Atomistic Simulation of the Elasticity of Polymers

DISSEPTION

submitted to the

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presented by
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Zürich, 1997
I dedicate this work to the memory of my father

Hubert Zehnder (1938-1997)
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Notation

\( a_i \)  \quad \text{acceleration vector} \ a \quad \text{m/s}^2

\( a_{ij} \)  \quad \text{transformation matrix} \ A

\( a_{mn} \)  \quad \text{acceptance probability from} \ m \ \text{to} \ n

\( A \)  \quad \text{Helmholtz free energy} \quad \text{J/mol}

\( A \)  \quad \text{general property}

\( a, b, c \)  \quad \text{cell edge lengths} \quad \text{m}

\( a_i, b_i, c_i \)  \quad \text{cell edge vectors} \ a, b, c \quad \text{m}

\( \alpha_A \)  \quad \text{polarizability of atom species} \ A \quad \text{m}^3

\( \alpha_{ij} \)  \quad \text{tensor of the thermal expansivity} \quad \text{K}^{-1}

\( \alpha_{mn} \)  \quad \text{attempt probability to go from} \ m \ \text{to} \ n

\( \alpha, \beta, \gamma \)  \quad \text{cell edge angles} \quad \text{°}

\( A_{\alpha\beta}, B_{\alpha\beta} \)  \quad \text{Lennard-Jones parameters between} \ \alpha \ \text{and} \ \beta \quad \text{J/mol} \cdot \text{m}^{6(12)}

\( b \)  \quad \text{bond length} \quad \text{m}

\( \beta \)  \quad \text{isothermal compressibility} \ (\text{=} \ K^{-1}) \quad \text{GPa}^{-1}

\( c_{0.5} \)  \quad \text{components of the quintic spline}

\( c_{ab} \)  \quad \text{normalized correlation function}

\( C_{AB} \)  \quad \text{correlation function between} \ A \ \text{and} \ B

\( c_{ijkl} \)  \quad \text{small strain/stress elasticity tensor} \quad \text{GPa}

\( C_{ij} \)  \quad \text{elasticity tensor in Voigt notation} \quad \text{GPa}

\( C_{ijkl} \)  \quad \text{finite strain/stress elasticity tensor} \quad \text{GPa}

\( C_v, C_p \)  \quad \text{isochoric, adiabatic heat capacity} \quad \text{J/(mol K)}

\( C_{6.10} \)  \quad \text{dispersion coefficients}

\( d_{ij} \)  \quad \text{stretching tensor} \ d

\( D \)  \quad \text{diffusion constant} \quad \text{cm}^2/\text{s}

\( \delta_{ij} \)  \quad \text{identity matrix} \ I

\( e_i \)  \quad \text{unit vector} \ e

\( \varepsilon \)  \quad \text{dielectric constant}

\( \varepsilon_i \)  \quad \text{principal values of} \ \varepsilon_{ij}

\( \varepsilon_0 \)  \quad \text{permittivity of vacuum} \quad \text{As/Vm}

\( \varepsilon_{ij} \)  \quad \text{symmetric small strain tensor} \ E, \ \varepsilon

\( \varepsilon_{\alpha\beta} \)  \quad \text{interaction energy between atom type} \ \alpha \ \text{and} \ \beta \quad \text{J/mol}

\( E \)  \quad \text{Young's modulus} \quad \text{GPa}

\( E \)  \quad \text{energy} \quad \text{J/mol}

\( f_i^\alpha \)  \quad \text{force} \ f \ \text{on atom} \ \alpha \quad \text{N}

\( \phi \)  \quad \text{torsion angle}

\( \phi_{ijk} \)  \quad \text{symmetrical tensor in the first pair of indices}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g_i$</td>
<td>gravitational force vector</td>
<td>N</td>
</tr>
<tr>
<td>$g(x)$</td>
<td>gradient of the potential energy with respect to $x$</td>
<td>J/(mol-m)</td>
</tr>
<tr>
<td>$g$</td>
<td>metric tensor</td>
<td>m$^2$</td>
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<tr>
<td>$g_{\alpha\beta}$</td>
<td>pair-distribution function of $\alpha$ and $\beta$</td>
<td></td>
</tr>
<tr>
<td>$G$</td>
<td>shear modulus</td>
<td>GPa</td>
</tr>
<tr>
<td>$G^{\alpha}$</td>
<td>lattice function of atom $\alpha$</td>
<td></td>
</tr>
<tr>
<td>$h$</td>
<td>Planck's number</td>
<td>Js</td>
</tr>
<tr>
<td>$h(s)$</td>
<td>structure factor</td>
<td></td>
</tr>
<tr>
<td>$h_i$</td>
<td>line search direction</td>
<td>m</td>
</tr>
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<td>$h_{ij}$</td>
<td>cell shape tensor $h$</td>
<td>m</td>
</tr>
<tr>
<td>$H_{ij}$</td>
<td>reference cell shape tensor $H$</td>
<td>m</td>
</tr>
<tr>
<td>$H$</td>
<td>Hamiltonian</td>
<td>J/mol</td>
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<tr>
<td>$H$</td>
<td>Hessian of the potential energy with respect to $x$</td>
<td>J/(mol-m$^2$)</td>
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<tr>
<td>$H$</td>
<td>displacement tensor</td>
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<td>$\eta$</td>
<td>shear viscosity</td>
<td>kg/(m-s)</td>
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<tr>
<td>$\eta_{ij}$</td>
<td>finite strain tensor in Voigt notation</td>
<td></td>
</tr>
<tr>
<td>$\eta_{ij}$</td>
<td>finite strain tensor</td>
<td></td>
</tr>
<tr>
<td>$I$</td>
<td>identity matrix</td>
<td></td>
</tr>
<tr>
<td>$j_{el}$</td>
<td>electrical flux</td>
<td>Cm/s</td>
</tr>
<tr>
<td>$J$</td>
<td>determinant of $J_{ij}$</td>
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<td>$J_{ij}$</td>
<td>Jacobian matrix $J$</td>
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<tr>
<td>$k$</td>
<td>Boltzmann factor</td>
<td>J/K</td>
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<td>$K$</td>
<td>bulk (compression) modulus</td>
<td>GPa</td>
</tr>
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<td>$K$</td>
<td>kinetic energy</td>
<td>J/mol</td>
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<td>$\kappa$</td>
<td>parameter of the Ewald summation</td>
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</tr>
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<td>$l_i$</td>
<td>invariants of the stress tensor</td>
<td>N/m$^2$</td>
</tr>
<tr>
<td>$L$</td>
<td>Lagrangian</td>
<td>J/mol</td>
</tr>
<tr>
<td>$\lambda_T$</td>
<td>thermal conductivity</td>
<td>W/(Km)</td>
</tr>
<tr>
<td>$\lambda_{n\times n}$</td>
<td>Eigenvalues of a $n\times n$ matrix</td>
<td></td>
</tr>
<tr>
<td>$\lambda, \mu$</td>
<td>Lamé constants</td>
<td>GPa</td>
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<tr>
<td>$\mu_i$</td>
<td>dipole moment</td>
<td>Cm</td>
</tr>
<tr>
<td>$\mu_\alpha$</td>
<td>chemical potential of specie $\alpha$</td>
<td>J/mol</td>
</tr>
<tr>
<td>$M_i$</td>
<td>number of systems in state $i$</td>
<td></td>
</tr>
<tr>
<td>$m_\alpha$</td>
<td>mass of atom $\alpha$</td>
<td>kg</td>
</tr>
<tr>
<td>$m_w$</td>
<td>molecular mass</td>
<td>g/mol</td>
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<tr>
<td>$m, n$</td>
<td>exponents of the Lennard-Jones $m$-$n$ potential</td>
<td></td>
</tr>
<tr>
<td>$m, n_i$</td>
<td>possible states in MC move</td>
<td></td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>( n_i )</td>
<td>unit vector ( n )</td>
<td></td>
</tr>
<tr>
<td>( n )</td>
<td>vector of integer numbers</td>
<td></td>
</tr>
<tr>
<td>( N_{(\alpha)} )</td>
<td>number of atoms (of type ( \alpha ))</td>
<td></td>
</tr>
<tr>
<td>( N_A )</td>
<td>effective number of electrons of atom species ( A )</td>
<td></td>
</tr>
<tr>
<td>( N_A )</td>
<td>Avogadro's number ( \text{mol}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( \nu )</td>
<td>Poisson's ratio</td>
<td></td>
</tr>
<tr>
<td>( p )</td>
<td>pressure ( \text{N/m}^2 ) (bar)</td>
<td></td>
</tr>
<tr>
<td>( p^\alpha )</td>
<td>momentum of atom ( \alpha ) ( \text{kg-m/s} )</td>
<td></td>
</tr>
<tr>
<td>( p, q )</td>
<td>arbitrary vectors</td>
<td></td>
</tr>
<tr>
<td>( p_i, q_i )</td>
<td>conjugate momenta, coordinates of atom ( i )</td>
<td></td>
</tr>
<tr>
<td>( P_i )</td>
<td>origin of the coordinate system ( x )</td>
<td></td>
</tr>
<tr>
<td>( P_{ij} )</td>
<td>symmetric microscopic stress tensor ( \text{N/m}^2 )</td>
<td></td>
</tr>
<tr>
<td>( \pi_{mn} )</td>
<td>transition probability</td>
<td></td>
</tr>
<tr>
<td>( q_i )</td>
<td>molecular conformation ( i )</td>
<td></td>
</tr>
<tr>
<td>( q_i^* )</td>
<td>selection probability of torsion angle ( i )</td>
<td></td>
</tr>
<tr>
<td>( q_i, q^{(j)}, Q )</td>
<td>partial charge on atom ( i ), total charge ( \text{electron charge, C} )</td>
<td></td>
</tr>
<tr>
<td>( Q )</td>
<td>coupling mass between ( T ) and ( \theta )</td>
<td></td>
</tr>
<tr>
<td>( Q_{THN} )</td>
<td>canonical partition function</td>
<td></td>
</tr>
<tr>
<td>( r_{(ij)} )</td>
<td>distance (between atom ( i ) and ( j )) ( \text{m (Å)} )</td>
<td></td>
</tr>
<tr>
<td>( r_i )</td>
<td>arbitrary vector ( r ) ( \text{m} )</td>
<td></td>
</tr>
<tr>
<td>( r_c, r_s )</td>
<td>cutoff/spline radius ( \text{m (Å)} )</td>
<td></td>
</tr>
<tr>
<td>( R )</td>
<td>reduced minimum distance</td>
<td></td>
</tr>
<tr>
<td>( R )</td>
<td>matrix or vector of random numbers</td>
<td></td>
</tr>
<tr>
<td>( \rho )</td>
<td>density ( \text{kg/m}^3 )</td>
<td></td>
</tr>
<tr>
<td>( s )</td>
<td>scaled coordinate of temperature coupling ( \text{m} )</td>
<td></td>
</tr>
<tr>
<td>( s_i )</td>
<td>arbitrary scaled vector ( s )</td>
<td></td>
</tr>
<tr>
<td>( s, S )</td>
<td>length of vector ( x_i, X_i ) ( \text{m} )</td>
<td></td>
</tr>
<tr>
<td>( s_{ijkl} )</td>
<td>small stress/strain compliance tensor ( \text{GPa}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( S_{ij} )</td>
<td>compliance tensor in Voigt notation ( \text{GPa}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( S_{ijkl} )</td>
<td>finite stress/strain compliance tensor ( \text{GPa}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( S )</td>
<td>Entropy ( \text{J/(mol-K)} )</td>
<td></td>
</tr>
<tr>
<td>( S(r) )</td>
<td>quintic spline function with components ( c_{0.5} )</td>
<td></td>
</tr>
<tr>
<td>( S_{AA} )</td>
<td>spectral density function of ( A ) ( \text{Ω}^{-1} \text{m}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( \sigma_e )</td>
<td>electrical conductivity ( \text{Ω}^{-1} \text{m}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>( \sigma_i )</td>
<td>finite stress tensor in Voigt notation ( \text{N/m}^2 )</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{ij} )</td>
<td>finite stress tensor ( \sigma ) ( \text{N/m}^2 )</td>
<td></td>
</tr>
<tr>
<td>( \sigma_{\alpha\beta} )</td>
<td>collision distance between atom type ( \alpha ) and ( \beta ) ( \text{m (Å)} )</td>
<td></td>
</tr>
<tr>
<td>( t )</td>
<td>time ( \text{s} )</td>
<td></td>
</tr>
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### Notation

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>$t_i$</td>
<td>thermodynamic tension tensor in Voigt notation</td>
<td>N/m²</td>
</tr>
<tr>
<td>$t_{ij}$</td>
<td>thermodynamic tension tensor $t$</td>
<td>N/m²</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_j$</td>
<td>torque</td>
<td>N/m</td>
</tr>
<tr>
<td>$T_{ij}$, $T_{ijkl}$</td>
<td>general tensor</td>
<td></td>
</tr>
<tr>
<td>$\theta$</td>
<td>bending angle</td>
<td>°</td>
</tr>
<tr>
<td>$\bar{\theta}$</td>
<td>conjugate scaled velocity</td>
<td>s⁻¹</td>
</tr>
<tr>
<td>$\Theta_{ij}$</td>
<td>quadrupole moment</td>
<td>Cm²</td>
</tr>
<tr>
<td>$u_j$</td>
<td>vector connecting two points before deformation</td>
<td>m</td>
</tr>
<tr>
<td>$U$</td>
<td>interaction energy</td>
<td>J/mol</td>
</tr>
<tr>
<td>$v_j^\alpha$</td>
<td>velocity $v$ of atom $\alpha$</td>
<td>m/s</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
<td>m³</td>
</tr>
<tr>
<td>$w_i$</td>
<td>Boltzmann weight $i$</td>
<td></td>
</tr>
<tr>
<td>$W$</td>
<td>coupling mass between stress and cell shape change</td>
<td>kg</td>
</tr>
<tr>
<td>$\Omega$</td>
<td>scaled momentum of pressure coupling</td>
<td></td>
</tr>
<tr>
<td>$\omega$</td>
<td>rotation angle</td>
<td></td>
</tr>
<tr>
<td>$\Omega_{ij}$</td>
<td>rotation tensor</td>
<td></td>
</tr>
<tr>
<td>$x_i$, $X_i$</td>
<td>cartesian coordinate vectors, reference frame</td>
<td>m</td>
</tr>
<tr>
<td>$X(\theta)$</td>
<td>Rotation matrix (Euler angles)</td>
<td></td>
</tr>
<tr>
<td>$\chi$</td>
<td>out-of-plane parameter (Wilson definition)</td>
<td>°</td>
</tr>
<tr>
<td>$\chi_{ijk}$</td>
<td>antisymmetric tensor in the last pair of indices</td>
<td></td>
</tr>
<tr>
<td>$\xi$</td>
<td>thermodynamic friction</td>
<td></td>
</tr>
<tr>
<td>$Z$</td>
<td>configuration integral</td>
<td></td>
</tr>
<tr>
<td>$Z(\psi)$, $Z(\psi)$</td>
<td>Rotation matrix (Euler angles)</td>
<td></td>
</tr>
</tbody>
</table>

### List of Acronyms

- **bcc**: body-centered cubic
- **BMFT**: Bundesministerium für Forschung und Technologie
- **BPA-PC**: Bisphenol-A-Polycarbonate
- **fee**: face-centered cubic
- **FDT**: Fluctuation Dissipation Theorem
- **GZS**: Gusev-Zehnder-Suter
- **hep**: hexagonally close packed
- **MC**: Monte Carlo
- **MD**: Molecular Dynamics
- **MRS**: Mechanical Relaxation Spectrum
- **MSI**: Molecular Simulations, Incorp.
<table>
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Abstract

In this work, the elastic constants of solids, in particular crystalline and amorphous polymers, are computed numerically.

The first part introduces in three chapters to the theory of elasticity, to atomistic modelling, and to the theory of fluctuations, laying the foundations for the second part, which presents the results of various computer simulations.

Starting from the stress and strain tensor, the properties of stiffness and compliance tensors are deployed in the first chapter. Special emphasis is put on symmetry operations and on coordinate transformations. In the chapter about atomistic modelling, the functional form and the computation of intra- and intermolecular forcefield terms are covered as well as algorithms for the canonical sampling of the phase space. The focus of the third chapter is on methods that compute the complete tensor of the elastic constants from fluctuations of global parameters. At the moment, there are two such formula: The first is from Parrinello and Rahman and uses the fluctuations of the cell shape (i.e. the strain with respect to a reference shape) only, whereas the second was established in the course of this work and takes into consideration both the fluctuations of the strain and the correlation of stress and strain.

The generation of atomistic models of argon, polyethylene, polypropylene, cellulose, polyamide, and polycarbonate is described in the second part of this work. These models were propagated by MC and MD algorithms through phase space to compare the convergence behaviour of the two fluctuation approaches and to test their applicability to real polymeric materials. Exact results are delivered by fluctuation approaches only in the limit of an ergodic sampling of the phase space, i.e. for infinitely long simulations. The convergence behaviour of these algorithms is therefore of prime interest to get useful approximations in a reasonable time. It could be shown, that the new fluctuation formula converges at least as good as the well established Parrinello-Rahman formula. In some cases - low temperatures and small oscillations - the new stress-strain correlation method is even much faster. Comparison between the results of the two approaches allows for an estimation of the accuracy of the elastic constants.

There is a good agreement between calculated and experimental elastic constants both for amorphous and crystalline polymers. In contrast to other methods like the static minimum energy method, it was even possible to predict the influence of small guest molecules and of temperature changes on the elastic behaviour. Besides this, it is possible to use the huge amounts of data produced in molecular dynamics simulations to compute dynamic properties like relaxation spectra.
Zusammenfassung

Diese Arbeit befasst sich mit der numerischen Berechnung von elastischen Konstanten von Festkörpern, insbesondere von amorphen und kristallinen Polymeren. Im ersten Teil werden in drei Kapiteln die Elastizitätstheorie, die atomistische Modellierung und die Fluktuationenrechnung dargelegt, welche die Grundlage des zweiten Teils bilden, in welchem die Resultate diverser Computersimulationen präsentiert werden.


Im zweiten Teil dieser Arbeit werden Festkörpermodelle von Argon, Polyethylen, Polypropylen, Cellulose, Polyamid und Polycarbonat erstellt und durch den Phasenraum propagiert, um einerseits das Konvergenzverhalten der Fluktuationenrechnungen zu vergleichen und um andererseits die Anwendbarkeit dieser Modelle auf reale Polymeren zu testen. Fluktuationenrechnungen liefern exakte Resultate nur für den Grenzfall der ergodischen Abtastung des Phasenraums, d.h. für unendlich lange Simulationen. Es konnte gezeigt werden, dass die neu entwickelte Fluktuationenformel zumindest gleich gut und unter gewissen Bedingungen - tiefe Temperaturen und kleine Dehnungen - viel besser konvergiert. Der Vergleich der Resultate der beiden Fluktuationenmethoden erlaubt zudem eine Abschätzung des Ungenauigkeit der erhaltenen Elastizitätstensoren.

Im Allgemeinen wurde eine sehr gute Übereinstimmung zwischen berechneten und experimentellen elastischen Konstanten für kristalline und amorphe Polymeren erzielt. Insbesondere sind die verwendeten Fluktuationenformeln in der Lage, den Einfluss von gelösten Stoffen und von Temperaturänderungen auf die elastischen Konstanten vorherzusagen. Bei diesen Simulationen fallen zudem große Mengen an Daten an, welche - mit Einschränkungen - für die Berechnung dynamischer Informationen, wie z. B. Relaxationsspektren, genutzt werden können.
Introduction

Only a few years after the establishment of the macromolecular character of polymers by Staudinger (1920)\textsuperscript{84}, Meyer and Lothmar\textsuperscript{36a} calculated the elastic modulus of isolated cellulose chains in 1936. They used spectroscopic data of low molar mass compounds to establish a forcefield of the cellulose backbone and computed the elastic constants from the spring constants of angles and valences. Basically the same forcefield approach was used twenty-five years later by Lyons\textsuperscript{58a} and Treloar\textsuperscript{60a} to estimate the elastic moduli of nylon, polyethylene terephthalate, and polyethylene chains. In 1966, Odajima and Maeda\textsuperscript{66a} used Born's lattice dynamics theory to compute the full matrix of the elastic constants of polyethylene crystals. They included the intermolecular forces (at least the nearest neighbour interactions), which they found to contribute only 0.2\% in the case of polyethylene crystals, and the influence of temperature on the elastic constants in their model. Four years later, Wobser and Blasenbrey\textsuperscript{70a} determined the elastic constants of PE single crystals using the theory of the dynamics of non-primitive lattices of Leibfried taking the first and second neighbour shell into consideration. In the following year, 1971, Shiro and Miyazawa\textsuperscript{71a} developed a general method to transform the potential energy matrix (i.e. the forcefield) to the matrix of the elastic constants. Both intra- and intermolecular forces were included. With the same general matrix method, but reduced to the asymmetric unit cell, Tashiro \textit{et al.}\textsuperscript{78a} perfected this methodology.

Another approach is the static minimum energy method, which uses the second derivative of the potential energy hypersurface with respect to strain to compute the elastic constants. There is no analytical computation of the forcefield Hessian, but a series of deformation and minimization steps are performed to discretize the energy surface. Two of the first applications for amorphous metals are described in the works of Maeda and Takeuchi\textsuperscript{81a} in 1981 and Srolovitz \textit{et al.}\textsuperscript{83a} in 1983. Three years later, Theodorou and Suter\textsuperscript{86a} applied this method to polymeric systems with extended statistical mechanical considerations. Furthermore, they used a force approach - i.e. the first derivative of the stress with respect to the strain - to estimate the elastic constants.

Brown and Clarke\textsuperscript{91a} introduced in 1991 a phenomenological method, that estimates the elastic constants from the elongation of a simulation cell during a molecular dynamics simulation with a constantly increasing stress component. This method was applied to various polymers by Qian and
All the methods presented above have certain disadvantages: The general matrix methods only work for ordered systems, whereas the static minimum energy approach completely neglects entropic effects, which makes its applicability to amorphous systems doubtful (see chapter 4.8.4.2). The molecular dynamics approach suffers from very high deformation rates and yields elastic constants which may considerably differ from experiment. It would therefore be desirable to have a method, that would take into account both entropic effects and the influence of small molecules on the elastic constants. Furthermore, the method should work both on crystalline and amorphous systems of any size and it should leave the microstructures close to their equilibrium conformations.

Already in 1969, Squire, Holt, and Hoover\textsuperscript{Squire69a} introduced a method to compute the elastic constants from 'kinetic', 'Born', and 'fluctuation' terms resulting from a Monte Carlo simulation. Parrinello and Rahman\textsuperscript{ParrinelloRahman81a/82a} published in 1981 and 1982 their pioneering works about constant stress molecular dynamics and the computation of the matrix of the elastic constants from strain fluctuations. This laid the basis for a number of works, that compared the efficiency of fluctuation algorithms in MC and various MD-ensembles. Of importance are here the work of Sprik, Impey, and Klein\textsuperscript{Sprik84a}, Ray, Moody, and Rahman\textsuperscript{Ray85a/86a}, and the papers of Ray\textsuperscript{Ray92a} and Fay and Ray\textsuperscript{Fay92a}. Most calculations in these papers dealt with nearest-neighbour Lennard-Jones solids and with sodium.

In this work, the strain fluctuation method was applied for the first time to various polymeric systems to compute the full matrix of the elastic constants of crystals, glasses, and glasses with small diffusants. It turned out, that this fluctuation method was capable of reproducing the elastic constants of all these systems remarkably well, with one problem remaining: the convergence of the elastic constants with simulation time was slow, requiring long simulations. It is therefore most valuable to find a convergence criterion to optimize the duration of the long molecular dynamics runs. This criterion was found by establishing a new fluctuation formula that uses both the stress and the strain fluctuations of a model cell to compute its elastic constants. Comparison of the results of the strain and the stress-strain fluctuation method allowed to estimate the degree of convergence of a simulation.
The following work is organized in two major sections:

The first three chapters comprise the *theory section*, in which the relevant concepts of elasticity, molecular modelling and fluctuations are outlined. Since this section is quite detailed, it might serve as a tutorial introduction to the field covered by this thesis.

The fourth chapter with eight subchapters presents the *results* of molecular dynamics and Monte Carlo simulations of argon, polyethylene, polypropylene, cellulose, polyamides and polycarbonate. Some introductory remarks at the beginning explain the choice of the polymers by methodological and historical arguments.

Comments, conclusions and an outlook finish the main body and some appendices provide more detailed informations on certain topics.
1 Theory I - Elasticity of Anisotropic Solids

1.1 Stress Tensor

Forces acting upon a solid elastic body may be categorized as body forces, originating from gravitational or magnetic fields, or as contact forces, exerted by the surrounding matter. While body forces are effective on individual particles of the system (atoms, dipoles, etc) and therefore are proportional to the size, the contact forces act on the surface of the body and are dependent on its shape and the location of the contact points. Consider a volume element within the stressed body (Fig. 1.1). From the contact points forces are transmitted on the sides of the element by the material around it. These forces are proportional to the area of the surface of the element, and the force per actual unit area is called the stress.

Figure 1.1: The stresses on the faces of a unit cube in a homogeneously stressed body

1.1.1 Homogeneous Stress

A stress can be called homogeneous, if the forces acting on the surface of an element of fixed shape and orientation are independent of the position of the element in the body. The volume element of Fig. 1.1 shows the stress acting on the three faces oriented towards the positive ends of the coordinate axes $x_1$, $x_2$ and $x_3$, with positive values given by the orientation of the vectors (tensile stress acting on the body is positive while compressive stress is negative). Since a homogeneous stress state is assumed, the stresses on the three opposite faces must be equal and opposite to those shown in the figure. This makes a total of nine different components of the stress.

If we further assume that the volume element is in static equilibrium, we
1.1 Stress Tensor

must have zero angular momentum around each coordinate axis. This is only fulfilled if

\[ \sigma_{12} = \sigma_{21} \quad \sigma_{12} = \sigma_{21} \quad \sigma_{12} = \sigma_{21} \]

or

\[ \sigma_{ij} = \sigma_{ji}. \]

We thus can write the six independent components of the stress in a symmetric 3x3-matrix:

\[
\begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{12} & \sigma_{22} & \sigma_{23} \\
\sigma_{13} & \sigma_{23} & \sigma_{33}
\end{bmatrix}
\]

1.1.2 Inhomogeneous Stress

A stress-state is called inhomogeneous, if the stress varies from point to point. The actual stress at a given point is arrived at by taking the forces per area of a volume element and letting the size of the volume element tend to zero. The inhomogeneity of the stress can be expressed by it's gradient \( \frac{\partial \sigma_{ij}}{\partial x_k} \).

The equations of motion of a small volume element in the presence of a (gravitational) body force \( g_i \) can be written as \( \text{Nye85} \)

\[
\frac{\partial \sigma_{ij}}{\partial x_j} + \rho g_i = \rho \ddot{x}_i, \quad (1-3)
\]

with \( \rho \) corresponding to the density of mass in the volume element. (Throughout the rest of this chapter, the summation convention is applied to indices occurring twice in a product).

Assuming statical equilibrium, all components of the acceleration \( \ddot{x}_i \) must be zero, which leads to the equations of equilibrium of the theory of elasticity

\[
\frac{\partial \sigma_{ij}}{\partial x_j} + \rho g_i = 0. \quad (1-4)
\]

In a small cube of size \( \delta \), the moment of inertia around an axis parallel to the edges through the center is \( \frac{\delta^5}{24} \). Since the torque exerted by the shear-stresses on the surface of this cube and by an additional body-torque \( G \) is

\[
T_k = (\sigma_{ij} - \sigma_{ji} + G_k) \delta^3 \quad (k \neq i, j), \quad (1-5)
\]
the angular acceleration will be proportional to \( \delta^{-2} \), becoming infinite as \( \delta \) tends to zero \( \text{KellyGroves70} \), unless
\[
\sigma_{ij} - \sigma_{ji} + G_k = 0. \tag{1-6}
\]

If body-torques are absent, the same relation as for homogeneous stresses (Eq. (1-1)) is obtained. With body-torques present, Hooke's law is still valid, if \( \sigma_{ij} \) is not the stress itself, but its symmetrical part \( \frac{1}{2} (\sigma_{ij} + \sigma_{ji}) \). Actually, it is always possible to find a transformation of the form

\[
\sigma'_{ij} = \sigma_{ij} + \frac{\partial \chi_{ijk}}{\partial x_k}, \quad \chi_{ijk} = -\chi_{ikj} \tag{1-7}
\]

where \( \chi_{ijk} \) is any tensor antisymmetric in the last pair of indices. If the antisymmetric part of \( \sigma_{ij} \) has the form

\[
\sigma_{ij} - \sigma_{ji} = 2 \frac{\partial \phi_{ijk}}{\partial x_k}, \quad \phi_{ijk} = \phi_{jik} \tag{1-8}
\]

then an asymmetrical \( \sigma_{ij} \) can be made symmetrical by a transformation of this type (Eq. (1-7)). The symmetrical tensor is

\[
\sigma'_{ij} = \frac{1}{2} (\sigma_{ij} + \sigma_{ji}) + \frac{\partial (\phi_{ikj} + \phi_{jki})}{\partial x_k} \tag{1-9}
\]

with

\[
\chi_{ijk} = \phi_{jki} + \phi_{ikj} - \phi_{ijk}. \tag{1-10}
\]

1.1.3 Tensor Properties of the Stress Matrix

The nine components of a second-rank tensor \( T \) connect the components of two vectors \( p \) and \( q \) in a linear relationship

\[
p_i = T_{ij} q_j \tag{1-11}
\]

If the coordinate system is transformed, the elements of a tensor transform according to

\[
T'_{ij} = a_{ik} a_{jl} T_{kl}, \tag{1-12}
\]

\( a_{ij} \) denoting the components of the transformation matrix \( A \) (Appendix A-1). Equation (1-12) thus represents a definition of a (second-rank) tensor.

It can be shown that the stress matrix \( \sigma_{ij} \) indeed forms a second-rank tensor that connects the normal \( n \) of a small surface element \( \delta S \) with the force vector \( p \delta S \) acting through this surface element (Fig. 1.2).

If the area of the surface element becomes infinitesimally small, the local stress vector \( p \) is given by
This equation still holds when the stress is not homogenous, when body forces are acting, and when the body is not in statical equilibrium for these extra terms become negligible as the surface is made vanishingly small.

1.1.4 Eigenvalues of the Stress Tensor, Invariants

Since the stress tensor is symmetric (Eq (1-1)), all its eigenvalues are real and the eigenvectors are orthogonal. It is thus possible to diagonalize the stress tensor by an appropriate transformation of the reference coordinate system using a transformation matrix \( a_{ij} \)

\[
\sigma'_{kl} = a_{ik} a_{lj} \sigma_{ij} = 
\begin{bmatrix}
\sigma_1 & 0 & 0 \\
0 & \sigma_2 & 0 \\
0 & 0 & \sigma_3
\end{bmatrix}
\]  

(1-14)

The unit vectors of the transformed coordinate system form an eigenspace, in which a volume element similar to that of Fig. 1.1 shows no shear stresses but only normal components.

Three invariants of the stress tensor are given by

\[
I_1 = \sigma_1 + \sigma_2 + \sigma_3 = \sigma_{11} + \sigma_{22} + \sigma_{33}
\]

\[
I_2 = \sigma_2 \sigma_3 + \sigma_3 \sigma_1 + \sigma_1 \sigma_2 = \begin{vmatrix}
\sigma_{22} & \sigma_{23} \\
\sigma_{23} & \sigma_{33}
\end{vmatrix} + \begin{vmatrix}
\sigma_{11} & \sigma_{13} \\
\sigma_{13} & \sigma_{33}
\end{vmatrix} + \begin{vmatrix}
\sigma_{11} & \sigma_{12} \\
\sigma_{12} & \sigma_{22}
\end{vmatrix}
\]

\[
I_3 = \sigma_1 \sigma_2 \sigma_3 = \begin{vmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{12} & \sigma_{22} & \sigma_{23} \\
\sigma_{13} & \sigma_{23} & \sigma_{33}
\end{vmatrix}
\]

(1-15)
1.2 Strain Tensor

1.2.1 Small or Linear-elastic Strain Tensor

1.2.1.1 Small Strain and Rotation Tensor

A material subject to a stress reacts by deforming until the internal stresses generated by this deformation counterbalance the external stress. If the material relaxes to its initial shape after removal of the external stress, the deformation is called elastic; if a permanent change in shape remains, a plastic deformation has occurred. In the present work, only the elastic, thermodynamically reversible behavior of matter is being concerned.

The local small-scale deformation of a body can be described by looking at an arbitrary infinitesimal line vector \(d\mathbf{x}\) connecting two points \(P\) and \(Q\) in the undeformed state (Fig. 1.3).

![Figure 1.3: Relative displacement \(du\) of \(Q\) relative to \(P\).

Upon deformation, the two points move by \(u\) to \(p\) and by \(u+du\) to \(q\), respectively. The unit relative displacement vector, \(\frac{du_i}{dS} = \frac{\partial u_i}{\partial x_j}dS_j\), can be written briefly as

\[
\frac{du}{dS} = J_u n, \tag{1-17}
\]
where \( J_u \) is the 3x3 Jacobian matrix or displacement gradient matrix and \( \mathbf{n} \) the unit vector in the direction of \( d\mathbf{X} \). The Jacobian matrix - the deformation process can be interpreted as a transformation from one coordinate system to another (Appendix A-6) - can be written as the sum of a symmetric matrix \( \mathbf{E} \) and a skew-symmetric matrix \( \Omega \),

\[
J_u = \mathbf{E} + \Omega, \tag{1-18}
\]

with

\[
\mathbf{E} = \begin{bmatrix}
\frac{\partial u_1}{\partial X_1} & \frac{1}{2} \left( \frac{\partial u_1}{\partial X_2} + \frac{\partial u_2}{\partial X_1} \right) & \frac{1}{2} \left( \frac{\partial u_1}{\partial X_3} + \frac{\partial u_3}{\partial X_1} \right) \\
\frac{1}{2} \left( \frac{\partial u_1}{\partial X_2} + \frac{\partial u_2}{\partial X_1} \right) & \frac{\partial u_2}{\partial X_2} & \frac{1}{2} \left( \frac{\partial u_2}{\partial X_3} + \frac{\partial u_3}{\partial X_2} \right) \\
\frac{1}{2} \left( \frac{\partial u_1}{\partial X_3} + \frac{\partial u_3}{\partial X_1} \right) & \frac{1}{2} \left( \frac{\partial u_3}{\partial X_2} + \frac{\partial u_2}{\partial X_3} \right) & \frac{\partial u_3}{\partial X_3}
\end{bmatrix}
\]

\[
\Omega = \begin{bmatrix}
0 & \frac{1}{2} \left( \frac{\partial u_1}{\partial X_2} - \frac{\partial u_2}{\partial X_1} \right) & \frac{1}{2} \left( \frac{\partial u_1}{\partial X_3} - \frac{\partial u_3}{\partial X_1} \right) \\
\frac{1}{2} \left( \frac{\partial u_1}{\partial X_2} - \frac{\partial u_2}{\partial X_1} \right) & 0 & \frac{1}{2} \left( \frac{\partial u_2}{\partial X_3} - \frac{\partial u_3}{\partial X_2} \right) \\
\frac{1}{2} \left( \frac{\partial u_1}{\partial X_3} - \frac{\partial u_3}{\partial X_1} \right) & \frac{1}{2} \left( \frac{\partial u_3}{\partial X_2} - \frac{\partial u_2}{\partial X_3} \right) & 0
\end{bmatrix}
\]

\[
\varepsilon_{ij} = \frac{1}{2} \frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i}, \tag{1-19}
\]

\[
\Omega_{ij} = \frac{1}{2} \frac{\partial u_i}{\partial X_j} - \frac{\partial u_j}{\partial X_i}. \tag{1-20}
\]

\( \mathbf{E} \) represents the (symmetric) small-strain tensor with its components \( \varepsilon_{ij} \). It can be shown\(^{Malvern69}\) that \( \Omega \) is a rotation tensor describing the rotation of a rigid body around an axis vector

\[
\omega = \begin{bmatrix}
-\Omega_{23} \\
-\Omega_{13} \\
-\Omega_{12}
\end{bmatrix}
\]

by an angle \(|\omega|\).

### 1.2.1.2 Diagonalization, Dilatation Strain Quadric and Ellipsoid

Since strain, as defined by (1-19), is a symmetrical tensor it may be referred to its principal axes. The shear components then vanish,
leading to a simple definition of the dilatation $\Delta$,

$$\Delta = (1 + \varepsilon_1)(1 + \varepsilon_2)(1 + \varepsilon_3) - 1 = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \text{tr} E.$$  \hfill (1-23)

The principal axes of strain only remain unchanged by deformation if the rotation tensor $\Omega$ is zero, otherwise they define three mutually perpendicular axes, which remain mutually perpendicular during the deformation.

It is possible to define a strain quadric

$$\varepsilon_{ij}x_ix_j = 1,$$  \hfill (1-24)

which is identical with the quadric $J_{ij}x_ix_j = 1$.

The strain ellipsoid

$$\frac{x_1^2}{(1 + \varepsilon_1)^2} + \frac{x_2^2}{(1 + \varepsilon_2)^2} + \frac{x_3^2}{(1 + \varepsilon_3)^2} = 1,$$  \hfill (1-25)

describes the shape of a sphere ($x_1^2 + x_2^2 + x_3^2 = 1$) after the deformation.

The invariants of the strain matrix can be found analogous to Eq. (1-15).

### 1.2.2 Finite Strain Tensor

If a body is heavily (but still elastically) deformed, the linear relationship between change in shape and strain is no longer valid, as will be shown in this paragraph.\textsuperscript{86a}

Considering again the deformation shown in Fig. 1.3, the vector $dx$, connecting the two points $P$ and $Q$, changes during the deformation to $dx = dX + du$. The squared distance between the two points is $dS^2 = dXjdX_j$ before and $ds^2 = dx_jdx_j = (dX_j + du_j)^2$ after the deformation. Substituting $du_j = (\partial u/\partial X)dx_j$, which is valid, if the strain is sufficiently homogeneous over the length scale given by $dX_j$, the length of the deformed connecting vector is

$$ds^2 = dS^2 + 2\frac{\partial u_i}{\partial X_j}dx_jdx_i + \frac{\partial u_i}{\partial X_j}\frac{\partial u_i}{\partial X_k}dx_i dx_k.$$  \hfill (1-26)

The second term can be brought into an explicitly symmetrical form, because the summation is taken over both suffixes $i$ and $j$:

$$2\frac{\partial u_i}{\partial X_j}dx_jdx_i \leftrightarrow \left(\frac{\partial u_i}{\partial X_j} + \frac{\partial u_i}{\partial X_j}\right)dx_i dx_j.$$  \hfill (1-27)
In the third term, the indices \( i \) and \( k \) are interchanged and \( ds^2 \) takes the final form

\[
ds^2 = dS^2 + 2\eta_{ij} dX_i dX_j,
\]

(1-28)

where the symmetric tensor \( \eta_{ij} \) is defined as

\[
\eta_{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} + \frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} \right).
\]

(1-29)

Comparing Eqs (1-19) and (1-29), one can clearly see that the small strain tensor is an approximation of the above equation neglecting the products of the derivatives. Equation (1-29) provides a correct mathematical description of the strain that is valid for small and large deformations.

Assuming that \( P \) in Fig. 1.3 is located at \( X \) and \( p \) at \( x \), the displacement \( u \) is given by

\[
u_i = x_i - X_i.
\]

(1-30)

Combining Eq. (1-29) and Eq. (1-30), we find

\[
\eta_{ij} = \frac{1}{2} \left( \frac{\partial x_k}{\partial X_i} \frac{\partial x_k}{\partial X_j} - \delta_{ij} \right),
\]

(1-31)

which, using the definition of the Jacobian (Eq. (A-17)), can be written as

\[
\eta_{ij} = \frac{1}{2} (J_{x_{ki}} J_{x_{kj}} - \delta_{ij}) \quad \text{or} \quad \eta = \frac{1}{2} \left( J_x^T J_x - I \right).
\]

(1-32)

The two tensors \( J_x \) and \( J_u \) are related by

\[
J_{u,ij} = \frac{\partial u_j}{\partial X_i} = \frac{\partial (x_i - X_i)}{\partial X_i} = \frac{\partial x_i}{\partial X_i} - \delta_{ij} = J_{x,ij} - \delta_{ij}.
\]

(1-33)

### 1.2.3 Finite Strain Tensor from Cell Shape Tensors

#### 1.2.3.1 Definition of the Cell Shape Tensor

The cell shape tensor \( h \) is simply constructed by taking the cell edge vectors \( a, b \) and \( c \) (Fig. 1.4) as columns of a 3x3 matrix

\[
h = \begin{bmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{bmatrix}.
\]

(1-34)

The cell shape tensor \( h \) is a scaling matrix that transforms all points in the cell into a cubic unit cell by

\[
r_\alpha = hs_\alpha \quad \text{or} \quad s_\alpha = h^{-1} r_\alpha.
\]

(1-35)
1.2.3.2 Strain from Cell Shape Tensors

The strain (deformation) between a reference cell shape tensor $H$ and an actual shape tensor $h$ (Fig. 1.4) can be expressed by

$$\eta = \frac{1}{2} \left[ h^T H^{-1} + H^T h^{-1} - I \right], \quad (1-36)$$

with $I$ representing the identity matrix ($I_{ij} = \delta_{ij}$, $\delta$: Kronecker symbol). (The derivation of this formula is given in Appendix B-1.)

Reference deformed

Figure 1.4: Scaling matrices linking unit cell with reference and deformed cell

1.2.4 Finite Stress (Thermodynamic Tension)

1.2.4.1 Relation Between Actual Stress and Thermodynamic Tension

As stated in chapter 1.1.1, stress is defined as force per unit surface of the actual, deformed body. In contrast to this, strain is referred to the natural, unstressed state. For this reason the stress power necessary to deform a body with a certain deformation rate is not equal to the stress components times the differentials of the corresponding strain components. Quantities $t_{ij}$ called thermodynamic tensions, are defined such that the power to stretch a medium non-dissipatively equals the sum $t_{ij} \eta_{ij}$ (per unit volume of undeformed body). This rate of change of the Helmholtz energy at constant temperature must equal the sum of the actual stress $\sigma_{ij}$ times the actual deformation rate $d_{ij}$.\textsuperscript{64}

$$U - TS = V_0 t_{st} \eta_{st} = V \sigma_{ij} d_{ij}, \quad (1-37)$$

where $U$ represents the internal energy, $T$ the temperature, and $S$ the entropy. $V$ and $V_0$ denote the volume of the deformed and undeformed body, respectively and the stretching tensor $d_{ij}$ is given by
1.2 Strain Tensor

\[ d_{ij} = \frac{1}{2} \left( \frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i} \right) = \frac{\partial X_s}{\partial x_i} \frac{\partial X_t}{\partial x_j} \]  \hspace{1cm} (1-38)

The second equality can be rationalized by taking the time derivative of Eq. (1-31),

\[ \dot{\eta}_{st} = \frac{1}{2} \left( \frac{\partial x_i}{\partial X_s} \frac{\partial x_j}{\partial X_t} + \frac{\partial x_j}{\partial X_s} \frac{\partial x_i}{\partial X_t} \right) = d_{ij} \frac{\partial x_i}{\partial X_s} \frac{\partial x_j}{\partial X_t} \]  \hspace{1cm} (1-39)

Plugging (1-38) into (1-37) and using the relation between \( V \) and \( V_0 \) given by Eq. (A-20), the thermodynamic tensions and the actual stress are connected by

\[ t_{st} = J \sigma_{ij} \frac{\partial x_i}{\partial x_j} \]  \hspace{1cm} or  \hspace{1cm} \[ \sigma_{ij} = \frac{1}{J} \frac{\partial x_i}{\partial x_j} t_{st} \]  \hspace{1cm} (1-40)

This equation can be written in terms of the cell shape tensors \( H \) and \( h^{Ray84a} \):

\[ t = JH^{-1} \sigma h^{-1} T \]  \hspace{1cm} (1-41)

with the Jacobi determinant \( J = \text{det}(hH^{-1}) \), and can also be found from comparison of Eqs. (1-32) and (1-36). (The derivation of these formulae can be found in Appendix B-2.) Since \( \sigma \) is a symmetric tensor, \( t \) must be symmetric too, as is shown in Appendix B-3.

1.2.4.2 Expressions for the Thermodynamic Tension

To find an expression for the \( t_{st} \), the first equality of Eq. (1-37) is written down, considering that \( A = U - TS \), Thurston64

\[ \rho_0 (A - TS) = t_{st} \dot{\eta}_{st} \]  \hspace{1cm} (1-42)

Assuming that the Helmholtz energy is a function of \( \eta_{st} \) and \( T \), its total derivative can be written as

\[ A = \left( \frac{\partial A}{\partial \eta_{st}} \right) \dot{\eta}_{st} + \left( \frac{\partial A}{\partial T} \right) \dot{T} \]  \hspace{1cm} (1-43)

By substitution into (1-42), it is found that

\[ \left( \rho_0 \frac{\partial A}{\partial \eta_{st}} - t_{st} \right) \dot{\eta}_{st} + \rho_0 \left( S + \frac{\partial A}{\partial T} \right) \dot{T} = 0 \]  \hspace{1cm} (1-44)

whence

\[ t_{st} = \rho_0 \left( \frac{\partial A}{\partial \eta_{st}} \right) \]  \hspace{1cm} (1-45)
Another formula for the thermodynamic tensions was presented by Ray\textsuperscript{Ray84a}.

\begin{equation}
\mathbf{t} = JHh^{-1}\mathbf{P}\mathbf{T}^{-1}H^T,
\end{equation}

where \(\mathbf{P}\) is the symmetric microscopic stress tensor

\begin{equation}
P_{ij} = V^{-1}\left[\sum_\alpha \frac{p_{\alpha i} p_{\alpha j}}{m_\alpha} - \sum_{\alpha < \beta} \frac{r_{\alpha \beta} r_{\alpha \beta} \partial U}{r_{\alpha \beta}}\right],
\end{equation}

with \(p_a\) denoting the momentum of atom \(a\) and \(r_{ab}\) representing the distance between atoms \(a\) and \(b\). \(U\) is a potential energy, which depends on the interatomic distances only but is not necessarily pairwise additive.

From the comparison of Eq. (1-41) and Eq. (1-46), it is found that

\begin{equation}
\sigma = \mathbf{P},
\end{equation}

which is equivalent to the virial theorem in the \(\mathcal{E}hN\)-constant energy, cell shape, and number of particles\) ensemble and a \(\mathcal{O}\left(\frac{1}{N}\right)\) approximation of it in the \(\mathcal{H}N\)-constant temperature, stress, and number of particles\) ensemble\textsuperscript{Ray84a}.

### 1.3 Stiffness and Compliance Tensors

#### 1.3.1 Definition of Stiffness and Compliance Tensor

As stated in chapter 1.2.1.1, a body subject to a stress deforms elastically until the internal forces generated by the emerging strain counterbalance the external stress. For sufficiently small stresses and strains, a linear (hookean) relationship between the two tensors can be observed. This is expressed by the following equations

\begin{equation}
\sigma_{ij} = c_{ijkl} \varepsilon_{kl} \quad \text{or} \quad \varepsilon_{ij} = s_{ijkl} \sigma_{kl},
\end{equation}

where the \(c_{ijkl}\) are called the stiffness and the \(s_{ijkl}\) the compliance of the material (note that the symbols of these two quantities are the reverse of the corresponding initial letters). The above equation is an example of a constitutive equation, describing the macroscopic behavior of the material under consideration.

It can be shown\textsuperscript{Nye85} that, since \(\sigma\) and \(\varepsilon\) both are second-rank tensors, \(c\) and \(s\) form fourth rank tensors, that transform like

\begin{equation}
T_{ijkl} = a_{im} a_{jn} a_{ko} a_{lp} T_{mnop},
\end{equation}

with \(a_{\alpha \beta}\) denoting the elements of the transformation matrix.

Dealing with relatively large stresses or strains, i.e. finite deformations, the stiffness and compliance tensors can be written as
1.3 Stiffness and Compliance Tensors

The isothermal elastic constants (= stiffnesses $C_{ijkl}$) can be written for infinitesimally small stresses and strains in differential form as

$$\sigma_{ij} = C_{ijkl} \varepsilon_{kl} \quad \text{or} \quad \varepsilon_{ij} = S_{ijkl} \sigma_{kl} \quad (1-51)$$

with the second equality given by (1-45). The elastic constants defined by the above equation are called second order because they involve the second derivatives of the energy. Third- and higher order elastic constants are defined in an analogous way to Eq. (1-52), but they are not of practical interest, since no experimental data is available.\footnote{CaginRay88a}

### 1.3.2 General Symmetry Relations

Since the stress (Eq. (1-1)) and the strain tensor (Eq. (1-29)) are symmetric, it follows from (1-51) that the indices in the first and the second pair of $C_{ijkl}$ and $S_{ijkl}$ can be exchanged

$$C_{ijkl} = C_{jikl} = C_{ijlk} = C_{ijlk}. \quad (1-53)$$

Furthermore, the order of differentiation in Eq. (1-52) is immaterial and thus the first pair of indices can be interchanged with the second pair:

$$C_{ijkl} = C_{klij}. \quad (1-54)$$

Eqs (1-53) and (1-54) provide a total of 60 independent equations, which reduce the maximum number of independent elements of the elasticity (= stiffness) tensor to 21.

Similar considerations are also valid for the compliance tensor $S_{ijkl}$, which has 21 independent elements, too.

### 1.3.3 Voigt Notation

The symmetry relations discussed in the previous chapter can be used to represent the forth-rank stiffness and compliance tensors by two-dimensional matrices.\footnote{Nye85}

The symmetric stress and strain tensors are converted into column vectors by writing them with a single suffix running from 1 to 6:

\[
\begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{12} & \sigma_{22} & \sigma_{23} \\
\sigma_{13} & \sigma_{23} & \sigma_{33}
\end{bmatrix} \leftrightarrow \begin{bmatrix}
\varepsilon_{11} \\
\varepsilon_{12} \\
\varepsilon_{13}
\end{bmatrix} \quad \text{or} \quad \begin{bmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\
\varepsilon_{12} & \varepsilon_{22} & \varepsilon_{23} \\
\varepsilon_{13} & \varepsilon_{23} & \varepsilon_{33}
\end{bmatrix} \leftrightarrow \begin{bmatrix}
\varepsilon_1 \\
\varepsilon_2 \\
\varepsilon_3
\end{bmatrix}. \quad (1-55)
\]
using the following rule to transform the 3x3-matrices to 6-dimensional vectors (compare Eq. (1-55)):

Table 1-1: Transformation rule of Voigt notation

<table>
<thead>
<tr>
<th>Two-suffix notation</th>
<th>11</th>
<th>22</th>
<th>33</th>
<th>23,32</th>
<th>31,13</th>
<th>12,21</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-suffix notation</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
</tbody>
</table>

The factors of $\frac{1}{2}$ in the off-diagonal strains are introduced to allow direct comparison of the elements of the matrix of the elastic constants with those of the elasticity tensor. The same conversion also holds for the finite stress ($t_{ij}$, Eq. (1-40)) and strain tensor ($\eta_{ij}$, Eq. (1-29)).

It is now possible to re-write the stiffness and compliance tensors, $C_{ijkl}$ and $S_{ijkl}$ of Eq. (1-51), as 6x6-matrices connecting the Voigt-stresses and -strains:

$$t_m = C_{mn} \eta_n \quad \text{or} \quad \eta_m = S_{mn} t_n.$$  \hspace{1cm} (1-56)

At the same time factors of 2 and 4 are introduced as follows:

$$S_{ijkl} = S_{mn} \quad \text{when } m \text{ or } n \text{ are 1, 2 or 3}$$
$$2S_{ijkl} = S_{mn} \quad \text{when either } m \text{ or } n \text{ are 4, 5 or 6}$$
$$4S_{ijkl} = S_{mn} \quad \text{when both } m \text{ and } n \text{ are 4, 5 or 6}$$  \hspace{1cm} (1-57)

For the $C_{ijkl}$ no factors of 2 and 4 are necessary, providing the simple relation

$$C_{ijkl} = C_{mn},$$  \hspace{1cm} (1-58)

which explains the introduction of the factors of $\frac{1}{2}$ in (1-55).

Both $C_{mn}$ and $S_{mn}$ are symmetric matrices as follows from Eq. (1-54), leading to

$$C_{mn} = C_{nm} \quad \text{or} \quad S_{mn} = S_{nm}.$$  \hspace{1cm} (1-59)

We can now write the matrix of the elastic constants (and the compliance matrix) as follows:

$$C_{mn} = C_{11} \ C_{12} \ C_{13} \ C_{14} \ C_{15} \ C_{16}$$
$$C_{12} \ C_{22} \ C_{23} \ C_{24} \ C_{25} \ C_{26}$$
$$C_{13} \ C_{23} \ C_{33} \ C_{34} \ C_{35} \ C_{36}$$
$$C_{14} \ C_{24} \ C_{34} \ C_{44} \ C_{45} \ C_{46}$$
$$C_{15} \ C_{25} \ C_{35} \ C_{45} \ C_{55} \ C_{56}$$
$$C_{16} \ C_{26} \ C_{36} \ C_{46} \ C_{56} \ C_{66}$$

$$S_{mn} = S_{11} \ S_{12} \ S_{13} \ S_{14} \ S_{15} \ S_{16}$$
$$S_{12} \ S_{22} \ S_{23} \ S_{24} \ S_{25} \ S_{26}$$
$$S_{13} \ S_{23} \ S_{33} \ S_{34} \ S_{35} \ S_{36}$$
$$S_{14} \ S_{24} \ S_{34} \ S_{44} \ S_{45} \ S_{46}$$
$$S_{15} \ S_{25} \ S_{35} \ S_{45} \ S_{55} \ S_{56}$$
$$S_{16} \ S_{26} \ S_{36} \ S_{46} \ S_{56} \ S_{66}$$  \hspace{1cm} (1-60)

These matrices contain the complete information about the elasticity of a
material and especially the matrix of the elastic constants is widely used in the following sections of this work. The two matrices are linked by the following relation, Shuvalov88

\[ t_{m} = C_{mn}n_{n} = C_{mn}S_{no}t_{o} \Rightarrow C_{mn}S_{no} = \delta_{mno} \Rightarrow S = C^{-1}. \]  

(1-61)

Although mathematical operations like inversion or multiplication with Voigt stress or strain vectors are quite straightforward, it has to be kept in mind that \( C_{mn} \) and \( S_{mn} \) do not represent tensors and that therefore the usual transformation law (Eq. (1-12)) is not valid. Instead of it, a more complicated transformation matrix described in Appendix A-2 has to be used.

1.3.4 Effect of Crystal Symmetry on the Matrix of the Elastic Constants

The relation between the symmetry of the physical properties of a crystal and its crystallographic symmetry is expressed by Neumann's Principle Nye85

The symmetry elements of any physical property of a crystal must include the symmetry elements of the point group of the crystal.

Therefore, the elastic constants have the same or a higher symmetry than the crystal they are measured on. The elasticity and stiffness tensors are inherently centrosymmetric (i.e. invariant, if all three cartesian axes are inverted), as can be easily seen from Eq. (1-56),

\[ t_{m} = C_{mn}n_{n} \quad \text{or} \quad n_{m} = S_{mn}t_{n}, \quad (1-56) \]

where a simultaneous change of the signs of the tensions \( t \) and the strains \( n \) is of no influence on the elastic constants.

If the crystal symmetry is higher than triclinic, the number of independent elastic constants is reduced from 21 to 13, 9, 7, 3 and 2 as the symmetry increases from monoclinic to cubic and isotropic.

There are several methods to introduce the crystal symmetry to the matrix of the elastic constants Nye85, Bhagavantam66, Lovett89, among which the one outlined next is the most systematic:

Each of the symmetry elements of the point group of the crystal is expressed as a transformation matrix \( A \) (Eq. (A-3)), operating on the elasticity or stiffness tensor,

\[ T_{ijkl} = a_{im}a_{jn}a_{ko}a_{lp}T_{mnop}. \]

(1-50)

Equating the old with the transformed moduli creates a set of equations describ-
ing the influence of the particular symmetry element on the elastic moduli. The combination of all the symmetry elements describes the point group and thus its influence on the elastic constants. In Table 1-2, the symmetry of the stiffness and compliance matrix as a function of the crystallographic crystal class is listed. A key to the notation can be found at the end of the table.

Table 1-2: Form of the $C_{ij}$ and $S_{ij}$ matrices

<table>
<thead>
<tr>
<th>Table 1-2: Form of the $C_{ij}$ and $S_{ij}$ matrices</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Triclinic</td>
</tr>
<tr>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td>$\alpha \neq 90^\circ$</td>
</tr>
<tr>
<td>$\beta \neq 90^\circ$</td>
</tr>
<tr>
<td>$\gamma \neq 90^\circ$</td>
</tr>
<tr>
<td>all classes:</td>
</tr>
<tr>
<td>$1, \bar{1}$</td>
</tr>
<tr>
<td>b) Monoclinic</td>
</tr>
<tr>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td>$\alpha = 90^\circ$</td>
</tr>
<tr>
<td>$\beta \neq 90^\circ$</td>
</tr>
<tr>
<td>$\gamma = 90^\circ$</td>
</tr>
<tr>
<td>all classes:</td>
</tr>
<tr>
<td>$2, m, 2/m$</td>
</tr>
<tr>
<td>Diad $</td>
</tr>
<tr>
<td>c) Tetragonal</td>
</tr>
<tr>
<td>$a = b \neq c$</td>
</tr>
<tr>
<td>$\alpha = 90^\circ$</td>
</tr>
<tr>
<td>$\beta = 90^\circ$</td>
</tr>
<tr>
<td>$\gamma = 90^\circ$</td>
</tr>
<tr>
<td>all classes:</td>
</tr>
<tr>
<td>$4, \bar{4},$</td>
</tr>
<tr>
<td>$4mm, \bar{4}2m, 422,$</td>
</tr>
</tbody>
</table>
### Table 1-2: Form of the $C_{ij}$ and $S_{ij}$ matrices

<table>
<thead>
<tr>
<th>Tensor</th>
<th>Condition</th>
<th>Axes</th>
<th>Symmetry</th>
</tr>
</thead>
</table>
| **d) Trigonal** | $a = b 
eq c$ | $\alpha = 90^\circ$ | 3, 3 |
| | $\beta = 90^\circ$ | $\gamma = 120^\circ$ | 32, 3m, |
| **e) Hexagonal** | $a = b 
eq c$ | $\alpha = 90^\circ$ | all classes: |
| | $\beta = 90^\circ$ | $\gamma = 120^\circ$ | 6, 6, 6/m, |
| | | | 622, 6mm |
| | | | 6mm2, |
| | | | 6/mmm |
| **f) Orthorhombic** | $a 
eq b = c$ | $\alpha = 90^\circ$ | all classes: |
| | $\beta = 90^\circ$ | $\gamma = 90^\circ$ | 222, mm2, |
| | | | mmm |
| **g) Cubic** | $a = b = c$ | $\alpha = 90^\circ$ | all classes: |
| | $\beta = 90^\circ$ | $\gamma = 90^\circ$ | 23, m3, |
| | | | 432, 43m, |
| | | | m3m |
Table 1-2: Form of the $C_{ij}$ and $S_{ij}$ matrices

<table>
<thead>
<tr>
<th>h) Isotropic</th>
<th>Key to notation</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Diagram" /></td>
<td><img src="symbols" alt="Symbols" /></td>
</tr>
</tbody>
</table>

### 1.3.5 Mechanical Stability

The elastic constants are only defined if the material under consideration is in a state of equilibrium, i.e., if small changes in shape do not result in plastic deformation. This imposes two restrictions to the structure of the energy hypersurface as a function of the applied strain: At zero strain, the first derivative of the strain energy is zero, i.e., no stresses act on the material and the second derivatives are positive. The second statement is equivalent to a mechanically stable system, where small deformations always increase the energy. \(^{54}\) BornHuang

The elastic constants are proportional to the second derivative of the (free) energy with respect to strain and therefore, the matrix of the elastic constants must be positive definite, which is equivalent to the requirement that all eigenvalues should be positive\(^{72}\) Gurtin or that all principal minors (Fig. 1.5) are positive\(^{54}\) BornHuang. (The computation of the eigenvalues and eigenvectors of a 4th rank tensor is described in Appendix A-3.) This requirement imposes further restrictions to the elastic constants of the different crystal systems.

\[
\begin{bmatrix}
C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\
C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\
C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\
C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\
C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\
C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66}
\end{bmatrix}
\]

Figure 1.5: Principal minors of the matrix of the elastic constants

The analytic computation of the eigenvalues of the matrix of the elastic constants is straightforward only for the cubic system, where the matrix
has the eigenvalues
\[ C_{11} - C_{12} \quad C_{11} - C_{12} \quad C_{11} + 2C_{12} \quad C_{44} \quad C_{44} \quad C_{44}. \] (1-63)

The requirement that all Eigenvalues should be positive, is equivalent to the following conditions:
\[ C_{44} > 0 \quad C_{11} > |C_{12}| \quad C_{11} + 2C_{12} > 0 \] (1-64)

A similar treatment of the hexagonal and trigonal symmetry results in the following restrictions:
\[ C_{44} > 0 \quad C_{11} > |C_{12}| \quad (C_{11} + C_{12})C_{33} > 2C_{13}^2, \] (1-65)
to which
\[ C_{66} > 0 \] (1-66)
is added for crystals of tetragonal symmetry.

For the triclinic, monoclinic and orthorhombic crystal classes, the eigenvalues are quite complicated, preventing the establishment of restrictions as compact as above. But numerically, the eigenvalues can be computed very efficiently from the matrix of the elastic constants, which allows a check of the mechanical stability of the system under consideration.

1.3.6 Voigt and Reuss Averages for Fibres and Powders

The elastic constants discussed so far are those of single crystals, but normally, matter is a conglomerate of crystallites of various size and orientation, embedded in a more or less amorphous matrix, which makes it very difficult to calculate the overall elastic behavior of a macroscopic body from the elasticity of its constituent domains. Two extreme approximations of the stress or strain field in a polycrystalline material are the Voigt and the Reuss limits:

- In the Voigt limit, it is assumed that all crystal elements are subject to the same strain and the elastic response of the material is obtained by taking the spatial average of the stiffness matrix.
• Equal stress is supposed to act on the crystallites in the Reuss limit and the overall compliance of the material is the spatial average of the individual compliances.

The spatial average of the stiffness or the compliance tensor equals the normalized integral over the distribution of orientation of the transformed tensor \( T_{ijkl} \) given by

\[
T_{ijkl} = a_{im} a_{jn} a_{ko} a_{lp} T_{mnop}
\]

with \( a_{ij} \) describing the orientation of the crystalline element using the Euler angle formalism (Appendix A-7).

There are two spatial orientations of practical interest:

- The cylindrical symmetry, where one coordinate axis is oriented uniformly in one direction and one of the other two axes (as the only degree of freedom), is randomly distributed in the plane perpendicular to the direction of orientation. This corresponds ideally to the orientation distribution in a polymeric fibre.
- The powder symmetry, where all orientations are equally probable, which is a model for any unoriented polycrystal.

### 1.3.6.1 Fibre symmetry

The transformation matrix \( a_{ij} \) of a fiber oriented in the \( x_3 \)-direction is

\[
A_\phi = \begin{bmatrix}
\cos \phi & \sin \phi & 0 \\
-\sin \phi & \cos \phi & 0 \\
0 & 0 & 1
\end{bmatrix}
\]

with \( \phi \) denoting the angular position of the crystal. Writing the 3x3x3x3-tensor of the elastic constants in reading order (i.e. by row) as a column vector (denoted by \( \{ \} \)) of 81 elements and multiplying the transformation matrices with the direct matrix product (\( \otimes \)) Eq. (1-50) can be written as

\[
\langle T_\phi \rangle = (A_\phi \otimes A_\phi \otimes A_\phi \otimes A_\phi) \langle T \rangle = A^{x4}_\phi \langle T \rangle
\]

\( A^{x4} \) being the self-direct product of degree \( n \) of the matrix \( A_\phi \). Then the cylindrical average over \( \phi \) becomes

\[
\langle \langle T_\phi \rangle \rangle = \frac{1}{2\pi} \int_0^{2\pi} A^{x4}_\phi \langle T \rangle \ d\phi = \langle A^{x4}_\phi \rangle \langle T \rangle.
\]

The result of the integration of the 4-fold product of the transformation matrix and
its subsequent multiplication with the stiffness tensor \( (T = C) \) is shown below:

\[
\langle C \rangle = \begin{bmatrix}
  A & B & C \\
  B & A & C \\
  C & C & D \\
  0 & 0 & E
\end{bmatrix}
\]

Voigt average \hspace{1cm} (1-69)

where

\[
\begin{align*}
A &= \frac{1}{8} (3C_{11} + 3C_{22} + 2C_{12} + 4C_{66}) \\
B &= \frac{1}{8} (C_{11} + C_{22} + 6C_{12} - 4C_{66}) \\
C &= \frac{1}{2} (C_{13} + C_{23}) \\
D &= C_{33} \\
E &= \frac{1}{2} (C_{44} + C_{55}) \\
F &= \frac{1}{8} (C_{11} + C_{22} - 2C_{12} + 4C_{66})
\end{align*}
\]

As a result of similar operations, the cylindrically averaged compliance matrix can be written as

\[
\langle S \rangle = \begin{bmatrix}
  A & B & C \\
  B & A & C \\
  C & C & D \\
  0 & 0 & E
\end{bmatrix}
\]

Reuss average \hspace{1cm} (1-71)

where

\[
\begin{align*}
A &= \frac{1}{8} (3S_{11} + 3S_{22} + 2S_{12} + S_{66}) \\
B &= \frac{1}{8} (S_{11} + S_{22} + 6S_{12} - S_{66}) \\
C &= \frac{1}{2} (S_{13} + S_{23}) \\
D &= S_{33} \\
E &= \frac{1}{2} (S_{44} + S_{55}) \\
F &= \frac{1}{8} (S_{11} + S_{22} - 2S_{12} + S_{66})
\end{align*}
\]
1.3.6.2 Powder symmetry

To have estimates of the lower and upper bounds of polycrystalline materials, the transformation matrix

\[
A_{\phi\psi} =
\begin{bmatrix}
\cos\psi\cos\phi - \cos\theta \sin\phi \sin\psi & \cos\psi \sin\phi - \cos\theta \cos\phi \sin\psi & \sin\psi \sin\theta \\
-\sin\psi \cos\phi - \cos\theta \sin\phi \cos\psi & -\sin\psi \sin\phi - \cos\theta \cos\phi \cos\psi & \cos\psi \sin\theta \\
\sin\theta \sin\phi & -\sin\theta \cos\phi & \cos\theta
\end{bmatrix}
\]

(A-24)

needs to be integrated over all possible orientations by

\[
\langle \{ T_{\phi,\psi} \} \rangle = \frac{1}{2\pi} \int_0^{2\pi} \int_0^{2\pi} A_{\phi,\psi}^{x4} \{ T \} \, d\psi \, d\phi = \langle A_{\phi,\psi}^{x4} \rangle \{ T \},
\]

leading to an average matrix of the elastic constants (stiffnesses) of

\[
\langle C_{\phi,\psi} \rangle =
\begin{bmatrix}
A & B & B \\
B & A & B \\
B & B & A
\end{bmatrix}
\]

Voigt average (1-74)

with the following elements

\[
A = \frac{1}{15} (3C_{11} + 2C_{12} + 2C_{13} + 4C_{66} + 4C_{55} + 3C_{22} + 2C_{23} + 4C_{44} + 3C_{33})
\]

\[
B = \frac{1}{15} (C_{11} + 4C_{12} + 4C_{13} - 2C_{66} - 2C_{55} + C_{22} + 4C_{23} - 2C_{44} + C_{33})
\]

\[
C = \frac{1}{2} (A - B)
\]

(1-75)

This corresponds exactly to the symmetry of an isotropic material (see Table 1-2), which will be discussed in the following chapter.

Averaging the stiffnesses, the Reuss average of the material is obtained as

\[
\langle S_{\phi,\psi} \rangle =
\begin{bmatrix}
A & B & B \\
B & A & B \\
B & B & A
\end{bmatrix}
\]

Reuss average (1-76)

with the following elements
\[ A = \frac{1}{15} (3S_{11} + 2S_{12} + 2S_{13} + S_{66} + S_{55} + 3S_{22} + 2S_{23} + S_{44} + 3C_{33}) \]
\[ B = \frac{1}{15} \left( S_{11} + 4S_{12} + 4S_{13} - \frac{1}{2}C_{66} - \frac{1}{2}C_{55} + C_{22} + 4C_{23} - \frac{1}{2}C_{44} + C_{33} \right) \]  
\[ C = 2(A - B) \]

### 1.3.7 Isotropic Materials: Lamé Constants, Elastic Constants

As shown in the previous chapter and in Table 1-2, the matrix of the elastic constants of an isotropic material can be written as

\[
\begin{bmatrix}
C_{11} & C_{12} & C_{12} \\
C_{12} & C_{11} & C_{12} \\
C_{12} & C_{12} & C_{11}
\end{bmatrix}
\leftrightarrow
\begin{bmatrix}
2\mu + \lambda & \lambda & \lambda \\
\lambda & 2\mu + \lambda & \lambda \\
\lambda & \lambda & 2\mu + \lambda
\end{bmatrix}
\]

with

\[ \lambda = C_{12} \quad \text{1st Lamé constant} \]
\[ \mu = C_{44} - \frac{1}{2}(C_{11} - C_{12}) \quad \text{2nd Lamé constant} \]

In order to be mechanically stable (chapter 1.3.5), \( \mu \) and \((3\lambda + 2\mu)\) must be positive.

Most engineering materials like metals, polymers, or ceramics behave macroscopically as isotropic elastic solids. Since in many cases only the elongation or the shear in relation to the acting normal or shear force is of interest, macroscopic elastic constants are often used for a more intuitive description of the behavior of elastic materials. The four most frequently used constants are

- **Young's modulus** \( E \) describes the elongation of a body in a direction in relation to the stress acting in the same direction:
  \[
  E = \frac{\sigma_i}{\varepsilon_i} = \frac{(3\lambda + 2\mu)\mu}{\lambda + \mu} \quad (i = 1, 2, \text{ or } 3)
  \]

- **The shear modulus** \( G \) is a measure of the shear deformation of a body in depends of the acting shear stress:
  \[
  G = \frac{\sigma_i}{\varepsilon_i} = \mu \quad (i = 4, 5, \text{ or } 6)
  \]
\[ G = \frac{\sigma_i}{\varepsilon_i} = \mu \quad (i = 4, 5, \text{or} 6) \quad (1-81) \]

- The bulk modulus \( K \) indicates the volume change \( \Delta V \) of a material (with an initial volume of \( V \)) under a hydrostatic pressure \( \Delta \rho \):
  \[ K = -V\frac{\Delta \rho}{\Delta V} = \lambda + \frac{2}{3}\mu \quad (1-82) \]

- Finally, Poisson's ratio \( \nu \) is defined as the ratio of the lateral contraction to the longitudinal extension of the cylinder:
  \[ \nu = \frac{\varepsilon_j}{\varepsilon_{i \neq j}} = \frac{\lambda}{2(\lambda + \mu)} \quad (i, j = 1, 2, \text{or} 3) \quad (1-83) \]

Taking the criteria for the mechanical stability \( (\mu > 0, 3\lambda + 2\mu > 0) \), it follows that
  \[ -1 < \nu < \frac{1}{2} \quad (1-84) \]

where \( \nu = \frac{1}{2} \) indicates a constant volume upon deformation and smaller values stand for material dilatation (for most materials, \( \nu \) lies between 0.25 and 0.35).

Relations between these macroscopic constants and other physical quantities can be found in Ref. [vanKrevelen80].
2 Theory II - Atomistic Modeling

2.1 Representation of Potential Energy by a Force Field

2.1.1 Introduction

In a many-particle system - e.g. an atomistic model of a solid polymer - a considerable number of internal degrees of freedom exists, i.e. the system can adopt a huge number of conformations \( q_i \) with energies \( E(q_i) \). To compute a macroscopic property \( \langle A \rangle \) of a system with a fixed number of particles, cell size and temperature (an \( TN \) or canonical ensemble, chapter 2.4.3), the individual conformations must be weighted with their Boltzmann factors

\[
w(q_i) = e^{-\frac{E(q_i)}{kT}}
\]

and averaged according to McQuarrie76, Huang87

\[
\langle A \rangle = \frac{\sum_i w(q_i) \cdot A(q_i)}{\sum w(q_i)}
\]

\( A(q_i) \) is the value of the property of interest obtained from an conformation with energy \( E(q_i) \) and \( k \) is the Boltzmann constant.

It is therefore of prime interest to find an expression of the energy of a system as a function of the conformation of its constituents. The basic and most general way to find such an expression is an ab initio quantum mechanical computation of the energy of a molecular system. The calculation of the elastic constants of a polymer model typically involves hundreds and thousands of atoms and spans over several tenthousand to several hundredthousand simulation steps. This is just beyond the capabilities of present quantum mechanical methods, although first principle molecular dynamics has recently become quite powerful Car95a.

In the Born-Oppenheimer approximation, the electronic degrees of freedom can be separated from the nuclear degrees of freedom. In an ab-initio quantum mechanical calculation, the electronic energy of a molecule is given first by the kinetic and potential energy of the electrons moving in the field of the nuclei, second by the electrostatic repulsion between all pairs of electrons, and third by the exchange interaction due to the correlation of parallel spins Leach96. All these
interactions together with the electrostatic interaction of the positive nuclei form a complex energy hypersurface depending on the positions of the nuclei.

In modern class-II force fields, this energy hypersurface and its derivatives are approximated by more or less complicated functions of the positions of the nuclei. The functional form of the different terms of these force fields is chosen such that the fit with the huge amount of quantum mechanically computed data is best with a reasonable number of parameters. This is in contrast to class-I force fields, where functional forms derived from classical models of the different molecular interactions are parametrized against a limited amount of experimental data (like crystallographic structures obtained by X-ray diffraction, IR-spectra, density measurements, etc.). Representatives of this class of force fields are CHARMM and AMBER, whereas MM and CFF belong to class-II.

2.1.2 The CFF93 Force Field

A good example of a class-II force field is the CFF93 force field, which is well described in the literature. The MSI-Discover simulation package uses a close relative of this force field - PCFF91 - that was extended to work with polycarbonates and that was used for most of the simulations reported in the following chapters.

2.1.2.1 Methodology

The methodology of obtaining a class-II force field involves the following steps:

- The minimal energy configurations of a representative group of small molecules belonging to a particular class of compounds (e.g. alkanes, amides, etc.) are computed quantum mechanically using a HF/6-31G* basis set.
- After a normal mode analysis, the molecules are deformed by a random amount in the direction of the normal modes and ab initio calculations are performed on these structures to find the total energy, the first and the second derivatives of the energy, the dipole moments, and the derivatives of the dipole moments for each structure.
- Since the Hartree-Fock approximation excludes dispersion energies (chapter 2.1.3.2), the van-der-Waals parameters are determined empirically by fitting to crystal structures and sublimation energies. Because the charges from ab initio calculations with moderate basis sets usually do not reproduce the experimental electrostatic properties, the ab initio charges need to be scaled by a scaling factor obtained from crystal structures, too.
• The valence parameters (bond, angle, torsion, out-of-plane and cross terms) are calculated by fitting to the \textit{ab initio} energy surface with both the charges and the van-der-Waals parameters held fixed. The resulting set of parameters is called the QMFF (quantum mechanical force field).

• Due to systematic deviations between experiment and quantum mechanical calculations, a small set of scaling factors (for bond, angle, torsion, out-of-plane and cross terms) is needed. In addition it is necessary to make minor adjustments to bond reference values, $b_0$, since these are calculated systematically too short in the HF approximation.

The functional form that allows a good fit to the quantum mechanical energy hypersurface while using a reasonable number of parameters is given in Fig. 2.1. The thirteen terms can be classified first into bonded ($a - k$) and non-bonded ($l, m$) interactions. The bonded interactions further split into diagonal ($a - d$) and cross terms ($e - k$).

2.1.2.2 Bonded Interactions

a) Bond stretching: The quartic polynomial approximates the morse potential function ($D_0[1-e^{-\alpha (r-b_0)}]$) well near the reference distance $b_0^{\text{Leach96}}$ and prevents bonds from breaking under large stress as can be observed for cubic polynomials. The anharmonicity in the potential is crucial for a good fit to the quantum mechanical energy hypersurface$^{\text{HaglerMaple94a}}$.

b) Angle bending: In contrast to the bond stretching potential, the anharmonic third and forth order terms of the bond angle $\theta$ seem to be of minor importance for the total energy and its first and second derivatives$^{\text{HaglerMaple94a}}$.

c) Torsion potential: The reference angle ($0^\circ$) of the fourfold potential is given by the trans state of the torsion angle $\phi$.

d) Out-of-plane: The Wilson definition of the out-of-plane angle is used to compute the energy of the deviation of the three bonds surrounding an $sp^2$-hybridized atom from planarity. The $\chi$-value is the average of the angle between one bond and a plane defined by the two other bonds.

The following cross terms are essential for a good fit of the QMFF to the \textit{ab-initio} energy surface and must not be omitted$^{\text{Hagler94a}}$

e) Bond-bond cross term: The interaction energy between two bonds sharing a common atom (i.e. between the two bonds that form an angle). The number of these interactions equals the number of angles found in a molecular system.

f) Angle-angle cross term: The interaction energy between two angles sharing a common bond and a common central atom.

g) Bond-angle cross term: Two bond-angle interactions per angle contribute to
The terms of the cff93 force field

- **Bond**
  \[ \sum_b K^b_b (b-b_0)^2 + K^b_3 (b-b_0)^3 + K^b_4 (b-b_0)^4 \]

- **Angle**
  \[ \sum_b K^b_b (\theta-\theta_0)^2 + K^b_3 (\theta-\theta_0)^3 + K^b_4 (\theta-\theta_0)^4 \]

- **Torsion**
  \[ \sum_b K^b_b (1-\cos\phi) + K^b_3 (1-\cos2\phi) + K^b_4 (1-\cos3\phi) \]

- **Out-of-plane**
  \[ \sum_b K^b_b x^2 \]

- **Bond-Bond**
  \[ \sum_b \sum_{b'} (b-b_0) (b'-b'_0) \]

- **Angle-Angle**
  \[ \sum_b \sum_{b'} K^b_{bb'} (\theta-\theta_0) (\theta'-\theta'_0) \]

- **Bond-Angle**
  \[ \sum_b K^b_b (b-b_0) (\theta-\theta_0) \sum_{b'} \sum_b K^b_{bb'} (\theta-\theta_0) (\theta'-\theta'_0) \]

- **End-Bond-Torsion**
  \[ \sum_b (b-b_0) [K^b_b \cos\phi + K^b_3 \cos2\phi + K^b_4 \cos3\phi] \]

- **Middle-Bond-Torsion**
  \[ \sum_b \sum_{b'} (b-b_0) [K^b_{bb'} \cos\phi + K^b_2 \cos2\phi + K^b_3 \cos3\phi] \]

- **Angle-Torsion**
  \[ \sum_b \sum_{\phi} K^b_{\theta\phi} (\theta-\theta_0) (\theta'-\theta'_0) \cos\phi \]

- **Angle-Angle-Torsion**
  \[ \sum_b \sum_{\phi} \sum_{\phi'} K^b_{\theta\phi\theta'} (\theta-\theta_0) (\theta'-\theta'_0) \cos\phi \]

- **Nonbonded interactions**
  \[ \sum_{i<j} \frac{1}{4\epsilon_{ij}} \left( \frac{q_i q_j}{r_{ij}} \right)^6 - \left( \frac{q_i q_j}{r_{ij}} \right)^4 \]
the cross term energy.

h) **End-bond-torsion** cross term: For each torsion angle, there are two end-bond-torsion cross terms and one

i) **Middle-bond-torsion** cross term.

j) **Angle-torsion** cross term: As with the bond-torsion interactions, there are two angle-torsion contributions and one

k) **Angle-angle-torsion** cross term per torsion angle.

### 2.1.2.3 Nonbonded Interactions

l) **Coulomb** interaction and

m) **van-der-Waals** interaction: These two interactions are computed between all pairs of nonbonded atoms. Two atoms are denoted nonbonded, if at least three bonds lie between them, i.e. there are nonbonded interactions between the first and last atom of a torsion angle. Since the nonbonded interactions are essential for the behavior of condensed systems, they will be discussed in greater detail below.

### 2.1.3 Nonbonded Interaction Potentials

#### 2.1.3.1 General Remarks

The interaction energy of an assembly of molecules \(i, j, k...\) can be written in form of a series of the sum of pairwise interaction terms, the sum of three-body terms, four-body terms and so on:

\[
U(r, \Omega) = \sum_{i>j} U_{ij} + \sum_{i>j>k} U_{ijk} + \sum_{i>j>k>l} U_{ijkl} + ... \tag{2-3}
\]

In the first instance, it is assumed that only the pairwise interaction term is of significance for the energy of the nonbonded interactions. Corrections to this picture are however necessary and will be outlined later.

#### 2.1.3.2 Quantum Mechanical Foundations

The functional form of the nonbonded interactions has been the subject of intense research since Boscovich formulated the first potential more than 200 years ago\(^{Kaplan86}\). In general, the interaction energy \(U(r, \Omega)\) between neighboring molecules is a sum of the following terms\(^{Stone96}\).

\[
U(r, \Omega) = U_{el}^{(1)} + U_{ex}^{(1)} + U_{ind}^{(2)} + U_{dis}^{(2)} + U_{ex-pot}^{(2)} + U_{(3...n)}, \tag{2-4}
\]

with \(U_{el}\) being the *electrostatic* interaction, which is composed of attractive terms between the nuclei of one molecule and the electrons of the other molecule and repulsive terms between the nuclei and between the electrons on the two mole-
molecules. $U_{\text{ex}}$ is the so-called exchange energy, which has its origins in the Pauli principle limiting the electron density. These two contributions are first-order approximations (as indicated by the superscript index) of the Rayleigh-Schrödinger perturbation theory applied to the total Hamiltonian. This Hamiltonian, the zeroth-order approximation, is obtained by a simple overlap of the molecular wave-functions $\Psi^A$ and $\Psi^B$. The induction, $U_{\text{ind}}$, and the dispersion term, $U_{\text{dis}}$, are second-order approximations of the perturbation caused by the mutual influence of the electrons in one molecule on the electrons in the other molecule. The induction can be explained classically as the formation of a dipole in a non-polar molecule due to a charge or a permanent dipole on the other molecule. The dispersion interaction has its origins in fluctuations of the electron density with time, which lead to the formation of momentary multipoles. These fluctuating multipoles induce charge separations in neighboring molecules and therefore interact with them in a analogous way to the mechanism of induction. Higher order approximations, symbolized by $U^{(3-n)}$, are not taken into consideration, and the second order approximation (polarization) of the exchange interaction, $U_{\text{ex-pol}}$, is regarded both as being marginal in effect and difficult to handle theoretically\cite{Kaplan86,Rataczak80a,Murrell76}.

All these terms depend of course on the distance $r$ and the mutual orientation $\Omega$ of the interacting molecules. The distance dependence of the various energy terms is of special interest and forms the topic of the next section.

### 2.1.3.3 Lennard-Jones Potential

If the molecules are very close to each other, their wave-functions overlap and the exchange interaction is the dominating term in the energy function. It is possible to show that this exchange term is proportional to $e^{-\alpha(R - 1)}$,\cite{Stone96} where $\alpha$ is a constant - typically between 12 and 15 - and $R = r/\sigma^*$, with $\sigma^*$ being the minimum energy distance (see Fig. 2.2).

At larger distances, the dispersion energy is the dominant term in the van-der-Waals energy, since the induction energy is much smaller in general. Using the simple dipolar model of Drude\cite{DrudeMaitlandRigby81}, the most important contribution in a power expansion of the interaction energy,

$$U_{\text{dis}}(r) = C_6/r^6 + C_8/r^8 + C_{10}/r^{10} + \ldots,$$

is the dispersion coefficient $C_6$, i.e. the electrostatic interactions decay with $r^6$ (Fig. 2.2). (The dispersion coefficients of higher order become more important, if quadrupoles, octupoles etc. are included in the Drude model.\cite{Leach96}) The dispersion coefficient $C_6$ can be approximated by the London formula,\cite{Kaplan86}
2.1 Representation of Potential Energy by a Force Field

\[ C_6 = \frac{3 U_A U_B}{2 (U_A + U_B)} \frac{\alpha_A \alpha_B}{(4 \pi \varepsilon_0)^2}, \]  

(2-6)

with \( \alpha_A \) and \( \alpha_B \) standing for the average polarizabilities and \( U_A \) and \( U_B \) denoting the average excitation energies, which in turn can be approximated in the Slater-Kirkwood formula as \(^{Stone96}\)

\[ U_A \approx \left( \frac{N_A}{\alpha_A} \right)^{\frac{1}{2}}. \]  

(2-7)

At very large distances above several hundred Å, the dispersion interaction is not proportional to \( r^{-6} \), but to \( r^{-7} \), because then the period of the charge fluctuations is comparable to the time required for the exchange of information by electromagnetic waves between the molecules (relativistic retardation effect) \(^{Kaplan86}\).

![Figure 2.2: Functional form of the exchange and dispersion energy as a function of the intermolecular distance r](image)

The combination of repulsive exchange and attractive dispersion and induction terms is denoted \( U_{tot} \) in Fig. 2.2 and is approximated in many applications by a Lennard-Jones \( m-n \)-potential function, \(^{AllenTildesley89}\)

\[ U_{LJ}^{\alpha\beta} = 4 \varepsilon_{\alpha\beta} \left[ \frac{(\sigma_{\alpha\beta})^m}{r} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^m \right], \]  

(2-8)

where the indices \( \alpha \) and \( \beta \) refer to the interacting atom types. Besides the above \( m-n \) form, exponential-6 potentials like the Hill and Buckingham
\( U_B = \frac{\varepsilon}{\alpha - 6} \left[ 6\varepsilon^{-\alpha}(x - 1) - \alpha x^6 \right] \) potential are also used.

For the attractive second term of Eq. (2-8), the exponential \( n \) is almost always 6, according to the distance dependence of the dispersion and induction interaction, whereas the exponential rise of the exchange interaction is approximated with a large value of \( m \), typically in the range of 9 - 12 (compare Fig. 2.2: the curve denoted by \( U_{\text{LJ}} \) is a 12-6-potential function, that approximates the quantum mechanical potential \( U_{\text{ex}} + U_{\text{dis}} \) quite well). The \text{ccf93} forcefield uses a 9-6 Lennard-Jones potential function to model the van-der-Waals interaction.

If the well depth \( \varepsilon \) and the radius of minimum energy \( \sigma^* \) (instead of the collision diameter \( \sigma \)) is used, Eq. (2-8) takes the form

\[
U_{\text{LJ}}^{\alpha \beta} = \varepsilon_{\alpha \beta} \left[ \frac{n}{m - n} \left( \frac{\sigma_{\alpha \beta}^*}{r} \right)^m - \frac{m}{m - n} \left( \frac{\sigma_{\alpha \beta}^*}{r} \right)^n \right] = \frac{A_{\alpha \beta}}{r^m} - \frac{B_{\alpha \beta}}{r^n},
\]

which is also used in some force fields. A comparison between Eq. (2-8) and (2-9) immediately reveals that

\[
A_{\alpha \beta} = 4\varepsilon_{\alpha \beta} \sigma_{\alpha \beta}^{12} \quad B_{\alpha \beta} = 4\varepsilon_{\alpha \beta} \sigma_{\alpha \beta}^6
\]

and

\[
\sigma_{\alpha \beta} = (A_{\alpha \beta} / B_{\alpha \beta})^{1/6} \quad \varepsilon_{\alpha \beta} = B_{\alpha \beta}^{2/4} A_{\alpha \beta}.
\]

The two adjustable parameters \( \sigma \) and \( \varepsilon \) are obtained from experimental densities, molecular beam cross sections, etc. For nonbonded interactions between two different types of atoms \( \alpha \) and \( \beta \), so called mixing rules have to be used. There are the commonly used Lorentz-Berthelot mixing rules,

\[
\sigma_{\alpha \beta} = \frac{1}{2} (\sigma_{\alpha \alpha} + \sigma_{\beta \beta}),
\]

\[
\varepsilon_{\alpha \beta} = \sqrt{\varepsilon_{\alpha \alpha} \varepsilon_{\beta \beta}},
\]

and the more recent rules form Hagler et al. \cite{HaglerWaldman93a}

\[
\sigma_{\alpha \beta} = \left( \frac{\sigma_{\alpha \alpha}^6 + \sigma_{\beta \beta}^6}{2} \right)^{1/6}
\]

\[
\varepsilon_{\alpha \beta} = 2 (\varepsilon_{\alpha \alpha} \varepsilon_{\beta \beta})^{1/2} \left[ \frac{\sigma_{\alpha \alpha}^3 \sigma_{\beta \beta}^3}{\sigma_{\alpha \alpha}^6 + \sigma_{\beta \beta}^6} \right]^{1/6}
\]

which seem to give consistently more accurate results.
2.1.3.4 Coulomb Interaction

Since electrons in molecules are not located at fixed points but distributed according to their wavefunctions over a (theoretically infinite) region in space, it is only possible to establish a probability density. However, the computation of nonbonded coulombic interactions between molecules based on quantum mechanical probability densities would be extremely time-consuming and difficult to perform. A number of methods to map this electron densities to a set of point charges or multipoles has been devised (Mulliken, Löwdin, Bader, etc.). Alternatively, the electrostatic potential in the vicinity of a molecule can be determined and a set of charges can be calculated that fits this electrostatic potential best. There also exist approaches based on the electronegativity of the atoms. In the cff93 force field, the charges are assigned incrementally bond per bond and located at the nuclear positions.

The result of such mapping is either a series of electronic moments - charges (monopoles), dipoles, quadrupoles, octupoles, and so on - that describe the molecule as a whole, the so-called central multipole expansion, or a set of point charges or distributed multipoles at various locations. If the point charges are placed at the positions of the nuclei, the calculation of the forces acting on the nuclei becomes particularly simple. On the other hand, it is not always possible to represent the complex electron density by a few point charges on the positions of the atoms.

An arbitrary distribution of charges $q_i$ at positions $x_{i,j}$ can be grouped into the following quantities:

<table>
<thead>
<tr>
<th>Moment</th>
<th>Tensor rank</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total charge $Q$</td>
<td>0 (scalar)</td>
<td>$Q = \sum q_i$</td>
</tr>
<tr>
<td>Dipole $\mu$</td>
<td>1 (vector)</td>
<td>$\mu_j = \sum q_i x_{i,j}$</td>
</tr>
<tr>
<td>Quadrupole $\Theta$</td>
<td>2</td>
<td>$\Theta_{jk} = \sum q_i x_{i,j} x_{i,k}$</td>
</tr>
<tr>
<td>higher moments</td>
<td>$n$</td>
<td>$M_{j,n} = \sum q_i(x_{i,j} \cdots x_{i,n})$</td>
</tr>
</tbody>
</table>
The classical electrostatic interaction between two scalar monopoles $q_i$ and $q_j$, given by Coulomb’s well-known formula,

$$U_{el} = \frac{1}{4\pi \varepsilon_0} \frac{q_i q_j}{r_{ij}},$$

depends as $r^{-1}$ on the distance. The interaction energy between a monopole and a dipole drops as $r^{-2}$, whereas dipole-dipole interactions are proportional to $r^{-3}$. In general, the interaction energy between two electronic moments of rank $m$ and $n$ decreases as $r^{-(m+n+1)}$. In the case of the interaction between neutral molecules or neutral groups of atoms, where only dipoles and higher moments exist, the energy is proportional to $r^{-3}$, if the distance between the groups is larger than the size of the groups themselves.

2.1.3.5 Many-Body Effects

As mentioned in chapter 2.1.3.1, three-body and higher interaction terms are neglected in most cases, the remarkable gain in computation time justifies this simplification. While the bonded interactions are proportional to $N$, the number of atoms in the system, the pairwise interactions are proportional to $N(N-1)/2$ operations and three-body terms to $N(N-1)(N-2)/6$.

There are, however, some cases where the three-body terms contribute significantly to the nonbonded energy or lead to completely different results. Examples comprise the well-known Ar-crystals, where the contribution of the Axilrod-Teller triple-dipole correction amounts to 10 - 20% Leach96, BellZucker76, Murrell76, and the modelling of ionic crystals of large halides and earth-alkaline metals, that leads to wrong structures if the polarization of the large halides due to Mg$^{2+}$ or Cd$^{2+}$ ions is neglected.Stone96

2.2 Modeling of Extended Dense Systems

With the force field derived in chapter 2.1, it is possible to model single molecules or assemblies of molecules in vacuo, but not extended solid or liquid matter. Even the smallest macroscopic bodies (grains or cells) contain $O(10^{10}-10^{20})$ atoms, which makes it impossible to simulate them as a whole. If only $O(10^2-10^3)$ atoms are used in a simulation - which is an appropriate number for current computers - most of them would be at or near the surface of the tiny body. The simulation of bulk properties would not be feasible this way. An elegant solution to this problem are the so-called periodic continuation conditions (PCC), also referred to as periodic boundary conditions (PBC).
2.2.1 Periodic Continuation Conditions

Periodic continuation conditions enable the modeling of bulk properties of solids or liquids with a relatively small number of atoms. Imagine a box with parallel walls (a parallelepiped) being replicated in all directions to give a periodic array. The walls of the box are pervious to the particles in it, so no physical boundaries are present. Particles leaving one side of the box, enter it at the opposite side immediately (compare Fig. 2.3), keeping the number of particles $N$ constant. In principle, there exist 5 cell shapes, that fill space completely by translation from a central cell: the parallelepiped (and its special form, the cube), the hexagonal prism, the truncated octahedron, the rhombic dodecahedron and the ‘elongated’ dodecahedron.\textsuperscript{96} Leach In this work, only the cube and the parallelepiped are used, because of the simple numeric implementation of these two conditions.\textsuperscript{89} Allen

The use of PCCs invokes some problems: First, fluctuations with wave-lengths greater than the dimensions of the box are not possible, the phonon spectrum is cut. Second, the radial distribution function $g_{ab}(r)$ is not exactly isotropic.\textsuperscript{96} Frenkel

The simulation cell is defined by $n$ vectors, with $n$ being the dimensionality of the simulation space (typically 3-dimensional), which form a $n \times n$ cell shape matrix $h$ (chapter 1.2.3.1):

$$
\mathbf{h} = \begin{bmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{bmatrix}
$$

\text{Fig. 2.3: Periodic continuation conditions in two dimensions}
2.2.2 Long-range Interactions

The introduction of the PCC creates a virtually infinite, quasi-crystalline simulation system without boundaries. Since this would imply an infinite number of interactions between the atoms in the central cell and all their replicas, the nonbonded interactions can not be evaluated explicitly. Several methods are used to circumvent this problem: for van-der-Waals interactions, a cutoff plus a correction term is reasonable, while more sophisticated methods like Ewald summation or cell multipole expansion are needed for the Coulomb interactions.

2.2.2.1 Cutoffs

A cutoff truncates the computation of nonbonded interactions between a central atom and the other atoms of a system at a certain distance. If the cutoff-radius is larger than the smallest cell extension ($r_d$ in Fig. 2.3), the central atom interacts with its replicas, causing unphysical finite-size effects. It is therefore useful to keep the radius of the interaction sphere smaller than half the smallest dimension of the box ($r_c$ in Fig. 2.3). In this case, the minimum image convention is applied, stating that each atom 'sees' at most just one image of every other atom in the system.

Using a step function (like the Heavyside function) to define a cutoff causes problems because of the discontinuities in the potential function and its derivatives (i.e. the forces). So a switching function $S(r)$ (Fig. 2.4) smoothly switches

![Diagram of 9-6 Lennard-Jones potential and switching function](image)

Figure 2.4: Cutoff applied to a 9-6 Lennard-Jones potential (Cutoff = 8Å, Spline = 2Å)
the nonbonded interactions from their full values at $r_f = r_c - r_s$ to zero at $r_c$. The most common switching function is a quintic spline, defined by the conditions, that the first and second derivatives at $r_f$ and $r_c$ are zero and $S(r_f) = 1$ and $S(r_c) = 0$:

$$S(r) = c_0 + c_1 r + c_2 r^2 + c_3 r^3 + c_4 r^4 + c_5 r^5$$

with

$$c_0 = r_c^6 \left( \frac{6 r_c^2 - 15 r_c r_s + r_s^2}{r_s^5} \right)$$

$$c_1 = -30 r_c^2 \left( \frac{r_c^2 - 3 r_c r_s + r_s^2}{r_s^5} \right)$$

$$c_2 = 30 r_c \left( \frac{2 r_c^2 - 3 r_c r_s + r_s^2}{r_s^5} \right)$$

$$c_3 = -10 \left( \frac{6 r_c^2 - 6 r_c r_s + r_s^2}{r_s^5} \right)$$

$$c_4 = -15 (r_s - 2 r_c) / r_s^5$$

$$c_5 = -6 / r_s^5$$

Even this smooth splining function causes considerable changes in the first and second derivatives of the interaction energy, which can lead to artifacts e.g. in the simulation of Ar-Crystals.a.

The cutting of the long-range interactions can be *atom-based* or *group-based*: If a cutoff is atom-based, the nonbonded interaction between two atoms is taken into account if the distance between the two atoms is smaller than the cutoff-distance. This check is made for every pair of atoms. Group-based algorithms perform the calculation of nonbonded interactions between two groups of atoms only if the two switching atoms are closer than the cutoff distance. If the groups of atoms are such, that the individual atomic charges sum up to zero, i.e. the group is neutral, the first term in the Coulombic energy potential is the dipole-dipole interaction, which is proportional to $r^{-3}$ (chapter 2.1.3.4). Furthermore, the unphysical situation of having a net charge in the sphere of the cutoff is avoided by this procedure.

### 2.2.2.2 Tail Correction for Lennard-Jones Potentials

The attractive part of the Lennard-Jones interaction energy beyond a cutoff $r_c$ is expressed by Theodorou85a:

---

a. S. Santos, private communication (1996)
\[ U_{\text{tail}} = \frac{1}{2} \sum_{\alpha=1}^{n} \sum_{\beta=1}^{n} N_{\alpha} \rho_{\beta} 4\pi \int_{r_{c}}^{\infty} g_{\alpha\beta}(r) U_{LJ}^{\alpha\beta}(r) r^2 dr - \int_{r_{c}}^{\infty} g_{\alpha\beta}(r) U_{LJ}^{\alpha\beta}(r) S(r) r^2 dr \]  

(2-16)

where \( \alpha \) and \( \beta \) run over all different forcefield-types of atoms, \( N_{\alpha} \) denotes the number of atoms \( \alpha \) and \( \rho_{\beta} \) the density of \( \beta \) atoms in the simulation cell. The volume element of the integration is a shell with a volume of \( 4\pi r^2 dr \) and \( g_{\alpha\beta} \) is the pair distribution function of \( \alpha \) and \( \beta \) (chapter 3.1.1).

Using a \( m-n \) Lennard-Jones interaction potential,

\[ U_{LJ}^{\alpha\beta} = 4\varepsilon_{\alpha\beta} \left[ \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{m} - \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{n} \right] \]  

(2-8)

where \( r = |r_{\beta} - r_{\alpha}| \), and the assumption, that \( g_{\alpha\beta} = 1 \) if \( r > r_{c} \), the integration of the shaded area in Fig. 2.4 leads to

\[ U_{\text{tail}} \approx \sum_{\alpha=1}^{n} N_{\alpha} \sum_{\beta=1}^{n} 8\pi \varepsilon \left[ \frac{r_{f}^3}{3-n} \left( \frac{\sigma_{\alpha}}{r_{f}} \right)^{n} - \frac{r_{f}^3}{3-m} \left( \frac{\sigma_{\beta}}{r_{f}} \right)^{m} - S \left( r_{c}, m \right) \left( \frac{\sigma_{\alpha}}{r_{c}} \right)^{m} \right] \]  

(2-17)

The integration at \( r = \infty \) is zero only if \( n,m > 3 \) (this makes it impossible to use this method to estimate the long-range corrections for Coulombic interactions, which decay as \( \frac{1}{r} \)). The function \( S(r,p) \) is defined by

\[ S'(r,p) = r^3 \left[ \frac{c_0}{3-p} + \frac{c_1 r}{4-p} + \frac{c_2 r^2}{5-p} + \frac{c_3 r^3}{6-p} + \frac{c_4 r^4}{7-p} + \frac{c_5 r^5}{8-p} \right] , \]  

(2-18)

with the singular term \( \left( \frac{c_n r^n}{n+3-p} \right) \), with \( n = p - 3 \) replaced by \( c_n r^n \ln r \).

This energy expresses itself in forces that are all attractive, because at \( r > r_{\text{cutoff}} \) the repulsive term is negligible. To include this long-range effect, an external pressure is applied to the system, so that its energy contribution equals the tail correction energy:

\[ \rho_{\text{corr}} V = U_{\text{tail}} \quad \rho_{\text{corr}} = \frac{U_{\text{tail}}}{V} \]  

(2-19)

The pressure \( \rho_{\text{corr}} \) is called the tail correction pressure. For dense polymeric systems and cutoffs of 8-9 Å, it is in the range of 500-2000 bar.
2.2.2.3 Tail Corrections for Coulombic Interactions

The long-range Coulombic interactions are far more difficult to deal with due to two reasons:

First, the Coulombic energy terms are farther-reaching than the van-der-Waals contributions; they decay as $r^{-1}$ for monopole-monopole interactions and still as $r^{-3}$ in the case of dipolar interactions, whereas the van-der-Waals energy drops as $r^{-6}$. The error introduced by cutting off the interactions at a relatively small distance of 8-10 Å is considerable.

Second, there are negative and positive interaction energies (attractive and repulsive forces) depending on the distribution of the monopoles or the mutual orientation of the dipoles. This prevents an integration of the neglected interactions as in Eq. (2-16) and leads to a quasi-random dependence of the coulombic energy from the cutoff distance (Fig. 2.5). This behavior is less pronounced for the group-based calculations than for the atom-based, but still too large to obtain reliable results for crystalline systems. Amorphous polymers with relatively small partial charges are not as problematic as the highly charged, dense polymer crystals of Cellulose, Nylon etc., which need special methods to deal with the long-range Coulombic interactions. One of the first of these methods, the Ewald summation, will be briefly discussed now:

For a cubic lattice (extension to general cell shapes is straightforward), with
$N$ charges $q_i$ in the simulation cell, the energy of the charge-charge interaction between all pairs of charges in the central cell and between the central cell and all surrounding cells is

$$U_{\text{Coul}} = \frac{1}{2} \sum_{|n| = 0}^{\infty} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{q_i q_j}{4\pi \varepsilon \varepsilon_0 |r_{ij} + n|}; \quad (2-20)$$

the position of a remote cell is given by the vector $n$. For $n=0$, the summation does not include terms, where $i=j$. The above sum is only conditionally convergent, i.e. the convergence rate is low and depends on the order of the summation of its terms.\cite{Heyes81a}

The idea behind the Ewald summation is, that the sum in Eq. (2-20) is replaced by two sums with better convergence properties. One of the summations is carried out in real space, namely the summation of the original point charges plus a neutralizing charge distribution of equal magnitude and opposite sign (Fig. 2.6). The added charge distribution is compensated by the second

![Figure 2.6](image)

Figure 2.6: The point charges are surrounded by gaussian distributed charge clouds in real space, which are cancelled by charge clouds of opposite sign in the reciprocal space.

summation, which adds up - in reciprocal space - a cancelling distribution of opposite sign. The distribution function is of minor importance, typically a Gaussian
2.2 Modeling of Extended Dense Systems

\[ \rho_i(r) = \frac{q_i \kappa^3}{\pi \frac{3}{2}} \exp \left( -\kappa^2 r^2 \right) \]  (2-21)

A third term is necessary subtracting the self-interaction of each Gaussian in real space. The forth term finally takes into account that there is a medium with a permittivity \( \varepsilon \) beyond the cells taken into the summation. The final form of the Ewald summation looks as follows \cite{Leeuw80, Leach96, Heyes81a}:

\[ U_{coul} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \left( \sum_{n=0}^{\infty} \frac{q_i q_j \text{erfc} \left( \kappa \left| r_{ij} + n \right| \right)}{4 \pi \varepsilon_0 \left| r_{ij} + n \right|} \right) + \sum_{k=0}^{N} \sum_{l=1}^{N} \frac{4 \pi^2}{k^2} \exp \left( -\frac{k^2}{4 \kappa^2} \right) \cos \left( \mathbf{k} \cdot \mathbf{r}_{ij} \right) - \frac{\kappa}{\sqrt{\pi}} \sum_{k=1}^{N} \frac{q_k^2}{4 \pi \varepsilon_0} \right. 
\]

\[ + \frac{2 \pi}{3 L^3} \sum_{k=1}^{N} \frac{q_k r_k^2}{4 \pi \varepsilon_0} \]  (2-22)

The parameter \( \kappa \) of the convergence function \( \text{erfc}(r, \kappa) = 1 - \text{erf}(r, \kappa) = 2/\sqrt{\pi} \int_r^\infty \exp(-t^2) dt \) and the Gaussian determines the number of terms in the real and reciprocal space summation: The smaller \( \kappa \), the faster the reciprocal space calculations converges, whereas a large \( \kappa \) improves the convergence of the real space calculations. Optimization of \( \kappa \) is therefore necessary to minimize computation times \cite{Karasawa89a}

For large systems, the Ewald summation is quite slow, since it scales as \( N^2 \). The cell multipole expansion exhibits a linear dependence on \( N \) and is therefore well suited for large systems with considerable partial charges. The idea of the method is to divide the central simulation cell into small cubic subcells of a few atoms and to compute the monopole, dipole and higher electric moments (Fig. 2.7). The interaction between the central cell and surrounding subcells is taken pairwise, if the distance between the central cell and the subcells is larger than the size of the subcells. For larger distances, the subcells are grouped into larger entities and their moments are added. With increasing distance, the influence of the larger cells becomes smaller and thus the error is kept at a more or less constant level.

Another way of taking the far reaching Coulomb terms into account is given by the reaction field method, where a sphere of the size of the cutoff radius is constructed around a dipole \( \mu_i \) containing \( N \) atoms with a total dipole moment of
\[ E_i = \frac{2(\varepsilon_s - 1)}{\varepsilon_s + 1} \left( \frac{1}{r_c^3} \right) \sum_{r_i \leq r_c}^N \mu_i. \]  

(2-23)

2.2.3 Introduction of Strain and Stress

The concept of a cell with PCCs allows the implementation of strains and stresses, which have already been discussed in chapter 1.

The finite strain of a cell \( h \) with respect to a reference cell \( H \) is given by

\[ \eta = \frac{1}{2} \left[ H^{-1} h' h H^{-1} - I \right]. \]  

(1-36)

and the finite stress by

\[ t = J H h^{-1} P h^{-1} H. \]  

(1-46)

2.3 Energy Minimization Methods

2.3.1 Introduction

Once an energy representation of an atomistic system with \( N \) atoms is established, the total potential energy \( U \), its gradient \( g \), and its second derivative \( H \) (the Hessian) as a function of the atomic coordinates \( x \) can be specified as
\[ U = U(x), \quad g = \nabla U = \frac{\partial U}{\partial x_i} \quad \text{and} \quad H = \nabla^2 U_{ij} = \frac{\partial^2 U}{\partial x_i \partial x_j}. \tag{2-24} \]

\( U(x) \) forms a complicated hypersurface in \( 3N - 5 \) dimensions, with maxima \( (g(x_M)=0, H(x_M)<0) \), minima \( (g(x_m)=0, H(x_m)>0) \) and saddle-points \( (g(x_s)=0, \ H_{ij}(x_s)>0, \ H_{kk}(x_s)<0) \). The minima are of special interest, because the system is most probably located at low energy conformations (Eq. (2-1)). This section therefore deals with numerical methods that minimize a high-energy structure. Except for the simulated annealing, all these methods just find the nearest local minimum, regardless how high its energy might be.

![Figure 2.8: Extrema of a function of an arbitrary coordinate in an interval \([x_1, x_2]\). The minima \( B, D, \) and \( F \) consist of the local minima \( B \) and \( F \) and the global minimum \( D \). \( A, C, \) and \( E \) are maxima with \( A \) being the global maximum and \( G \) is a saddle-point.](image)

If, for example, the starting point of the minimization of the simple function in Fig. 2.8 lies between \( A \) and \( C \), the high-energy, local minimum \( B \) will be the result of the numerical evaluation. Since this local minimum contributes nearly nothing to the average of Eq. (2-2), it would be of interest not only to find local minima but to specify the global minimum. Except for the smallest systems of a few atoms, the high dimensionality of the conformation space prohibits the necessary systematic search.

The minimization methods can be categorized by the order of the derivatives involved in the computation. There are simple methods that need only function evaluations, so-called zeroth-order algorithms, whereas more efficient ones require the computation of gradients (first-order) and the fastest, yet least robust ones demand the matrix of the second derivatives, the Hessian. In the last para-
(2.3.5) the method of simulated annealing is discussed, which tries to find the global minimum instead of a local one.

In general, all the methods summarized below do not find an exact minimum, but approach it more or less. From a numerical point of view, convergence is achieved, if the change in energy between successive steps is smaller than $\varepsilon$ (the computer's floating point precision). This limits the exactness of the position of the atoms to about $\sqrt{\varepsilon}$. \cite{Pressetal92}

### 2.3.2 Zeroth-order Algorithms

Zeroth-order algorithms rely only on direct function evaluations without the use of gradients or derivatives of higher order. They are therefore quite simple to program and efficient in memory usage. The most simple line search algorithm finds a minimum in a one-dimensional curve by bracketing and is used by first-order methods too. The more advanced simplex routine is able to find a local minimum in an $M$-dimensional conformation space, but will not be discussed here.

#### 2.3.2.1 Line-search Algorithm

Consider a function of one variable and three initial points $x_1$, $x_2$ and $x_3$ given by Fig. 2.9. This function might well be a one-dimensional cross-section through a multidimensional hypersurface.

![Figure 2.9: Bracketing the minimum of a one-dimensional function $f(x)$](image)

Since the function value $f(x_2)$ is smaller than the neighboring $f(x_1)$ and $f(x_3)$, the minimum must be between $x_1$ and $x_3$. The bracketing algorithm now chooses a new point $x_4$ in this interval on one or the other side of $x_2$. If this new point is
smaller than \( x_2 \), the new interval lies between \( x_1 \) and \( x_2 \) (in the above figure). The same procedure is repeated at \( x_5 \) and \( x_6 \). If the function value at the new point is higher than the central value, the border of the interval is shifted to this new position, otherwise the new point becomes the central point and the border is moved to the former central point.\textsuperscript{Pressetal92}

The optimal bracketing interval

\[
\frac{x_3 - x_2}{x_3 - x_1} = \frac{x_4 - x_1}{x_2 - x_1} = \ldots = \frac{3 - \sqrt{5}}{2} \approx 0.38197
\]

allows to control the precision of finding the minimum by varying \( \sigma \): \( \sigma=0 \) enforces an exact search for the algorithm, whereas \( \sigma>0 \) produces a weak line search.\textsuperscript{Harley86}

### 2.3.3 First-order Algorithms

These algorithms are widely used in atomistic simulations, because they combine robustness with efficiency and thus normally lead to well converged structures. The most straightforward method is the

#### 2.3.3.1 Steepest Descent Method

where the local gradient \( \nabla U(x) \) is taken as the direction, in which a line search (section 2.3.2.1) is performed. The minimum of this one-dimensional cross-section is the new starting point \( x_n \) of the next iteration. At \( x_n \), the gradient \( \nabla U(x_n) \) is orthogonal to the initial gradient. This behavior can lead to slow convergence, if the potential energy surface forms a long narrow valley, in which the algorithm performs a zig-zag (Fig. 2.10).\textsuperscript{MDIScover1}

At every step, part of the information obtained in the previous minimization is lost again due to an overcorrection of errors. This can be prevented by the

#### 2.3.3.2 Conjugate Gradient Minimization

Here, the directions \( h_i \) and \( h_{i+1} \) of two successive line minimizations are not
orthogonal but form a conjugate set, with mutually orthogonal local gradients \( g_i \). This is achieved by taking \( h_{i+1} \) as

\[
h_{i+1} = g_{i+1} + \gamma_i h_i
\]

(2-27)

with

\[
\gamma_i = \frac{g_{i+1} \cdot g_{i+1}}{g_i \cdot g_i}
\]

(Polak-Ribiere) \hspace{1cm} (2-28)

or

\[
\gamma_i = \frac{(g_{i+1} - g_i) \cdot g_{i+1}}{g_i \cdot g_i}
\]

(Fletcher-Reeves). \hspace{1cm} (2-29)

With the above set of line search directions \( h_i \), the nearest local minimum of an energy function in \( M \) dimensions is reached exactly in \( M \) steps, if the function \( U(x) \) has a quadratic form like

\[
U(x) = U(P) + g(P) \cdot x + \frac{1}{2} x \cdot H(P) \cdot x,
\]

(2-30)

with \( P \) being at the origin of the coordinate system \( x \). If the energy function is not exactly quadratic, repeated cycles of \( M \) line minimizations are necessary, but the convergence to the minimum is quadratic.

### 2.3.4 Second-order Algorithms

#### 2.3.4.1 The Newton-Raphson Method

Taking Eq. (2-30), the gradient of \( U(x) \) at \( x \) can be expressed as

\[
g(x) = H(P) \cdot x - g(P).
\]

(2-31)

Using the fact, that at a local minimum the gradient \( g(x_m) \) is zero, solving the equation

\[
H(P) \cdot x_m = g(P) \quad \Leftrightarrow \quad x_m = H^{-1}(P) \cdot g(P)
\]

(2-32)

would lead immediately to the minimum of a quadratic energy function. For
anharmonic potentials, a number of iterations would be necessary, but convergence would be achieved quadratically.\textsuperscript{Harley86}

However, this method has a number of drawbacks, which prevent a unmodified implementation. The second derivatives are sometimes difficult to compute and the full Hessian requires $O(N^2)$ memory, which can be prohibitive for large ($M\sim 3N >1000$) systems. Furthermore, the minimization can become unstable, if the forces (gradients) are large and the curvature (second derivative) is small, as is the case on the steep repulsive wall of a van-der-Waals potential. In this situation, a large step is computed, that may overshoots the minimum, leading to a divergent behavior.\textsuperscript{MSIDiscover1}

However, if the gradients are already small and the system is of moderate size, the above Newton-Raphson method leads to a rapid convergence to an extremely precise minimum, as is needed for a vibrational normal mode analysis.

### 2.3.4.2 Quasi Newton-Raphson

The idea behind the quasi-Newton methods is it, to use an approximation $A$ of the Hessian $H$. This approximation is by construction positive definite and symmetric, which is necessary if the solution of Eq. (2-32) should be descendent. Close to the minimum, $A$ approaches the true Hessian $H$, and the fast convergence of the Newton-Raphson algorithm can be used.

Since the derivation of the matrix $A$ is not straightforward, only the final result will be given here, details can be found in [Harley86]. With

\[
\Delta x = x_{i+1} - x_i \quad \text{and} \quad \Delta g = g_{i+1} - g_i
\]

as the changes in coordinates and gradients between successive steps, the approximate matrix $A_{i+1}$ is given in the DFP (Davidson, Fletcher, and Powell)-method by\textsuperscript{Acton90}

\[
A_{i+1} = A_i + \left[ \frac{(\Delta x \cdot \Delta x^T) A_i \cdot \Delta g \cdot \Delta g^T A_i}{\Delta x^T \cdot \Delta g} \right] - \frac{(\Delta x \cdot \Delta x^T) A_i \cdot \Delta g \cdot \Delta g^T A_i}{\Delta x^T \cdot \Delta g}.
\]

and in the BFGS (Broyden, Fletcher, Goldfarb, and Shanno)-method by

\[
A_{i+1} = A_i + \left( I + \frac{(\Delta g^T \cdot A_i \cdot \Delta g)}{\Delta x^T \cdot \Delta g} \right) \frac{\Delta x \cdot \Delta x^T}{\Delta x^T \cdot \Delta g} - \frac{A_i \cdot \Delta g \cdot \Delta g^T A_i}{\Delta x^T \cdot \Delta g}.
\]

In general, all minimization routines must be somehow terminated, because the
exact minimum can only be approximated with machine precision at best. It is either possible to monitor the energy decrease or the change in coordinates from one iteration to the next or to calculate the root-mean-square gradient,

\[ RMS = \sqrt{\frac{g^T g}{3N}} \]  

and to stop the computation if either of these values drops below a certain limit.

### 2.3.5 Simulated Annealing

All methods mentioned so far are only capable of finding the nearest local minimum. Except for molecular crystals, that have a limited number of local minima and eventually one deep global minimum, the high dimensionality of the conformation space especially of polymers makes it very improbable that the nearest local minimum is a global minimum or even just a 'good' minimum.

It is therefore necessary to search the conformation space for probable structures, i.e. structures of reasonably low energy. As the Boltzmann weight of a conformation depends exponentially on its energy \( E_i \),

\[ w_i = e^{-\frac{E_i}{kT}} \]

typically only a few of the many possible conformations are important for the ensemble average. But the energy of a minimum alone does not tell the whole truth: Comparing minimum \( D \) and \( F \) of Fig. 2.8 on p. 45, it is not a priori clear, which one has a larger weight, because the integral

\[ w^{\text{site}} = \int_{E}^{x_2} e^{-\frac{E(x)}{kT}} dx^M \]

may be larger for the interval \( E \) to \( x_2 \) (minimum \( F \)) than for the interval \( C \) to \( E \) (minimum \( D \)). It is therefore of interest to find the most probable conformations, not just the deepest minima. The necessary sampling of the conformation space is the topic of chapter 2.5, and just the principle idea of the so-called simulated annealing will be outlined here.\(^{89}\)

Annealing in metallurgy consists in a slow cooling down of a material from above melting temperature to low temperatures in order to equilibrate it. After annealing, the material is in a state of low internal energy. This process is simulated on the computer by starting a sampling procedure (Monte Carlo, Molecular Dynamics etc.) at a high temperature, where the conformation space is sampled
efficiently because the saddle-points between local minima are lower than the energy of the assembly. The temperature of the sampling procedure is gradually lowered, restricting the available conformation space to smaller and smaller volume. If the cooling process is sufficiently slow, the structure is able to reach a well equilibrated (= minimized at 0 K) state. This procedure can be used in a variety of problems, that are not tractable with other methods, the most famous of them being the travelling salesman (connection of randomly placed cities by a route of minimal length).}

2.4 Ensembles

The following section provides a short introduction to statistical mechanics, basically introducing the terminology and the concepts of relevance. More detailed descriptions can be found in standard textbooks like [McQuarrie76, Friedman85]

2.4.1 Introduction

In the computation of macroscopic properties from atomistic simulations – the domain of statistical mechanics – the concept of phase space is of prime importance. For a molecule of \(N\) atoms with a Lagrangian \(L\) (Eq. (2-62)), the classical phase space \(\Gamma(q,p)\) contains \(6N\) dimensions, \(3N\) for the coordinates \(q_i\) and \(3N\) for the conjugate momenta \(p_i = \partial L / \partial q_i\).\(^{\text{AllenTildesley}}\) The state of a molecule at a time \(t\) is completely described by these \(6N\) generalized coordinates, which define a point \(\Gamma(t)\) in the phase space. In the course of time, this point moves through phase space on a trajectory \(\Gamma(t)\), governed by the equations of motion. These equations are different for the different ensembles that exist and link the macroscopic parameters of the system as a whole with the regions of the phase space accessible to the molecule. An ensemble is a set of points in phase space that obey certain restrictions, e.g. the volume of the unit cell is the same or the kinetic energy follows a Boltzmann distribution. Relevant ensembles will be shortly introduced in section 2.4.3.

The above description was based on classical mechanics, where the phase space is continuous. The atomistic systems described here obey, in principle, the laws of quantum mechanics and thus the phase space is not continuous, but is made up of a countably infinite set of quantum states. In the following discussion it is assumed that the classical and the quantum mechanical representation can be both used interchangeably.
2.4.2 The Ergodic Hypothesis and the Liouville Theorem

The ergodic hypothesis is of central importance for the molecular dynamics and Monte Carlo sampling methods (chapter 2.5). It states that the set of ensemble points in phase space compliant with the restrictions posed by the different ensembles can be obtained by following the trajectory of one initial point. It is now possible to replace the ensemble average of Eq. (2-40) by a time average. An exact average, however, is only obtained for infinitely long trajectories that sample all relevant parts of the phase space. This is not a priori given and can not be proved rigorously: The phase space is maybe such that trajectories form closed loops or remain trapped for a very long time in a region surrounded by narrow saddle points.\textsuperscript{AllenTildesley89}

The points in phase space belonging to an ensemble have a density \( \rho(q,p,t) \) in the phase space volume \( dq dp \) around \( q,p \). The Liouville equation\textsuperscript{McQuarrie76},

\[
\frac{\partial \rho}{\partial t} + \sum_{j=1}^{3N} \left( \frac{\partial \rho}{\partial p_j} \right) \dot{p}_j + \sum_{j=1}^{3N} \left( \frac{\partial \rho}{\partial q_j} \right) \dot{q}_j = 0, \tag{2-38}
\]

which is equivalent to

\[
\frac{d\rho}{dt} = 0, \tag{2-39}
\]

conserves the density of these phase space points as they move along their trajectories. This is equivalent to the statement, that the size (but not necessarily the shape) of the volume element \( dq dp \) in phase space remains constant.

2.4.3 Relevant Ensembles

2.4.3.1 Microcanonical (EhN)-Ensemble\textsuperscript{a}

This ensemble is equivalent to a container with solid, thermally insulating walls (e.g. a dewar), because the number of particles \( N \), the shape of the simulation cell \( h \) and the energy \( E \) are kept fixed during the simulation. The temperature, on the other hand, is allowed to fluctuate during the simulation around a constant mean value, because only the sum of the potential and the kinetic energy remains constant. This ensemble is actually the microcanonical ensemble, which is commonly denoted as \( NVE \)-ensemble, neglecting the difference between constant shape and constant volume.\textsuperscript{Ray84a}

\textsuperscript{a} Throughout this work, the notation found in Ref. [GrabenRay93] and [Ray88a] was used.
2.4.3.2 Canonical ($T_N$)-Ensemble

If an experiment is performed in a container with heat conducting walls and the container is immersed in a bath of constant temperature $T$, the phase space points are distributed according to the canonical ensemble. Commonly, this ensemble is denoted $TVN$-ensemble (see the remark in the previous paragraph).

2.4.3.3 Constant Stress-Constant Temperature ($T_tN$)-Ensemble

A solid body at a constant external thermodynamic tension $t$ (quite often $t_{ext}=0$) and constant temperature $T$ belongs to the $T_tN$-ensemble. Since this is a common state of solids, most of the simulations of this work were carried out in this ensemble.

2.4.3.4 Other ensembles

In total, there exist eight commonly used ensembles, which are depicted in Figure 2.11.

![Diagram of eight thermodynamic ensembles](image)

Figure 2.11: Eight thermodynamic ensembles, that are in contact with a temperature, pressure and chemical potential reservoir. Ensembles on the left are adiabatically insulated, those on the right are in thermal contact with the reservoir.

Fig. 2.11. For all these ensembles, sampling methods have been devised. The microcanonical, canonical, and constant temperature - constant stress ensemble have already been introduced. Of importance in simulations is furthermore the grandcanonical ensemble, which allows changes in the number of particles to keep the chemical potential constant. Panagiotopoulos87
2.4.4 The Partition Function

The relationship between an arbitrary microscopic property \( A \), which can be expressed as a function of the generalized coordinates \( A(\Gamma) \), and its macroscopic observable \( A_{\text{obs}} \) is given simply by

\[
A_{\text{obs}} = \langle A(\Gamma) \rangle_{\text{ens}},
\]

(2-40)

where \( \langle \cdot \rangle_{\text{ens}} \) denotes the ensemble average of \( A(\Gamma) \). This ensemble average as well as the observable property are different for the different ensembles. Using the principle of a priori equal probabilities \(^{McQuarrie76}\), the average for the canonical ensemble is given by (Eqs (2-1) and (2-2))

\[
\langle A \rangle_{\text{ThN}} = \frac{\sum_{\Gamma} A(\Gamma) e^{\frac{H(\Gamma)}{kT}}}{\sum_{\Gamma} e^{\frac{H(\Gamma)}{kT}}},
\]

(2-41)

with a denominator

\[
Q_{\text{ThN}} = \sum_{\Gamma} e^{\frac{H(\Gamma)}{kT}} = \frac{1}{N!} \frac{1}{h^{3N}} \int e^{\frac{H(q,p)}{kT}} dq dp
\]

(2-42)

called the (canonical) partition function. The second approximate equality is the classical description of the partition function in the continuous phase space. The leading quantum correction \( Q_{\text{quantum mechanical}} - Q_{\text{classical}} \) is small for high temperatures and weak interactions. \(^{Friedman85}\)

Since, for a system obeying classical statistics, the Hamiltonian \( H \) (in cartesian coordinates) can always be written as the sum of kinetic (\( p \)-dependent) and potential (\( q \)-dependent) contributions, the partition function factorizes into a product of kinetic (ideal gas) and potential (excess) parts \(^{AllenTildesley89}\):

\[
Q_{\text{ThN}} = \frac{1}{N!} \frac{1}{h^{3N}} \int e^{\frac{K(p)}{kT}} dp \int e^{\frac{U(q)}{kT}} dq = Q_{\text{ThN}}^{\text{id}} Q_{\text{ThN}}^{\text{ex}}.
\]

(2-43)

Instead of the excess partition function \( Q_{\text{ThN}}^{\text{ex}} \), often, the configuration integral

\[
Z = V^N Q_{\text{ThN}}^{\text{ex}} = \int e^{\frac{U(q)}{kT}} dq
\]

(2-44)

is computed in a configuration-space MC simulation and the ideal gas properties are added onto the results afterwards.
In the microcanonical ensemble, the energy is constant and each point has therefore equal weight. The partition function is simply the number of microscopic instances of the property \( A \), provided the energy \( E(\Gamma) \) of the microstate is exactly \( E \):

\[
Q_{EhN} = \sum_{\Gamma} \delta \left( E(\Gamma) - E \right) = \frac{1}{N!^3} \frac{1}{\hbar^{3N}} \int \delta \left( E(q, p) - E \right) dq dp . \tag{2-45}
\]

The partition functions of the isothermal-isobaric ensemble, AllenTildesley89

\[
Q_{TN} = \sum_{\Gamma} \sum_{N} e^{\frac{\text{tr}(\eta_n) - E(\Gamma)}{kT}} e^{-\frac{E(\Gamma)}{kT}} = \sum_{N} \frac{1}{N!^3} \frac{1}{\hbar^{3N}} \int e^{\frac{\text{tr}(\eta_n) - E(q, p)}{kT}} dq dp \tag{2-46}
\]

and the grand-canonical ensemble,

\[
Q_{ThN} = \sum_{\Gamma} \sum_{N} \frac{\mu N}{kT} e^{\frac{\text{tr}(\eta_n) - E(\Gamma)}{kT}} = \sum_{N} \frac{1}{N!^3} \frac{1}{\hbar^{3N}} \int e^{\frac{\mu N - E(q, p)}{kT}} dq dp . \tag{2-47}
\]

The partition function and its temperature derivative are of interest, because all macroscopic thermodynamic properties can be derived from it, as the following equations show for the canonical ensemble: ReedGubbins73

\[
\begin{align*}
U &= kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V, N_a} \tag{a) } \\
p &= kT \left( \frac{\partial \ln Q}{\partial V} \right)_{T, N_a} \tag{b) } \\
H &= kT \left( \frac{\partial \ln Q}{\partial T} \right)_{V, N_a} + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_{T, N_a} \tag{c) } \\
C_V &= \left( \frac{\partial U}{\partial T} \right)_{V, N_a} \tag{d) } \\
C_p &= \left( \frac{\partial H}{\partial T} \right)_{p, N_a} \tag{e) } \\
S &= k \ln Q \tag{f) } \\
A &= -kT \ln Q \tag{g) } \\
G &= -kT \ln Q + kTV \left( \frac{\partial \ln Q}{\partial V} \right)_{T, N_a} \tag{h) } \\
\mu_\alpha &= -kT \left( \frac{\partial \ln Q}{\partial N_\alpha} \right)_{T, V, N_{\beta \neq \alpha}} \tag{i) }
\end{align*}
\]
Similar relations exist for the other ensembles. Except for the smallest systems, it is, however, not possible to evaluate the partition function analytically or numerically, because the high dimensionality \( \mathcal{O}(10^2-10^4) \) of typical simulations prevents a systematic sampling of the phase space. It is therefore necessary to use specialized sampling methods (chapter 2.5).

### 2.4.5 Equipartition of the Hamiltonian

For any two degrees of freedom \( x_i, x_j \) of a system with a Hamiltonian \( H \), it can be shown \(^{Pathria72}\) that

\[
\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} kT. \tag{2-49}
\]

If \( H \) (the sum of the kinetic and potential energy) is of a quadratic form \(^{McQuarrie76}\)

\[
H(p_1, p_2, \ldots, q_s) = \sum_{i=1}^{m} a_i p_i^2 + \sum_{j=1}^{n} b_j q_j^2 + H(p_{m+1}, \ldots, p_{s}, q_{n+1}, \ldots, q_s), \tag{2-50}
\]

each of the harmonic degrees of freedom contributes \( \frac{1}{2} kT \) to the average energy of the system. The theorem is also valid if the 'constants' \( a_i \) and \( b_j \) are functions of the coordinates and momenta \( p_{m+1}, \ldots, p_{s}, q_{n+1}, \ldots, q_s \) not involved in the quadratic terms.

### 2.5 Sampling Methods

The sampling procedure stands in the center of every atomistic simulation. Specification of the force field, the simulation cell, and the ensemble (i.e. the macroscopic variables that are constant) allows the computation of the energy and, if necessary, of the forces acting on the atoms in the simulation. Using one of the subsequently described methods, the phase space of the system can be explored and thermodynamical and mechanical properties can be calculated afterwards from microscopic configurations.

Basically, there are two different methods to sample the phase space. The more intuitive way is maybe molecular dynamics (MD), which solves the equations of motion compliant with the ensemble being used and tries thus to mimic nature. A more abstract, but equivalent, way is to generate conformations in a more or less random fashion and to select those that fit into the chosen ensemble. Due to the randomness in the generation process, this method is termed Monte Carlo.\(^{Metropolis49}\)
2.5.1 Monte Carlo

As pointed out in chapter 2.4.4, the classical partition function in cartesian coordinates can be split into a term depending on the momenta, which is known from kinetic gas theory, and a term that depends solely on the coordinates \( q \) - the configurational integral - the approximate computation of which is the task of the MC algorithm.

2.5.1.1 Simple sampling

The most straightforward way to integrate (2-44) would be the use of an equispaced grid spanning the whole configuration space. Since the total number of points equals \( p^{3N} \), \( p \) giving the number of grid points in one dimension and \( N \) the number of atoms, this method is impractical except for the smallest molecules. Furthermore, virtually all grid points would lay in areas of the phase space where the interaction energy is so high that the Boltzmann factor almost vanishes.

The same inefficiency can be observed, if the points in phase space are chosen at random rather than on a grid. In dense atomic systems, a fraction of only about \( 10^{-260} \) of all points makes significant contributions to the conformational integral.\(^{96}\)

It would be much better to chose the phase space points with a probability corresponding to their Boltzmann factor and to weight them evenly instead of selecting them with equal probability and to weight them afterwards. This is the fundamental concept of importance sampling.

2.5.1.2 Importance sampling

Given a distribution \( \rho \) of \( N \) states (Fig. 2.12) with a set of transitions \( \pi \)

![Diagram](image)

Figure 2.12: Transition probabilities between \( N \) (= 5) different states

between all possible states. In particular, \( \pi_{mn} \) denotes the transition probability
to go from state $m$ to state $n$, and $\pi_{n,m}$ the probability of going from $n$ to $m$. The transition probabilities form a $N \times N$ matrix whose rows add to one. The number density of state $i$ is given by

$$\rho_i = \frac{M_i}{M},$$  \hspace{1cm} (2-51)

where $M_i$ is the number of systems that are in state (configuration) $i$ out of an ensemble of $M \gg N$ configurations. In thermodynamic equilibrium, the number densities are distributed according to their Boltzmann factors:

$$\rho_i \propto e^{-\frac{H(q_i)}{kT}}.$$  \hspace{1cm} (2-52)

Starting with a given density $\rho_{old}$, the new number densities $\rho_{new}$ can be evaluated by matrix multiplication as

$$\rho_{new} = \rho_{old} \pi.$$  \hspace{1cm} (2-53)

It is required that the limiting distribution resulting from repetition of (2-53) equals the one given by (2-52). This is fulfilled, if the sum of all transitions from, say, state $m$ to the other states $n_i$ (solid lines in Fig. 2.12) equals the transitions from these states to $m$ (dashed lines in Fig. 2.12),

$$\sum_i \rho_m \pi_{mn_i} = \sum_i \rho_{n_i} \pi_{n,m}. $$  \hspace{1cm} (2-54)

In normal simulations, this sufficient condition is replaced by the unnecessarily strong requirement of *detailed balance* of all possible transitions,

$$\rho_m \pi_{mn_i} = \rho_{n_i} \pi_{n,m}.$$  \hspace{1cm} (2-55)

The transition probability $\pi_{mn}$ is the product of a probability $\alpha_{mn}$ to attempt to change the configuration from $m$ to $n$ and a probability $a_{mn}$ to accept this move,

$$\pi_{mn} = \alpha_{mn} \cdot a_{mn}.$$  \hspace{1cm} (2-56)

Assuming a symmetric underlying matrix $\alpha$, the acceptance probability $^{53}$Metropolis

$$a_{mn} = \begin{cases} 1 & \rho_n \geq \rho_m \\ \frac{\rho_n}{\rho_m} & \rho_n < \rho_m \end{cases},$$  \hspace{1cm} (2-57)

is able to generate with a Markov$^a$ chain a set of canonically distributed configu-
Although there are other solutions to Eq. (2-55), Eq. (2-57) - known as the asymmetrical Metropolis solution - is the most common one. Averages obtained from transition matrices such as (2-57) differ from the true canonical average by a term $O(n_{steps}^{-1/2})$.

The asymmetrical Metropolis solution shown above is equivalent to accepting a trial move with a probability of $\exp\left(-\frac{\Delta H}{kT}\right)$. In a practical simulation, a random number $\eta$ is drawn from the interval $(0,1)$ and the move is accepted if

$$\eta \leq e^{-\frac{\Delta H_{mn}}{kT}}.$$  \hspace{1cm} (2-58)

It is of great importance to use reliable random number generators not only for the acceptance step, but also for all different kinds of moves presented in the next section. A short discussion of the random number generators used in this work is therefore given in Appendix C.

For ensembles other than the canonical, the same acceptance probability can be used as above, but the Hamiltonian in the evaluation of the number densities is different. In the $Tt/V$ ensemble, for example, the configurational Hamiltonian is

$$H_{Tt/V} = U(q) + V_0 tr(t_\eta) + kT/N \ln V,$$  \hspace{1cm} (2-59)

the last term correcting for the fact that different volumes are sampled and thus the kinetic configurational part is different for each point contributing to the ensemble. Alternatively, the momenta can be included explicitly.\(^{192a}\)

### 2.5.1.3 Umbrella Sampling

Figure 2.13 shows the distribution of the cell edge length in the $c$-direction during the last 500 ps of a 1 ns $Tt/V$-simulation of a PP crystal (chapter 4.3). The quantity of interest is the width of the cell edge length distribution, since it is proportional to the compliance in this direction. In contrast to the mean value, the width converges rather slowly, because it is more dependent on the tails of the distribution. The tails of the distribution, however, are only rarely sampled by the MD algorithm, which weights the individual conformations according to their Boltzmann weights. Normally, MC samples the phase space in the same manner, but it needn't necessarily do so. A number of schemes have been devised to

---

a. (A Markov chain is a sequence of trial moves that satisfies two conditions:
- The outcome of each trial belongs to a finite set of outcomes $\{m, n_1, ..., n_N\}$, called the state space
- The outcome of each trial depends only on the outcome of the trial that immediately precedes it.)
introduce a bias - that needs to be removed in the averaging process - which enhances the probability of accepting configurations at the tails. AllenTildesley89

The one-half umbrella sampling algorithm used in this work originates from Lee and ScottLee80a and accepts a new MC conformation if

\[ \eta \leq W(\Delta U_{mn}) \, e^{\frac{\Delta U_{mn}}{kT}} \],

where \( \eta \) is a random number in the interval \([0,1]\) and \( W(\Delta U_{mn}) = e^{\frac{\Delta U_{mn}}{2kT}} \). The correct averages are computed from the weighted ones by

\[ \langle A \rangle_0 = \frac{\langle A/W \rangle_W}{\langle 1/W \rangle_W} \].

\[ (2-61) \]

2.5.1.4 Monte Carlo Moves

Up to now the structure of the underlying matrix \( \alpha \), the probability of attempting a move, has not been specified, except that it should be symmetric. It is the great advantage (and difficulty) of the Monte Carlo method that this matrix can be chosen with great freedom, allowing all kinds of moves in a variety of ensembles.

In principle, the moves performed by \( \alpha \) should be ergodic, i.e. any state \( n \) should be reachable from any state \( m \) by an (infinite) number of steps. In practice, the choice of \( \alpha \) is a compromise between the necessity to sample a representative part of the configurational space with a finite number of steps and the desire to obtain a statistically sufficient number of configurations. The first argu-
ment requires large moves, that quickly decorrelate the structure and the second one demands a certain fraction of accepted moves. Typically, the stepwidth is chosen such that an acceptance ratio of about 50% is obtained. There is evidence, however, that lower acceptance ratios often lead to better performance. Frenkel96, Leontidis94a, AllenTildesley89

It is beyond the scope of this work to discuss the nearly numberless types of moves that have been created for all kinds of problems. A good overview can be found in [Widmann96a, Leontidis94a, Binder92a] and references therein. In the simulation of dense polymeric systems, the simple scheme of randomly changing any degree of freedom leads only to a slow sampling of the phase space. A number of other techniques have therefore been developed Leontidis94a, some of which are mentioned now, neglecting coarse-grained lattice models, which operate on other time- and length-scales.

As already mentioned, the simple random change of one (local move) or all degrees of freedom simultaneously (global move) exhibits poor efficiency in equilibrating dense polymer structures. For systems of individual atoms or small molecules, local moves make better use of computational effort than global updates of the coordinates. In the case of dense polymers, the situation is reversed. Due to the dense packing and entanglement of the chains, global changes of the configuration seem to be more efficient in finding a way through bottlenecks in phase space. Forrest94a

The reptation of chain molecules by one or several repeat units yields a good equilibration for chains of relatively short length. If the molecules are longer or contain bulky side groups, cage effects reduce the acceptance ratio unacceptably or lead to a stationary vibration of the chain due to forth and back moves.

A similar algorithm is Continuum-Configurational-Bias Monte Carlo (CBMC), in which a polymer chain is cut at a randomly chosen segment and rebuilt in a step-wise fashion. At each step, the Boltzmann weight of a number of torsion angles is computed and one of the angles chosen proportional to its weight. This bias has to be removed at the end of the regrowth process by comparing the statistical weight of the old and the new changed part of the chain.

The Concerted-Rotation method tries to move four segments in the middle part of the chain by changing a torsion angle while holding all other segments constant. This requires to solve a set of constraint equations numerically and to compute the Jacobian of the transition from the torsion angle space to the space of the constraint equations in order to achieve detailed balance.

A similar algorithm is used by the Variable-Connectivity method to create bridges between different molecules. Therefore, a distribution of chain lengths is
generated and the simulation samples the semigrand \((NnPT\mu^*)\) ensemble.\(^{95a}\)

A new, yet unpublished idea is the Parallel-Rotation, in which a driver angle and three dependent torsion angles are used to shift the remaining part of the polymer chain parallel to itself.\(^{3}\)

All the above methods, however, change the polymer matrix only locally. As already stated, it would be advantageous to update the degrees of freedom globally. Hybrid Monte Carlo methods use short MD runs to create new configurations and apply a Metropolis criterion to accept or reject them. Before presenting shortly this approach, the MD method will be introduced.

2.5.2 Molecular Dynamics

2.5.2.1 Equations of Motion

The Lagrangian \(L\) of a system of \(N\) particles is its kinetic minus its potential energy\(^{86b}\)

\[
L = K(\mathbf{q}) - U(\mathbf{q}),
\]

(2-62)

where \(\mathbf{q}\) and \(\mathbf{q}'\) are the \(n = 3N\) generalized coordinates and \(n\) generalized velocities.

Applying the principle of least action, the equations of motion are obtained as

\[
\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0 \quad i = 1, 2, \ldots, n.
\]

(2-63)

Integration of these equations allows to propagate the system through the phase space.

Depending on the ensemble (i.e. fixed macroscopic variables) the Lagrangian has a different form. Two examples, the microcanonical \((EhN)\) and the isothermal-isotension \((\mathcal{T}N)\)-ensemble, are given. The microcanonical ensemble is the natural ensemble of MD (as the canonical is for MC), while the \(\mathcal{T}N\)-ensemble is the one, in which most of the simulations presented in this work were carried out.

The Lagrangian of the microcanonical ensemble is just

\[
L_{\text{\(\mathcal{H}\)E}} = \frac{1}{2} \sum_{i,k} \alpha_{ik}\mathbf{q}_i \mathbf{q}_k - U(\mathbf{q}) = \sum_{\alpha} \frac{p_{\alpha}^2}{2m_{\alpha}} - U(\mathbf{r}).
\]

(2-64)

---

a. S. Santos, private communication (1996)
The first equality is valid for arbitrary generalized coordinates and velocities, the second only for cartesian coordinates, \( a_{ik} \) is a function of the coordinates \( q \) only and \( m_\alpha \) and \( p_\alpha \) are the mass and the momentum of atom \( \alpha \), respectively. Deriving the equations of motion from the second equality, one obtains

\[
\frac{1}{m_\alpha} \frac{dp_\alpha}{dt} = -\frac{\partial U}{\partial r_\alpha} \quad \Rightarrow \quad m_\alpha \ddot{r}_\alpha = F_\alpha \tag{2-65}
\]

exactly Newton's equations of motion.

In case of the \( TnN \)-ensemble, the Lagrangian in cartesian coordinates is much more complicated: \( \text{Lill93a} \)

\[
\tilde{L}_{TnN} = \sum_\alpha \frac{\pi^{(\alpha)} T - 1}{2m^{(\alpha)} \pi^{(\alpha)}} - U(r) + \frac{\text{Tr} \left( \Omega' T \Omega' \right)}{2W^2} - V_0 \text{Tr} (\eta) + \frac{\eta^2}{2Q} - nkT \ln \pi, \tag{2-66}
\]

where the first term expresses the kinetic energy of the particles as a function of their scaled, virtual momenta \( \pi^{(\alpha)} = \hbar p^{(\alpha)}/s \) and the metric tensor \( g \) (Eq. (A-14)). \( U(r) \) is the potential energy, that depends only on the interparticle distances. The kinetic energy of the simulation cell is given by the third term. \( \Omega' \) is the virtual momentum \( (\Omega/s) \) and the parameter \( W \) has the dimension of mass and governs the coupling between the net pressure and the rate, with which the cell changes its shape. The fourth term is the potential energy of the elastically deformed cell, with the thermodynamic tension \( t \) given by Eq. (1-41) and the strain \( \eta \) by Eq. (1-36). The volume \( V_0 \) is given by \( V_0 = |H| \), the determinant of the reference cell shape \( H \). The third and fourth term together form an additional degree of freedom, originally introduced by Parrinello and Rahman.\( \text{ParrinelloRahman81a} \) The fifth and sixth term are the kinetic and potential energy of a similar additional degree of freedom with coordinate \( s \) and mass \( Q \) and a conjugate momentum \( \theta \) originating from the Nosé-Hoover thermostat.\( \text{Nose84a,Nose84b,Nose91a} \) (Note the difference between the coordinate \( s \) of the Nosé-Hoover thermostat and the scaled coordinates \( s_\alpha \).) The quantity \( n \) denotes the number of degrees of freedom \( (3N+3) \). The Lagrangian is tilded, because a term \( m^{(\alpha)} \hbar s^{(\alpha)} \), which is considered to be small, was neglected in the expression of the particle momentum in a fluctuating cell.\( \text{Ray84a} \)

The equations of motion are obtained as described above; transforming them to physical time introduces a thermodynamic friction \( \dot{\varepsilon}^{\text{Hoover85a}} \) into the atomic and lattice dynamics.\( \text{Lill93a} \)
\[
\dot{s} = \xi s \\
\dot{\xi} = \frac{1}{Q} \left[ \sum_{\alpha} N \pi_{ij}^{(\alpha)} g_{ij}^{-1} \pi_j^{(\alpha)} \right] + \frac{\Omega_{ij}}{W} \dot{\Omega}_{ij} - nkT \\
\pi_i^{(\alpha)} = \frac{g_{ij}^{-1} \pi_j^{(\alpha)}}{m_\alpha} \\
J_{ij} = \frac{\Omega_{ij}}{W} \\
\Omega_{ij} = (P - \Pi)_{ik} h |J_{jk}^{-1} - \xi \Omega_{ij} \\
\Omega_{ij}^s = \frac{1}{2} (\Omega_{ip} J_{pk}^{-1} + \Omega_{kp} J_{pi}^{-1}) J_{kj} \\
\Pi_{ij} = -\frac{1}{|J|} [\delta_{ij} (t_{kp} \pi_{kp}) + J_{kl}^{-1} t_{kp} J_{jp}] = -\left[ \delta_{ij} (\sigma_{kp} \mu_{kp}) + J_{kl}^{-1} J_{kp} \sigma_{pl} \right] 
\]

The internal virial pressure \( P \) is defined by Eq. (1-47), \( \Pi \) is the effective external pressure, and \( \sigma \) the stress imposed on the system. The strain \( \mu \) is defined as

\[
\mu_{ij} = \frac{1}{2} (\delta_{ij} - \xi J_{kl}^{-1} J_{kj}) 
\]

Bulgac and Kosnezev\(^{Bulgac90a}\) found that it is sufficient to control the ratio of two quantities to achieve a constant temperature condition and the canonical distribution. Since any pair of quantities, the ratio of whose canonical ensemble averages is \( kT \), could be chosen, the Lagrangian of Eq. (2-66) is only one of many possible representations of a \( \mathcal{TN} \)-ensemble.

### 2.5.2.2 Manostats

Equation (2-67-f) describes the relation between the change in the cell momentum and the difference between the internal stress \( P \) and the external stress \( \Pi \), which is defined by Eq. (2-67-h). To prevent an unphysical rotation of the cell, its momentum tensor is symmetrized by Eq. (2-67-g).

The Parrinello-Rahman algorithm produces a canonical distribution if the step-width of the integration is infinitely small. However, at finite step-sizes the average of the actual stress during a simulation is always lower than the target stress, as can be seen in Table 2-2. This deviations become very large with increasing time-step, making simulations of fully flexible polymeric systems with a stepwidth larger than about 0.5 fs questionable.

The above equations of motion let the cell change its volume and shape without restrictions. For structures far from mechanical equilibrium, this can lead
to large distortions in the cell shape, which prevent further use in simulations. In the initial stage of simulation, it is therefore often desirable to use a constant-pressure algorithm\cite{Anderson80a} that changes only the size of a model box, while leaving the shape orthogonal. Constant pressure algorithms using uniform cell dilation and flexible cells with isotropic external tension are discussed in Ref. \cite{Martyna94a}.

A more direct coupling between the internal stress $\mathbf{P}$ and the particle coordinates $\mathbf{r}_i$ and the cell shape tensor $\mathbf{h}$ was suggested by Berendsen.\cite{Berendsen84a} In his weak-coupling scheme, $\mathbf{r}_i$ and $\mathbf{h}$ are scaled according to

$$r'_i = \mu r_i$$

$$h' = \mu h'$$

where the scaling tensor $\mu$ is proportional to the difference between the internal stress tensor and the externally imposed stress $\mathbf{P}_0$:

$$\mu = 1 - \frac{\beta \Delta t}{3 \tau_p} (\mathbf{P}_0 - \mathbf{P})$$

($\beta$ is the isothermal compressibility, $\Delta t$ the time-step, and $\tau_p$ a parameter).

### 2.5.2.3 Thermostats

Omitting the kinetic energy of the cell in Eq. (2-67-b), the change of the thermodynamic friction coefficient is proportional to the difference between the actual and the target kinetic energy,

\[ \Delta f \]

\[ 0.2 \]

\[ 0.5 \]

\[ 1.0 \]

\[ 1.5 \]

\[ 2.0 \]

<table>
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<th>$\Delta t$ [fs]</th>
<th>$\sigma_{xx}$</th>
<th>$\sigma_{yy}$</th>
<th>$\sigma_{zz}$</th>
<th>$\sigma_{yz}$</th>
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<td>104.3</td>
<td>68.5</td>
<td>36.0</td>
<td>61.7</td>
</tr>
</tbody>
</table>
\[ \xi = \frac{1}{Q} \left[ \sum_{a}^{N} \pi_i^{(\alpha)} g_{ij}^{-1} \pi_j^{(\alpha)} \right] - nkT = \frac{1}{Q} [K - nkT]. \quad (2-70) \]

If the temperature is too high, the thermodynamic friction \( \xi \) increases and the momenta of the particles are reduced by the last term of Eq. (2-67-d).

As observed with the Parrinello-Rahman algorithm, the average temperature of a Nosé-Hoover thermostat depends heavily on the time step used for the MD integration. As Fig. 2.14 shows, the actual temperature approaches the target temperature as the integration step gets smaller and the width of the fluctuations becomes

\[ \langle \delta T^2 \rangle = \frac{2}{3N} \langle T \rangle^2, \quad (2-71) \]

which is, for the above example, about 7.6 K. As a compromise between speed and accurate temperature and pressure control, a stepsize of 0.5 fs was used in all simulations that used one of the two extended control mechanisms. The coupling parameter \( Q \) is suggested to be proportional to \( 3NkT(T_0)^2 \), where \( T_0 \) represents a characteristic time of the system. The proportionality factor has been set empirically to \( 1.41 \times 10^{-7}/(T_0)^2 \), with \( T_0 \) set to 1. MSIDiscover
In Berendsen’s thermostat\(^{84a}\), an expression quite similar to Eq. (2-70) is used, but instead of \( \dot{\xi} \), it is \( \xi \) directly, which is controlled:\(^{91a}\)

\[
\xi = \frac{1}{Q} \left[ \sum_{\alpha} \frac{N_j^{(\alpha)} g_{ij}^{(\alpha)} m_{i}}{m_{\alpha}} - nkT \right] = \frac{1}{Q} [K - nkT] .
\] (2-72)

In contrast to the Nosé-Hoover thermostat, the above equation is not capable of generating a canonical ensemble.\(^{85a,85a}\)

The first and most straightforward temperature control method is the velocity scaling algorithm of Woodcock\(^{71a}\), where the velocities are simply scaled after each integration step by a factor \( \lambda \), which is given by

\[
\lambda = \left( \frac{T}{T_{\text{act}}} \right)^{\frac{1}{n}}
\] (2-73)

\((T\) is the target simulation temperature and \( T_{\text{act}} \) is the actual temperature, obtained from the kinetic energy).

A further possibility to control the temperature consists in stochastic collisions of imaginary particles with individual atoms, that redistribute the kinetic energies.\(^{80a}\) Both the velocity scaling and the stochastic collision method do not fulfill the requirement stated at the end of chapter 2.5.2.1 and are therefore not canonical.

### 2.5.2.4 Integrators

The above equations of motion (Eqs (2-65) or (2-67)) define a trajectory of the system in phase space. Except for the simplest cases (e.g. two interacting bodies), the trajectory can not be computed analytically but must be obtained numerically using a finite difference method.

All methods of this kind start at a given time \( t \), at which the locations \( r(t) \), the velocities \( v(t) \) and - via the evaluation of the forces \( f(t) \) - the accelerations \( a(t) \) of all particles are known. The integrator propagates the system by a small timestep \( \Delta t \) of \( O(10^{-15} \text{s}) \) to a new time \( t + \Delta t \) and so on.

For an integrator to be useful in MD, it should be:

- fast (only one force evaluation per timestep)
- small (minimal consumption of computer memory)
- robust (good energy conservation even at large \( \Delta t \))
- time reversible and canonical.

A necessary condition to achieve canonicity is the conservation of the phase space volume in the course of the MD simulation according to the Liouville theo-
rem (chapter 2.4.2). A more detailed discussion about this topic can be found in Appendix D, where it becomes manifest that - for MD simulations - the velocity Verlet algorithm is a better choice than the complicated and slow predictor-corrector algorithms, especially the ABM4 method. Since the velocity Verlet algorithm was used for all MD simulations in this work, it will be briefly derived from its ancestor, the Verlet integrator.\textsuperscript{Frenkel96}

A Taylor expansion of the coordinates at \( t + \Delta t \) and \( t - \Delta t \) yields

\[
\begin{align*}
\mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \mathbf{v}(t) \Delta t + \frac{1}{2} \mathbf{a}(t) \Delta t^2 + \frac{1}{3!} \frac{d^3}{dt^3} \mathbf{r} \Delta t^3 + O(\Delta t^4) \\
\mathbf{r}(t - \Delta t) &= \mathbf{r}(t) - \mathbf{v}(t) \Delta t + \frac{1}{2} \mathbf{a}(t) \Delta t^2 - \frac{1}{3!} \frac{d^3}{dt^3} \mathbf{r} \Delta t^3 + O(\Delta t^4),
\end{align*}
\]

which sum up as

\[
\mathbf{r}(t + \Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \mathbf{a}(t) \Delta t^2 + O(\Delta t^4). \tag{2-75}
\]

Neglecting the last term in Eq. (2-75), one obtains the Verlet integrator. Remarkably, the new positions can be estimated with an accuracy of \( \Delta t^4 \), without knowledge of the velocities. But in many cases, the velocities are needed to define an actual temperature. A first variant of the Verlet algorithm that includes the velocities is the so-called Leapfrog scheme,\textsuperscript{Berk70a} which got its name from the fact that the velocities and positions are leaping over each other, separated by \( \frac{\Delta t}{2} \):

\[
\begin{align*}
\mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \mathbf{v}(t) \frac{\Delta t}{2} \\
\mathbf{v}
\left( t + \frac{\Delta t}{2} \right) &= \mathbf{v}
\left( t - \frac{\Delta t}{2} \right) + \mathbf{a}(t) \Delta t.
\end{align*}
\]

This asynchronicity prevents direct modifications of the velocities, as required by a thermostat. Therefore, an algorithm of the Verlet type was developed, which evaluates the positions and velocities at the same time - the velocity Verlet algorithm,\textsuperscript{Swope82a}

\[
\begin{align*}
\mathbf{r}(t + \Delta t) &= \mathbf{r}(t) + \mathbf{v}(t) \Delta t + \frac{1}{2} \mathbf{a}(t) \Delta t^2 \\
\mathbf{v}(t + \Delta t) &= \mathbf{v}(t) + \frac{1}{2} [\mathbf{a}(t) + \mathbf{a}(t + \Delta t)] \Delta t.
\end{align*}
\]

As a last remark about integrators, it should be noted that it is not important that an algorithm is able to follow the 'true' trajectory extremely well. This is due to the fact that even an extremely small difference in the initial conditions of two
otherwise identical simulations will lead to completely uncorrelated trajectories after a few hundred or thousand steps. This effect is called the Lyapunov instability and can be quantified as

\[ |\Delta r(t)| = \varepsilon \cdot \exp(\lambda t) \]  

(2.78)

with \( \lambda \) being the largest Lyapunov exponent.

Figure 2.15 shows the effects of this 'chaotic' behaviour on a 'real' example. A DISCOVER simulation was performed and in the course of the simulation, a '.xdyn' file was created. A second simulation was now started, using the data of the '.xdyn' file and the potential and the kinetic energy of the continued and the restarted run were compared. The only difference between the two simulations was the precision of the initial data: The continued run was using the 64 bit data format, with which numbers are stored in the memory, while the '.xdyn' file was written with a smaller (although unknown) precision to the disk. The effects of this small difference are well visible: After approximately 10'000 MD steps, the small initial difference has increased so much that the trajectories became completely uncorrelated. The fluctuation of the difference becomes twice as large as the fluctuations of the individual values.

2.5.3 Hybrid Monte Carlo (HMC)

One of the main disadvantages of Molecular Dynamics simulations is that the stepsize of the integration has to be quite small in order to achieve a reason-
able conservation of quantities of interest such as energy and temperature. Furthermore, constant-temperature MD methods are only canonical in the limit of infinitely small time steps.

In contrast to this, Monte Carlo methods are numerically stable and canonical, but suffer from the fact that it would be often necessary to use collective instead of isolated moves to pass certain barriers in the equilibration of structures. Random global moves, however, normally lead to very low acceptance ratios.\cite{Mehlig87a}

A solution to this dilemma is the use of Hybrid Monte Carlo (HMC)\cite{Duane87a}, which combines the advantages of both MD and MC. The framework of this method is a standard Monte Carlo algorithm (chapter 2.5.1), in which the change of the coordinates is performed by a relatively short MD simulation. In contrast to 'normal' MC, the Hamiltonians (potential plus kinetic energy) and not the potential energies of the initial and final structure are compared and the new configuration is accepted according to the criterion stated in Eq. (2-57). Detailed balance can only be maintained, if the integration algorithm is both time reversible and area preserving.\cite{Forrest94a} Since the numerical instability of longer time steps always leads to an increase $\Delta H$ in the energy, the acceptance ratio, which is proportional to

\[ P_{\text{acc}} \propto e^{-\frac{\Delta H}{kT}} \]  

always drops. These two tendencies - better decorrelation and lower acceptance ratio with larger time steps - must be balanced for optimum performance.

Among the technical details of interest is the fact that the velocities are randomized at the beginning of each MD run, whether or not its predecessor has been accepted (otherwise detailed balance cannot be satisfied)\cite{Forrest94a}.

In contrast to this, another Hybrid-MC scheme, the stochastic dynamics - Monte Carlo (SD-MC) algorithm\cite{Guarnieri94a} leaves the velocities unaffected by the acceptance or rejection of the MC step. The algorithm seems to be capable of sampling the phase space efficiently, but without proof of canonicity.
3 Theory III: Correlations and Fluctuations

3.1 Correlation Functions in Space and Time

Correlation functions are of outstanding importance in atomistic modeling since they provide the necessary link between quantities computed by the simulation (e.g. velocity and location of the atoms) and experimentally observable properties (diffusion coefficient, electrical conductivity, etc.). In this subchapter, the correlation functions in space and time will be introduced, some of their properties investigated, and a few applications mentioned.

3.1.1 The Radial Distribution Function

A 'lattice' function $G^\alpha (r)$ is introduced, which describes the probability of finding an atom of kind $\alpha$ at the position $r$. The analytical form of $G$ depends on the atomistic system being investigated. A structure at very low temperature or an individual frame of an MC or MD simulation produces a sum of delta functions:

$$G^\alpha (r') = \sum_{i=1}^{N^\alpha} \delta \left( r' - r^{(i)} \right), \quad (3-1)$$

with $N^\alpha$ being the number and $r^{(i)}$ the position of the atoms of kind $\alpha$. If structures at higher temperatures or a large number of simulation frames are considered, the distribution of the individual atomic positions is gaussian - provided, the underlying interaction potential is harmonic:

$$G^\alpha (r') = \sum_{i=1}^{N^\alpha} \frac{1}{\sqrt{2\pi\sigma}} e^{-\frac{\|r' - r^{(i)}\|^2}{2\sigma^2}}, \quad (3-2)$$

Other 'lattice' functions than (3-1) and (3-2) are possible, but their normalization constant is always

$$\int_{\mathbb{R}^3} G^\alpha (r') \, dr' = N^\alpha. \quad (3-3)$$

Using the 'lattice' functions, the pair distribution function $g_{\alpha\beta}(r)$ can be defined as

$$g_{\alpha\beta} (r) = \frac{1}{N^\alpha N^\beta} \int_{\mathbb{R}^3} G^\alpha (r' - r) \, G^\beta (r') \, dr', \quad (3-4)$$
which, integrated over all \( r \) of equal length, results in the radial distribution function

\[
g_{\alpha\beta}(r) = \frac{1}{4\pi} \int_0^{\pi} \int_{-\pi}^{\pi} \sin \theta \, d\phi \, g_{\alpha\beta}(r)
\]

with \( r = f(r, \vartheta, \varphi) \).

Using the convolution theorem, \( g_{\alpha\beta}(r) \) can be expressed by the Fourier transforms (Eq. (3-15)) of \( G^\alpha \) and \( G^\beta \) as

\[
g_{\alpha\beta}(\omega) = G^\alpha(\omega) G^\beta(\omega).
\]

An example of calculated radial distribution functions is given in Fig. 3.1, where the distributions in a nearest-neighbour Lennard-Jones crystal (which is quite similar to an argon crystal) at a reduced temperature \( T^* \) of 0, 0.125, and 0.31 are compared (the melting point of the crystal is at about \( T^* = 0.5 \)). The broadening and shift of the peaks to higher values with increasing temperature can be well observed.

The radial distribution function is of central importance in the theory of disordered systems for two reasons: \(^{86}\text{Hansen,}^{76}\text{McQuarrie}\)

First, the radial distribution function can be measured experimentally both by X-ray diffraction and by neutron scattering methods. The structure factor

![Figure 3.1: Radial distribution function of an nearest-neighbour Lennard-Jones crystal at three different reduced temperatures (2048 atoms with variable-shape MC after 3·10^6 global updates)](image-url)
3.1 Correlation Functions in Space and Time

\[ h(s) = \rho \int_{-\infty}^{\infty} [g(r) - 1] e^{is \cdot r} dr, \]  

(3-7)

the Fourier transform of \( g(r) - 1 \), can be evaluated directly with radiation-scattering experiments.

Second, thermodynamical quantities such as the potential energy \( U \), the pressure \( \rho \), and the chemical potential \( \mu \) can be calculated, once the radial distribution function is known.

3.1.2 The Time-Autocorrelation Function

In Molecular Dynamics as well as in Monte Carlo simulations, successive conformations are normally highly correlated (i.e. differ only little). A convenient measure of the fading of the correlation of a dynamical variable \( A(t) \) (e.g. the velocity \( \mathbf{v}(t) \) or the position \( r(t) \) of a particle) is the time-autocorrelation function \(^6\)

\[ C_{AA}(\tau) = \frac{1}{t_{\text{max}}} \int_0^{t_{\text{max}}} A(t + \tau) A(t) \, dt = \frac{1}{n_{\text{max}}} \sum_{i=1}^{n_{\text{max}}} A_i + \tau / \Delta t A_i = \langle A(\tau) A \rangle. \]  

(3-8)

The first equality is valid for continuous values of \( A(t) \) whereas the second equality defines the autocorrelation function of \( A \) at discrete values of \( t \), assuming constant time intervals \( \Delta t \) between successive samples; \( A_k \) is defined as \( A(k \cdot \Delta t) \). The third equality is only valid, if the process that governs the time evolution of \( A(t) \) is ergodic \(^{76}\), because the angular brackets denote an ensemble average. In the subsequent derivations, however, this notation will be used both for time and ensemble averages.

If \( A(t) \) fluctuates around a non-zero mean value \( \langle A \rangle \), only its deviations from this mean value are of interest, giving

\[ a(t) = A(t) - \langle A \rangle. \]  

(3-9)

The correlation function of this quantity can be normalized by dividing it by \( C_{aa}(0) \),

\[ c_{aa}(\tau) = \frac{\langle a(\tau) a \rangle}{\langle a(0) a \rangle} = \frac{\langle a(\tau) a \rangle}{\langle a^2 \rangle}. \]  

(3-10)

The normalized correlation function \( c_{aa} \) has the following important properties: \(^{96,76}\)
with the second equation following from Schwarz's inequality and the third from
the definition of $a(t)$ (Eq. (3-9)). The time-autocorrelation function is thus a mea-
sure how long it lasts until the system has lost its 'memory' of the previous con-
formations or states. A value of 1 indicates complete correlation with the state of
reference, whereas 0 indicates complete loss of all information about the initial
state.

A typical autocorrelation function looks similar to the one given in Fig. 3.2.

![Autocorrelation function of the γ-angle of Cellulose at 325 K (TIP4P-MD simulation
with Ewald summation of the coulombic interactions, data from 0 to 132 ps)](image)

At short times (< 10 fs), there is hardly any change in the quantity of interest (the γ
angle of the cell shape), whereas, at about 100 fs, a quick decorrelation starts,
corresponding to a fluctuation of the cell with a period of about 350 fs. This
period is reflected too in the oscillations at long times and is linked to the cell
mass $W$ of the constant-pressure MD algorithm (Eq. (2-66)). At very long times,
these oscillations become smaller and smaller because the fluctuations of the
cell are not monochromatic. The relaxation time $\tau_R$, i.e. the time where $c_{\gamma}(t)$ has
dropped to $\frac{1}{e^2}$, is about 70 fs in the above example.

### 3.1.3 The Time-Crosscorrelation Function

The temporal dependence between two different variables $A(t)$ and $B(t)$ is
expressed by the crosscorrelation function
which can be normalized by subtracting the mean values from the variables \( A(t) \) and \( B(t) \) and dividing the correlation function by \( \langle a(0)b \rangle \):

\[
C_{AB}(\tau) = \frac{\langle a(\tau)b \rangle}{\langle a(0)b \rangle},
\]

(3-13)

with \( a(t) = A(t) - \langle A \rangle \) and \( b(t) = B(t) - \langle B \rangle \). Again \( C_{AB}(\tau) \) is proportional to the probability of \( a(t+\tau) \) evolving parallel with \( b(t) \).

According to Eqs. (3-8) and (3-12), the correlation functions are functions of the time difference \( \tau \) only and are thus said to be stationary. Therefore, the relations

\[
\langle \dot{A}(\tau)B \rangle = -\langle A(\tau)b \rangle,
\]

(3-14)

\[
\langle \dot{A}A \rangle = 0
\]

\[
\langle \dot{A}(\tau)B \rangle = -\langle \dot{A}(\tau)b \rangle
\]

are valid.\(^{Hansen86}\)

### 3.1.4 The Wiener-Khinchin Theorem

If \( A(\omega) \) denotes the Fourier-transform of the familiar dynamic variable \( A(t) \),

\[
A(\omega) = \lim_{T \to \infty} \int_{-T}^{T} A(t) e^{i\omega t} dt,
\]

(3-15)

the spectral density function of \( A(t) \) is defined as

\[
S_{AA}(\omega) = \lim_{T \to \infty} \frac{1}{2T} \int_{-T}^{T} A(\omega) A^*(\omega) dt,
\]

(3-16)

where \( A^*(\omega) \) stands for the complex conjugate of \( A(\omega) \).

The Wiener-Khinchin theorem now connects the spectral density and the time-correlation function of \( A(t) \) by stating that\(^{Reichl80a}\)

\[
S_{AA}(\omega) = \int_{-\infty}^{\infty} e^{i\omega \tau} \langle A(\tau)A \rangle d\tau = \int_{-\infty}^{\infty} e^{i\omega \tau} C_{AA}(\tau) d\tau.
\]

(3-17)

This is equivalent to the more general 'Correlation Theorem'\(^{Presseetal92}\)

\[
C_{AB}(\tau) = A(\omega) B^*(\omega),
\]

(3-18)
which allows to compute the correlation function by multiplication of the Fourier transform of the fluctuating variable(s).

### 3.1.5 Kubo-Green Formula

The well-known Einstein formula for the self-diffusion coefficient

\[ D = \lim_{t \to \infty} \frac{1}{6t} \langle [r^{(i)}(t) - r^{(i)}(0)]^2 \rangle \quad (3-19) \]

can be generalized to the following form:

\[ K = \langle \Delta A(t) \rangle = \frac{1}{kTV} \lim_{t \to \infty} \frac{1}{2t} \langle [A(t) - A(0)]^2 \rangle. \quad (3-20) \]

This equation is equivalent to

\[ K = \langle \Delta A(t) \rangle = \lambda \int_{t}^{\infty} \chi_{AB}(\tau) \, d\tau \quad (3-21) \]

with \( \lambda \) being the constant external perturbation and \( \chi_{AB} \) the 'after effect' function

\[ \chi_{AB}(t) = \begin{cases} \frac{1}{kT} \langle B(0) \dot{A}(t) \rangle & \text{for } t > 0 \\ 0 & \text{for } t \leq 0 \end{cases} \quad (3-22) \]

(3-22) is the so-called Green-Kubo relation between a transport coefficient and an integral over a time-correlation function. There exists a number of such relations, some of which are given in the next equations:

\[ D = \int_{0}^{\infty} \langle v^{(i)}(\tau) \cdot v^{(i)}(0) \rangle \, d\tau \]

\[ \eta = \frac{1}{kTV} \int_{0}^{\infty} \langle \sigma_{ik}(\tau) \sigma_{ik}(0) \rangle \, d\tau \quad (3-23) \]

\[ \lambda_{T} = \frac{1}{kT^2V} \int_{0}^{\infty} \langle \dot{j}^{(i)}(\tau) \dot{j}^{(i)}(0) \rangle \, d\tau \quad (3-23) \]

\[ \sigma_{e} = \frac{1}{kTV} \int_{0}^{\infty} \langle \dot{j}^{(\alpha)}(\tau) \dot{j}^{(\alpha)}(0) \rangle \, d\tau \quad (3-23) \]

As stated in the remarks of Eq. (3-8), the angular brackets actually denote
ensemble averages. The notation of the variables is given at the beginning of this work. Assuming ergodicity to hold, the ensemble averages can be replaced by time averages (chapter 2.4.2). For Eqs. (3-23) to be exactly valid, it would actually be necessary to simulate for an infinite amount of time. Since this is not possible in practical computer simulations, all quantities calculated from the above equations are just finite-time approximations of the 'real' values. It is therefore necessary to check whether or not the simulation has been long enough for the results to converge.

3.2 The Fluctuation-Dissipation Theorem and the Elastic Constants

3.2.1 The Fluctuation-Dissipation Theorem

The famous fluctuation-dissipation theorem \(^8\text{Landau}^8\),

\[
\langle x^2 \rangle = \frac{h}{2\pi^2} \int_0^\infty \alpha''(\omega) \coth \frac{\hbar \omega}{4\pi k T} d\omega,
\]

connects the imaginary part of the generalized susceptibility \(\alpha(\omega)\) to the mean square of the fluctuations of a general physical quantity \(x\). The generalized susceptibility is the Fourier-transform of the proportionality \(\dot{x}\) of the linear response \(\ddot{x}(t)\) of a physical quantity \(x(t)\) to an external perturbation force \(f(t)\):

\[
\ddot{x}(t) = \dot{x} f(t).
\]

The perturbation force \(f(t)\) and the physical property \(x(t)\) can be any pair of conjugate quantities (e.g. electrical field and dipole moment); in the case of the elastic properties, \(f(t)\) is a mechanical force (or stress) acting on a solid body that invokes a deformation (or strain) response \(x(t)\). The proportionality factor \(\dot{x}\) between these two quantities is the familiar elastic compliance (Eq. (1-56)).

In the limit of high temperatures \(kT \gg \hbar \omega/2\pi\) - the classical case - the fluctuation-dissipation theorem (FDT) can be simplified to \(^8\text{Landau}^8\)

\[
\langle x^2 \rangle = kT\alpha'(0).
\]

The first formulation (3-24) of the FDT allows to obtain informations about the underlying atomistic processes from macroscopic measurement of the imaginary part of the general susceptibility. By reformulating the FDT, it is also possible to compute a general susceptibility from the fluctuations of the corresponding physical quantity. The following equation for the generalized susceptibility is due
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Kubo\textsuperscript{Kubo66a}

\[
\alpha(\omega) = \frac{i2\pi}{\hbar} \int_0^\infty e^{i\omega t} \langle \dot{x}(t) (\dot{x}(0) - x(0)) (\dot{x}(t)) \rangle dt. \tag{3-27}
\]

In the classical limit, this formula is equivalent to Eqs. (3-23) (and of course Eq. (3-26)).

3.2.2 The Fluctuation Equations of the Elastic Constants

The strain-strain fluctuation formula of the elastic constants,

\[
\langle \eta_{ik} \eta_{lm} \rangle = \frac{kT}{\langle V \rangle} S_{iklm} \tag{3-28}
\]

can be directly derived from (3-26). Using the stiffnesses instead of the compliances leads to the familiar form of the equation\textsuperscript{ParrinelloRahman82a}.

\[
C_{iklm} = \frac{kT}{\langle V \rangle} \langle \eta_{ik} \eta_{lm} \rangle^{-1}. \tag{3-29}
\]

The stress-strain fluctuation formula of the elastic constants is obtained in the following way\textsuperscript{Gusev96a}:

In the absence of external stresses, the Hamiltonian $H$ of a $N$-particle system can be written as

\[
H = \sum_\alpha \frac{p_\alpha^2}{2m_\alpha} + U(r_{\alpha\beta}), \tag{3-30}
\]

where $p_\alpha$ and $m_\alpha$ are the momentum and mass of particle $\alpha$ and $U(r_{\alpha\beta})$ is the potential energy, which depends only on the distances $r_{\alpha\beta}$ between the particles. Considering six independent components of the strain tensor $\eta_{ik}$ (Eq. (1-36)) as 'generalized coordinates' (degrees of freedom) the following identity holds:

\[
\left\langle \eta_{ik} \frac{\partial H}{\partial \eta_{lm}} \right\rangle = kT \delta_{il} \delta_{lm}. \tag{3-31}
\]

Equations (3-31) and (2-49) are examples of the general form $\langle A \partial H / \partial q \rangle = kT (\partial A / \partial q)$ that holds\textsuperscript{Münster69,Pathria72} for any generalized coordinate $q$ and function $A$ in the canonical ensemble and is valid to $O(N^{-1})$ in any other ensemble.

To calculate the derivatives of the Hamiltonian with respect to the strain components, Eq. (1-28) takes the form
\[ r^2 = R^2 + 2\eta_{ik}X_iX_k, \quad (3-32) \]

which is actually the definition of the strain tensor for homogeneous deformations. Differentiating both sides of (3-32) with respect to \( \eta_{ik} \) and noting that \( X_i = H_ih_{ik}X_k \) (Eq. (B-1)), we obtain from (3-30) - (3-32)

\[ \langle \eta_{ik} \sum_{\alpha > \beta} \frac{\partial U}{\partial \eta_{\alpha \beta}} \frac{H_{lp}h_{pq}^{-1}(x_{\alpha \beta})_q H_{mt}h_{ts}^{-1}(x_{\alpha \beta})_s}{r_{\alpha \beta}} \rangle = \frac{1}{2}kT(\delta_{il}\delta_{km} + \delta_{lm}\delta_{kl}). \quad (3-33) \]

The kinetic term of the Hamiltonian was left out in the above equation, because it does not contribute, since \( \langle \eta_{ik} \rangle = 0 \). From Eqs (3-29) and (3-33) a new fluctuation formula for the elastic constants follows:

\[ C_{iklm} = \frac{1}{\langle V \rangle} \langle \eta_{ik} t_{nj} \rangle \langle \eta_{nj} \eta_{lm} \rangle^{-1}. \quad (3-34) \]

According to Eqs (1-46) and (1-47), the summation term is equivalent to the thermodynamic tension \( t \). This results in the following notation of the fluctuation formula for finite stress and strain:

\[ C_{iklm} = \langle \eta_{ik}\sigma_{nj} \rangle \langle \eta_{nj} \eta_{lm} \rangle^{-1}. \quad (3-35) \]

If the difference between the instantaneous scaling matrix \( h \) and the average scaling matrix \( \bar{H} \) is small (e.g. at low temperatures), the linear stress tensor \( \sigma \) can be used instead:

\[ C_{iklm} = \langle \eta_{ik}\sigma_{nj} \rangle \langle \eta_{nj} \eta_{lm} \rangle^{-1}. \quad (3-36) \]

In the limit of thermodynamic equilibrium, both fluctuation approaches yield the same result, leading to the following convergence criterion:

\[ \langle \eta_{ik} t_{lm} \rangle = \frac{1}{2\langle V \rangle} \langle \delta_{ij}\delta_{km} + \delta_{im}\delta_{jk} \rangle, \quad (3-37) \]

which is equivalent to (3-33). If linear stresses are assumed, the convergence criterion can be written as

\[ \langle \eta_{ik}\sigma_{lm} \rangle = \frac{1}{2\langle V \rangle} \langle \delta_{ij}\delta_{km} + \delta_{im}\delta_{jk} \rangle. \quad (3-38) \]

Equation (3-37) shows, that formally the constant term \( kT/\langle V \rangle \) of Eq.(3-29) is replaced by the fluctuating components of the stress-strain correlation. Unless the instantaneous stresses and strains are correlated, this would not improve the
convergence of the elastic constants calculation. But they indeed are correlated, as is most obvious in the limit of low temperature, where the entropic contributions are negligible and the instantaneous stresses are unambiguously determined by the instantaneous strains via Hooke's law

$$\sigma_{ij} = c_{ijk}\epsilon_{kl}. \quad (1-49)$$

As discussed in Ref. [Gusev96a], this correlation between the instantaneous stresses and strains allows for an evaluation of the elastic constants by using (3-35) or (3-36) without fully converged second moments \(\langle \eta_{ij}\eta_{lm} \rangle \) of the strain fluctuations, as explicitly required by (3-29).

### 3.2.3 Size Dependence of the Elastic Thermal Fluctuations

The amplitude of the thermal fluctuations of a body with Young's modulus \(E\) is increasing with decreasing sample dimension \(l\), approximately like

$$\sqrt{\langle \delta F^2 \rangle} = \frac{kT}{\sqrt{E}}. \quad (3-39)$$

This can be rationalized by considering \(l\) as a degree of freedom of the system as a whole and assigning an average energy of \(\frac{1}{2}kT\) to it. The average elastic energy of a cubic cell due to the fluctuation of the cell size \(l\) matches this value in thermodynamic equilibrium, as is expressed by

$$\langle \frac{1}{2}E\delta l^2 \rangle = \frac{1}{2}kT. \quad (3-40)$$

Figure 3.3 gives an example of the absolute value of the thermal fluctuations of a

![Figure 3.3: Root mean squared fluctuations of a body with a Young modulus of 3 GPa as a function of its size \(l\).](image-url)
cubic body with a Young modulus of $E = 3 \text{ GPa}$. It is clearly visible that, at macroscopic dimensions of centimeters ($10^8 \text{ Å}$), the fluctuations are vanishingly small. At very small dimensions of $10 - 30 \text{ Å}$ typically present in simulations, the fluctuations are in the range of a few percent of the cell dimension $l$. This considerable absolute value guarantees an accurate numerical registration of the effect, i.e. a good signal/noise ratio. On the other hand, dynamical instabilities occur if the cell size is very small or Young's modulus very low. It furthermore often requires the use of finite instead of linear stresses and strains.
4 Results

This section contains the description of the various atomistic model systems that were simulated in the course of this Ph. D. thesis and of the results obtained from these simulations.

Chronologically, the first polymer that was investigated was polycarbonate (BPA-PC) in its glassy state. In order to have a more simple system and to avoid the imponderabilities of generating amorphous structures, a monocrystal of polyethylene was the next system of interest. Polypropylene followed, because it allowed to get insights into the elasticity of helical chains. The final step in the direction of more simple and computationally well tractable systems was reached by simulating a crystal of nearest-neighbour Lennard-Jones particles. This system allowed to compare the different fluctuation formulae and to have a close look at the influence of the temperature on the elastic constants. Due to the experience gained in this system, it became possible to aim for more complicated structures: crystalline polyamide-6 and Cellulose-Iβ were modeled at various temperatures. The whole work ended with an extensive simulation of amorphous polyamide-6 and -12 in dry and water-saturated state at different temperatures to quantify the influence of these parameters on the mechanical behaviour.

The model systems, however, will be presented starting from the most simple and best understood going to more and more complicated problems:

- Lennard-Jones solid - nearest neighbours
- Polyethylene - planar zig-zag chains
- Polypropylene - helical chains
- Cellulose-Iβ - chains with hydrogen bonds
- Polyamide-6 - chains with hydrogen bonds
- Polyamide-6 - amorphous, with and without water
- Polyamide-12 - amorphous, with and without water
- Polycarbonate - amorphous

For each system, a short description about the structure and its generation process is given, followed by details about the simulation procedure. Problems encountered during the simulation and the results obtained from the trajectories are discussed. Finally a comparison with other numerical approaches and with experimental values (if available) is made and conclusions are drawn.
4.1 Lennard-Jones Solid - Nearest-Neighbours

4.1.1 Introduction

Crystals of the rare gases Ne, Ar, Kr, and Xe have been studied particularly well\textsuperscript{Horton76} due to their extremely simple structure: they consist of individual atoms which form an fcc (face-centered cubic) lattice. This lattice is held together only by van-der-Waals forces (dispersion and exchange terms); Coulombic or bonded interactions as well as induction terms are completely missing. Nevertheless, theoretical and experimental determination of the precise form of the interaction potential is by no means trivial. One of the best approximations is the so-called Barker-Fisher-Watts (BFW) potential\textsuperscript{Barker76}

$$U(r) = \varepsilon \left( \sum_{i=1}^{5} A_i (R - 1)^i - \frac{C_6}{R^6 + \delta} - \frac{C_8}{R^8 + \delta} - \frac{C_{10}}{R^{10} + \delta} \right)^{\alpha} \tag{4-1}$$

As already mentioned in chapter 2.1.3.5, many-body interactions contribute substantially to the total energy, making it necessary to include at least the triple-dipole contribution to obtain reliable results.\textsuperscript{Barker76} It is also worth noting that all calculations predict an extremely small energy difference between the hexagonally close packed (hcp) and the fcc lattice. This difference is a fraction of a percent of the crystal potential energy and by far not enough to explain the fact that the above mentioned rare gases crystallize in the fcc structure.\textsuperscript{BellZuck76}

Since the above potential is quite complicated, the more simple 12-6 Lennard-Jones function of Eq. (2-8) is used for model calculations. This so-called Lennard-Jones solid (which - by reasons stated above - is not identical to a solid rare gas) is a widely used model system. In many simulations, the simplicity of this model is further increased by neglecting all but the nearest-neighbour interactions. The result is the Nearest-neighbour Lennard-Jones solid, a well-investigated reference system against which new sampling methods can be tested.\textsuperscript{Rahman64a,Verlet67a,Sprik84a,Rutledge94b}

The intention of the following work was to study the convergence behaviour of different fluctuation approaches, in particular the Parrinello-Rahman strain-strain correlation formula (Eq. (3-36)) and the new stress-strain correlation formula (Eq. (3-34)). Another objective was it to establish the influence of the simulation box size and the temperature on the convergence rate and the 'final'

\begin{itemize}
  \item $R = \sigma^*$ (chapter 2.1.3.3), $\sigma^* = 3.7612 \, \text{Å}$, $\varepsilon/k = 142.095 \, \text{K}$, $R_0 = 3.3605 \, \text{Å}$,
  \item $A_0 = 0.27783$, $A_1 = -4.50431$, $A_2 = -8.331215$, $A_3 = -25.2696$, $A_4 = -102.0195$, $A_5 = -113.25$, $C_6 = 1.10727$, $C_8 = 0.16971325$, $C_{10} = 0.013611$, $\alpha = 12.5$, and $\delta = 0.01$
\end{itemize}
results. Therefore, Monte Carlo and molecular dynamics simulations of a variety of systems from 32 to 2048 and even 23328 atoms were performed at different temperatures. This was possible because the extreme simplicity of the interaction function (Eq. (E-2)) allowed to write highly efficient code (an example: one global-update MC step of a 108-atom system took 1.3 milliseconds on a workstation).

The results of these simulations will be examined in detail in order to introduce the methodology for the subsequent polymeric systems.

4.1.2 Description and Cell Generation

With an fcc unit cell of 4 atoms (Fig. 4.1 a)) and a cubic overall shape the simulation system contains \(n^3 \times 4\) atoms (\(n\) being integer). In the literature, all possible systems from 32 \((n = 2)\) to 864 \((n = 6)\) particles have been described and used. Due to the cubic symmetry, there are only three independent elastic constants, \(C_{11}, C_{12}, \text{ and } C_{44}\), as indicated in Table 1-2 on page 18. Many of the results in the following sections are thus given as an average over the symmetry-equivalent components of the matrix of the elastic constants. The standard deviation serves as an indication of the precision of the calculation, as do the elements that should be zero.

The generation of cubic simulation boxes of arbitrary size was done by a small program (makecar.f), which calculated the size of the box, the positions of the individual atoms, and the list of nearest-neighbour interactions from the number of unit cells per dimension, \(n\). It was not necessary to specify the Lennard-Jones parameter \(\sigma\) because reduced units were used (Appendix E). To convert
from reduced to SI units, \( \sigma = 3.805 \text{ Å} \) and \( \varepsilon = 119.8 \text{ kJ mol}^{-1} \) have been used.

To speed up equilibration, it is favourable to multiply the \( h \) matrix describing the box shape with an empirical, temperature-dependent constant which accounts for the thermal expansion of the simulation box. Typical values of this constant lie between 1.1 and 1.2 \(^{83a}\). The file created by the above program, and used as the input of the subsequent MC simulation, had a structure that is given in Table 4-1.

Table 4-1: The data file of the nearest-neighbour Lennard-Jones solid

| \( a_1 \) | \( b_1 \) | \( c_1 \) | \( h \)-matrix \([a,b,c]\) |
| \( a_2 \) | \( b_2 \) | \( c_2 \) |
| \( a_3 \) | \( b_3 \) | \( c_3 \) |
| \( s_{11} \) | \( s_{12} \) | \( s_{13} \) | scaled coordinates of the 4\( n^3 \) atoms |
| \( s_{21} \) | \( s_{22} \) | \( s_{23} \) |
| .. | .. | .. |
| .. | .. | .. |
| \( a_{ti} \) | \( a_{tk} \) | list of 6-4\( n^3 \) pairs of nearest neighbours |
| .. | .. |

### 4.1.3 Simulation Procedure

#### 4.1.3.1 Monte Carlo Simulations

A simple global-update Monte Carlo move was used to simulate a \( T_N \)-ensemble: In one move both the cell shape matrix \( h \) and the coordinates \( x^{(a)} \) of all atoms were changed randomly. The cell shape matrix was altered symmetrically by

\[
h_{\text{new}} = h_{\text{old}} + \Delta h_{\text{max}} (2R - 1) \quad R_{ik} = R_{ki}
\]  

(4-2)

to prevent rotations of the cell as a whole. The positions of all atoms were changed by

\[
x_{\text{new}}^{(a)} = x_{\text{old}}^{(a)} + \Delta x_{\text{max}} (2R - 1)
\]  

(4-3)

with \( R \) denoting a symmetric 3x3 matrix (Eq. (4-2)) or a vector (Eq. (4-3)) of random numbers between 0 and 1 and \( \mathbf{1} \) being a matrix or a vector full of 1's. All random numbers were generated by the Lagged Fibonacci algorithm described in Appendix C-2.

The maximum possible change of the cell parameters and of the coordinates, \( \Delta h_{\text{max}} \) and \( \Delta x_{\text{max}} \), were set to the same proportion by
with \( N \) being the number of atoms. \( \Delta h_{\text{max}} \) was not a true degree of freedom since it was adapted during the simulation to yield a certain acceptance ratio. An auto-adjustment procedure was introduced that modified these values to keep the acceptance ratio \( \rho_{\text{acc}} \) between \( \rho_{\text{acc, min}} \) and \( \rho_{\text{acc, max}} \). If the actual acceptance ratio - computed over at least 100 steps - was smaller than \( \rho_{\text{acc, min}} \), \( \Delta h_{\text{max}} \) was reduced by 10% (multiplied with 0.9). If it exceeded \( \rho_{\text{acc, max}} \), \( \Delta h_{\text{max}} \) was multiplied with 1.1 instead. Stationary values of \( \Delta h_{\text{max}} \) were reached after \( 2 \times 10^4 - 4 \times 10^5 \) MC steps. Typically, this initial period with varying \( \Delta h_{\text{max}} \) comprised less than a percent of the total simulation and its influence on the final result should therefore be negligible. However, in some cases a faster convergence would have been achieved by starting with a better guess of \( \Delta h_{\text{max}} \).

After a random change of the cell shape and atom coordinates, \( E_{\text{new}} \) the sum of the interaction energies between the nearest neighbours was calculated. A move was accepted if

\[
\min\left(1, \left( \frac{V_{\text{new}}}{V_{\text{old}}} \right)^N \cdot \exp\left( -\frac{E_{\text{new}} - E_{\text{old}}}{kT} \right) \right) > \frac{1}{2}
\]

was larger than a random number between 0 and 1. In this case, the new configuration replaced the old one and was added to the ensemble average. Otherwise, the old configuration contributed again to the ensemble average. The ensemble sampled in this way was the \( TN \)-ensemble and the elastic constants are the isothermal ones.

Tables 4-2 and 4-3 show the simulations that were performed using the \( TN \)-MC algorithm. The linear form of the stress-strain correlation function (Eq. (4-16)) was used to compute the elastic constants in Table 4-2. In Table 4-3, the finite-stress-strain correlations were computed by Eq. (4-20). In each cell, the number of equilibration steps is indicated in the upper left and the number of sampling steps in the lower right half. The last row in the first table lists the CPU time per MC step on a workstation (SGI Crimson). Since only nearest-neighbour interactions were considered, the computation time scales linearly with \( N \). There is no significant difference in the computation time if finite stresses were assumed.

Besides these simulations, the influence of the acceptance probability on the convergence of the elastic constants was investigated by a series of three runs with 32 atoms at \( T^* = 0.3 \), each of \( 10^6 \) steps. The maximum possible
Table 4-2: $TtN$-MC simulations of nearest-neighbour Lennard-Jones solid of various size at a range of temperatures, linear stresses were assumed in all calculations

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$N$</th>
<th>32</th>
<th>108</th>
<th>256</th>
<th>2048</th>
<th>23328</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>10^6</td>
<td>10^8</td>
<td>10^8</td>
<td>10^6</td>
<td>10^7</td>
<td>2.10^6</td>
</tr>
<tr>
<td>0.225</td>
<td>-</td>
<td>10^8</td>
<td>10^8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>10^8</td>
<td>10^8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.31</td>
<td>10^6</td>
<td>10^8</td>
<td>-</td>
<td>2.10^6</td>
<td>10^7</td>
<td>2.10^6</td>
</tr>
<tr>
<td>0.5</td>
<td>10^6</td>
<td>10^8</td>
<td>-</td>
<td>10^6</td>
<td>10^7</td>
<td>10^6</td>
</tr>
<tr>
<td>$t_{CPU}$ [s]</td>
<td>0.0013</td>
<td>0.0043</td>
<td>0.0095</td>
<td>0.1180</td>
<td>0.8946</td>
<td></td>
</tr>
</tbody>
</table>

Table 4-3: $TtN$-MC simulations of nearest-neighbour Lennard-Jones solid of various size at a range of temperatures, in all calculations, finite stresses were taken into account

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$N$</th>
<th>32</th>
<th>108</th>
<th>256</th>
<th>2048</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>-</td>
<td>10^7</td>
<td>10^7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.02</td>
<td>-</td>
<td>1.5.10^7</td>
<td>1.5.10^7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.05</td>
<td>-</td>
<td>1.5.10^7</td>
<td>1.5.10^7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.125</td>
<td>-</td>
<td>10^8</td>
<td>2.10^8</td>
<td>10^8</td>
<td>-</td>
</tr>
<tr>
<td>0.225</td>
<td>-</td>
<td>2.10^8</td>
<td>10^8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.3</td>
<td>-</td>
<td>2.10^8</td>
<td>10^8</td>
<td>10^7</td>
<td>2.10^6</td>
</tr>
<tr>
<td>0.5</td>
<td>-</td>
<td>2.10^8</td>
<td>10^8</td>
<td>10^7</td>
<td>2.10^6</td>
</tr>
</tbody>
</table>

change of the cell parameters, $\Delta h_{max}$, was set such, that the acceptance probabilities were 5 - 10%, 45 - 50%, and 90 - 95%, respectively.

### 4.1.3.2 Molecular Dynamics Simulations

To check the results of the MC algorithm and to get an idea of its efficiency, some MD simulations were performed. For this purpose, argon structures of 108 atoms were built with InsightII and minimized with Discover94. The forcefield used for the minimization and the subsequent MD simulations contained only a 12-6 Lennard-Jones interaction term with $\sigma = 3.805\ \text{Å}$ and $\varepsilon/k = 119.8\ \text{K}$ (the
value of \( \sigma \) was taken from ref. [Sprik84a] and is somewhat too large). Runs in the 
T\textsubscript{oN} ensemble were made with a stepsize of \( \Delta t = 0.0025 \) (6.024 fs), approxi-
mately half the typical value found in the literature, which ranges from 8.6 fs\textsuperscript{Sprik84a} to 12.05 fs\textsuperscript{Ray85a,Ray88a}. This small value was chosen because the 
Nosé-Hoover thermostat used for the temperature control requires relatively 
small timesteps (chapter 2.5.2.3).

Consecutive simulations of several \( 10^4 \) steps wrote the cell size and the 
stresses to a table file from where these values were read by essentially the 
same program which computed the elastic constants of the MC runs. A descrip-
tion of this program will be given in chapter 4.1.4. Because it would have been 
too complicated to access the forces acting on the individual atoms, the stress-
strain correlation term in the Gusev-Zehnder-Suter formula was only calculated 
assuming linear (Eq. (3-36)) and not finite (3-35) stresses. So the results were 
just compared with MC calculations using linear stresses, too.

All MD and the MC simulations mentioned in this chapter were performed 
on a 108-atom Lennard-Jones crystal at a reduced temperature \( T^* = 0.3 \) and 
consisted of \( 10^7 \) steps. To circumvent the inability of the Discover MD-software 
to compute just nearest-neighbour interactions (as described in chapter 4.1.3.3), 
a set of runs with cutoffs of 5.35 Å without splines and 5.2 Å with various spline 
widths was used for both the MD and the MC simulations. The following table 
gives an overview of all simulations performed:

<table>
<thead>
<tr>
<th></th>
<th>cutoff [Å]</th>
<th>spline [Å]</th>
<th>runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>5.35</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>5.4</td>
<td>0.4</td>
<td>2</td>
</tr>
<tr>
<td>MD</td>
<td>5.4</td>
<td>0.4</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>5.8</td>
<td>1.2</td>
<td>1</td>
</tr>
</tbody>
</table>

### 4.1.3.3 Hybrid Monte Carlo

As a third independent sampling method, Hybrid Monte Carlo runs were 
done with Discover 94 for the structures of 108 and 500 atoms. Two different 
ensembles were sampled hereby: the canonical ThN\textsubscript{c} and the isothermal-isos-
tress T\textsubscript{oN}-ensemble. In both cases, an input-script for Discover 94 generated 
the necessary random numbers (Appendix C-1), extracted the energies from 
output files, and controlled the writing of conformations and cell stresses. How-
ever, various technical problems and limitations of Discover 94 prevented the use of this method for calculating elastic constants.

One of the first problems arouse with the cutoffs: For MD and HMC simulations, the interactions between nearest-neighbour interactions were replaced by those within a cutoff of 5.35 Å. This value was found by plotting a histogram of the interparticle distances at the desired simulation temperature of $T^* = 0.3$. As Fig. 3.1 reveals and as was confirmed by subsequent simulations, the first and second neighbour shells are so close that atoms from one or the other shell occasionally cross the sharp cutoff and change the energy by $-0.1232$ kcal/mole abruptly (Fig. 4.2 a)). No way was found to influence the update rate of the neighbour list in order to alter this unphysical behaviour. Hybrid-MC simulations of the nearest-neighbour Lennard-Jones solid were therefore not possible because a jump of $0.12$ kcal/mole is equal to a reduction of the acceptance down to 18%.

![Figure 4.2: Potential energy during an EhN-MD simulation of a Lennard-Jones solid (500 atoms, $T^* = 0.3$, $\Delta T^* = 0.005$) with a) a sharp cutoff at 5.35 Å and b) a splined cutoff between 5.0 and 5.4 Å](image)

The above jumps in the potential energy could be made much smaller by the introduction of a spline between 5.0 and 5.4 Å. As can be seen in Fig. 4.2 b), the fluctuations in the potential energy become approximately two orders of magnitude smaller and are less abrupt. These small fluctuations are hardly influencing the HMC algorithm anymore (influence on the acceptance rate is less than 3 %). But by introducing this spline of 0.4 Å width, one is no longer able to simulate a nearest-neighbour Lennard-Jones solid which has a strong impact on the elastic constants (chapter 4.1.5.5).

To sample conformations in the $\mathcal{T}\mathcal{N}$-ensemble, a hybrid scheme was
devised that consists of two parts: In one part, the cell is deformed by a random amount according to Eq. (4-2) without change of the atom coordinates; in the other part, a short Ehn-MD run is performed. In order to achieve detailed balance (microreversibility), the sequence of the two parts must not always be the same. It is possible to use a 50-50 mixture of moves that perform first a deformation and afterwards a MD simulation and moves that do the opposite. The other - equal - solution consists of a mixture of pure deformation and pure Hybrid-MC processes:

![Diagram](image)

Figure 4.3: TNA-HMC schemes: a) equal probability of dynamics/deformation and deformation/dynamics moves; b) adjustable proportion of deformation and dynamics

In Discover 94, however, the velocities can not be scaled simultaneously with the change of the cell shape matrix, so that the dynamics/deformation move can not be programmed straightforwardly.

To avoid these problems, variable shape (EaN)-MD simulation runs with relatively large timesteps (90.36 fs with a Nosé-Hoover thermostat) were used to sample the phase space on the limit of stability of MD. The acceptance criterion was modified by an 'umbrella' sampling technique described in chapter 2.5.1.3. The test system was again a 108-atom nearest-neighbour Lennard-Jones solid at T* = 0.3.

Again for comparison, the same system was used in a self-made MC code,

Table 4-5: Simulations with N = 108 and T* = 0.3, nearest-neighbour interactions only

<table>
<thead>
<tr>
<th></th>
<th>MD steps</th>
<th>global steps</th>
<th>runs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deformation only</td>
<td>-</td>
<td>8\times10^7</td>
<td>1</td>
</tr>
<tr>
<td>Deformation + MD</td>
<td>100</td>
<td>10^7</td>
<td>1</td>
</tr>
<tr>
<td>MD + Deformation</td>
<td>100</td>
<td>10^7</td>
<td>1</td>
</tr>
</tbody>
</table>

which was extended to follow a short Ehn-MD trajectory with a velocity-Verlet integrator (Appendix E). Using this code, the calculations listed in Table 4-5 were
4.1.4 Evaluation of the Elastic Constants

In order to calculate the elastic constants with the Parrinello-Rahman formula,

\[ C_{iklm} = \frac{kT}{\langle V \rangle} \langle \eta_{ik} \eta_{lm} \rangle^{-1}, \quad (3-29) \]

or with the Gusev-Zehnder-Suter approach,

\[ C_{iklm} = \langle \eta_{ik} t_{lj} \rangle \langle \eta_{lj} \eta_{lm} \rangle^{-1}, \quad (3-35) \]

it is necessary to evaluate the averages of the strain-strain and of the stress-strain correlation matrices, \( \langle \eta_{ik} \eta_{lm} \rangle \) and \( \langle \eta_{ik} t_{lj} \rangle \). But both the definition of the finite strain,

\[ \eta = \frac{1}{2} [H^{-1} h^T h H^{-1} - I], \quad (1-36) \]

and the finite stress,

\[ t = J^{-1} h^{-1} \sigma h^{-1} H^T, \quad (1-46) \]

contain the reference cell shape \( H \), which is not known \textit{a priori}, but can be set equal to the average cell shape \( \langle h \rangle^{\text{Parrinello-Rahman}81a} \). For the average cell shape in a \( \bar{T}tN \)-simulation is the cell shape formed by the average stress, and the net stress in all simulations was set to zero bar, this average cell shape should represent an equilibrium (i.e. strain-free) cell.

If the cell shape \( h(t) \) and the actual stress \( \sigma(t) \) are known as a function of time - MD simulation time or sequence of MC frames - the elastic constants can be expressed as a function of \( t \), too. The easiest and most straightforward way to do this is to store the cell parameters and the stress of all relevant frames and to obtain first the average cell shape and the average stress and to use these values in Eqs. (1-36) and (1-46) to compute the actual strain and stress, which themselves are needed to obtain the strain-strain and the stress-strain correlation matrices.

Although the correlation between successive frames makes it necessary to save, say, only every 10th frame, long simulations easily produce \( 10^7 \) (MD) or \( 10^8 \) (MC) frames. Even if the 64-bit binary representation is used, the storage of the 6 cell parameters and the 6 stress values consumes 100 to 1000 MBytes of...
data per run. It is therefore necessary to find an algorithm, which computes the
double averages of $h$ and $\alpha$ 'on the fly':

The strain of a cell matrix $h$ with respect to the average cell $\langle h \rangle$ is
expressed as

$$\eta = \frac{1}{2} \left[ \langle h^T \rangle^{-1} h^T h \langle h \rangle^{-1} - I \right] = \frac{1}{2} [H - I]$$  \hspace{1cm} (4-6)

(Note the difference between $H$, the reference cell shape, now replaced by $\langle h \rangle$, and $H$, given by the above equation.) The strain-strain correlation can be expanded now as

$$\langle \eta_{ij} \cdot \eta_{kl} \rangle = \frac{1}{4} \left[ \delta_{ij} \cdot \delta_{kl} - \delta_{ij} \cdot \langle H_{kl} \rangle - \delta_{kl} \cdot \langle H_{ij} \rangle - \langle H_{ij} \cdot H_{kl} \rangle \right]$$  \hspace{1cm} (4-7)

The important quantities to keep account of are $\langle H_{ij} \rangle$ and $\langle H_{ik} H_{jl} \rangle$. These quantities can be expressed as functions of the $\langle h \rangle$ and $h$ matrices that describe the average and the actual shape of the simulation cell. Using matrix multiplication algebra, the individual elements of the $H$ matrix can be written as:

$$H_{ij} = \sum_{k=1}^{3} \langle h_i^T \rangle^{-1}_{ik} \sum_{l=1}^{3} \left[ \sum_{m=1}^{3} h_{mk} h_{ml} \right] \langle h_j \rangle^{-1}_{ij}$$  \hspace{1cm} (4-8)

Due to the interchangeability of inversion and transposition and the fact that
$h_i^T = h_{ki}$, it is possible to write $H_{ij}$ in the form

$$H_{ij} = \sum_{k=1}^{3} \langle h_i \rangle^{-1}_{ki} \sum_{l=1}^{3} \langle h_j \rangle^{-1}_{lj} \sum_{m=1}^{3} h_{mk} h_{ml}$$  \hspace{1cm} (4-9)

The following rules,

$$\langle \sum_{\alpha} X_{\alpha} \rangle = \frac{1}{t} \sum_{t} \sum_{\alpha} X_{\alpha}^t = \frac{1}{t} \sum_{\alpha} \sum_{t} X_{\alpha}^t = \sum_{\alpha} \frac{1}{t} \sum_{t} X_{\alpha}^t = \sum_{\alpha} \langle X_{\alpha} \rangle$$,  \hspace{1cm} (4-10)

and

$$\langle \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \langle x_{\alpha \beta} \rangle x_{\alpha \gamma} x_{\beta \gamma} \rangle = \frac{1}{t} \sum_{t} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \langle x_{\alpha \beta} \rangle x_{\alpha \gamma} x_{\beta \gamma} =$$

$$\frac{1}{t} \sum_{t} \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \langle x_{\alpha \beta} \rangle \sum_{\gamma} x_{\alpha \gamma} x_{\beta \gamma} = \sum_{\alpha} \sum_{\beta} \langle x_{\alpha \beta} \rangle \frac{1}{t} \sum_{t} \sum_{\gamma} x_{\alpha \gamma} x_{\beta \gamma} =$$

$$\sum_{\alpha} \sum_{\beta} \langle x_{\alpha \beta} \rangle \sum_{\gamma} \frac{1}{t} \sum_{t} x_{\alpha \gamma} x_{\beta \gamma} = \sum_{\alpha} \sum_{\beta} \langle x_{\alpha \beta} \rangle \sum_{\gamma} \langle x_{\alpha \gamma} x_{\beta \gamma} \rangle$$  \hspace{1cm} (4-11)
allow to obtain the average of Eq. (4-9) as

$$
\langle H_{ij} \rangle = \sum_{k=1}^{3} \sum_{l=1}^{3} \langle h^{-1}_{ki} \rangle \langle h^{-1}_{lj} \rangle \sum_{m=1}^{3} \langle h_{mk} h_{ml} \rangle.
$$

The right side of Eq. (4-12) contains 3·9=27 elements over which the averages have to be summed. The last term of Eq. (4-7), $\langle H_{ij} H_{kl} \rangle$, is much more complicated: no less than 738 terms have to be watched:

$$
\langle H_{ij} \cdot H_{kl} \rangle = \sum_{m=1}^{3} \sum_{n=1}^{3} \sum_{o=1}^{3} \sum_{p=1}^{3} \langle h^{-1}_{mj} \rangle \langle h^{-1}_{nj} \rangle \langle h^{-1}_{ok} \rangle \langle h^{-1}_{pl} \rangle \sum_{q=1}^{3} \sum_{r=1}^{3} \langle h_{qm} h_{qn} h_{ro} h_{rp} \rangle.
$$

Inserting the above terms into Eq. (4-7), the average of the product of the strains is expressed in quite a lengthy expression:

$$
\langle \eta \cdot \eta \rangle_{ijkl} = \frac{1}{4} \delta_{ij} \cdot \delta_{kl} \cdot \frac{1}{4} \delta_{ij} \cdot \sum_{m=1}^{3} \sum_{n=1}^{3} \langle h^{-1}_{mk} \rangle \langle h^{-1}_{nl} \rangle \left( \sum_{o=1}^{3} \langle h_{om} h_{on} \rangle \right)
$$

$$
- \frac{1}{4} \delta_{kl} \cdot \sum_{m=1}^{3} \sum_{n=1}^{3} \langle h^{-1}_{mk} \rangle \langle h^{-1}_{nl} \rangle \left( \sum_{o=1}^{3} \langle h_{om} h_{on} \rangle \right) +
$$

$$
\frac{1}{4} \sum_{m=1}^{3} \sum_{n=1}^{3} \sum_{o=1}^{3} \sum_{p=1}^{3} \langle h^{-1}_{ml} \rangle \langle h^{-1}_{nj} \rangle \langle h^{-1}_{ok} \rangle \langle h^{-1}_{pl} \rangle \sum_{q=1}^{3} \sum_{r=1}^{3} \langle h_{qm} h_{qn} h_{ro} h_{rp} \rangle.
$$

The corresponding expression for the stress-strain correlation term in the limit of linear elasticity,

$$
\eta_{ij} \sigma_{kl} = \frac{1}{2} \left( \sum_{m=1}^{3} \langle h^{-1}_{mj} \rangle \sum_{n=1}^{3} \langle h^{-1}_{nj} \rangle \sum_{o=1}^{3} \langle h_{om} h_{on} \rangle \delta_{ij} \right) \cdot \sigma_{kl},
$$

can be found in an analogous way,

$$
\langle \eta_{ij} \sigma_{kl} \rangle = \frac{1}{2} \sum_{m=1}^{3} \sum_{n=1}^{3} \sum_{o=1}^{3} \langle h^{-1}_{mj} \rangle \langle h^{-1}_{nj} \rangle \langle h_{om} h_{on} \sigma_{kl} \rangle \frac{1}{2} \delta_{ij} \langle \sigma_{kl} \rangle.
$$

The above equation is correct in the limit of linear elasticity. To account for non-linear behaviour, the theory of finite elasticity needs to be applied. This is
done in the following steps.

Equation (3-34),

\[
C_{iklm} = \frac{1}{\langle V \rangle} \langle \eta_{ik} \sum_{\alpha > \beta} \frac{\partial U}{\partial r_{\alpha \beta}} H_{np} h_{pq}^{-1}(x_{\alpha \beta})_{q} H_{lt} h_{ts}^{-1}(x_{\alpha \beta})_{s} \rangle \langle \eta_{lj} \eta_{ml}^{-1} \rangle^{-1}, \quad (3-34)
\]

is slightly rewritten by using the fact that \( h_{ik}^{-1} x_{k} = s_{i} \) and that \( H \) can be replaced by \( \langle h \rangle \):

\[
C_{iklm} = \frac{1}{\langle V \rangle} \langle \eta_{ik} \sum_{\alpha > \beta} \frac{\partial U}{\partial r_{\alpha \beta}} \langle (h)_{np}(s_{\alpha \beta})_{p} \cdot (h)_{lt}(s_{\alpha \beta})_{l} \rangle \rangle \langle \eta_{lj} \eta_{ml}^{-1} \rangle^{-1}. \quad (4-17)
\]

Without summation convention, the first term on the right side is

\[
\langle \eta_{ij} \sum_{\alpha > \beta} \frac{\partial U}{\partial r_{\alpha \beta}} \langle (h)_{np}(s_{\alpha \beta})_{p} \cdot (h)_{lt}(s_{\alpha \beta})_{l} \rangle \rangle = \langle \eta_{ij} \sum_{\alpha > \beta} \sum_{p=1}^{3} \sum_{l=1}^{3} \langle (h)_{np}(h)_{lt} s_{\alpha \beta} s_{\alpha \beta} \rangle \frac{\partial U}{\partial r_{\alpha \beta}} \frac{1}{r_{\alpha \beta}} \rangle. \quad (4-18)
\]

Using Eq. (4-10) and writing Eq. (4-6) with explicit summations,

\[
\eta_{ik} = \frac{1}{2} \sum_{u=1}^{3} \sum_{v=1}^{3} \sum_{w=1}^{3} \langle h \rangle_{iu}^{T-1} h_{uv}^{T} h_{vw}^{T-1}(h)_{wk}^{T-1} \frac{1}{2} \delta_{ik}, \quad (4-19)
\]

the average stress-strain fluctuation term can be written (after reordering the indices) as

\[
\langle \eta_{ij} \sum_{\alpha > \beta} \frac{\partial U}{\partial r_{\alpha \beta}} \langle (h)_{km} s_{\alpha \beta m} \cdot (h)_{ln} s_{\alpha \beta n} \rangle \rangle = \frac{1}{2} \sum_{m=1}^{3} \sum_{n=1}^{3} \sum_{p=1}^{3} \sum_{q=1}^{3} \langle (h)_{km} (h)_{ln} (h)_{pq}^{-1} \rangle \frac{\partial U}{\partial r_{\alpha \beta}} \frac{1}{r_{\alpha \beta}} \langle \delta_{ij} \rangle \quad (4-20)
\]

All terms in Eq. (4-14) and (4-20) together need less than 1.5 kBytes of memory when stored as 64-bit numbers, independent of the number of frames processed. This allows the accurate calculation of the strain-strain and the stress-strain fluctuation term and thus the precise determination of the matrix of
the elastic constants.

4.1.5 Results

4.1.5.1 Influence of the Acceptance Ratio

As mentioned at the end of chapter 4.1.3.1, the influence of the acceptance probability, which is a function of the maximum allowed change in the cell shape, on the convergence of the elastic constants was investigated. A cell of 32 atoms at $T^* = 0.31$ was used for this purpose. The upper and the lower limit of the acceptance probabilities were set to 5 - 10%, 45 - 50%, and 90 - 95%, respectively. Figure 4.4 shows the relative error of $(C_{11} + C_{22} + C_{33})/3$. The relative error of this figure is defined as

$$\Delta_{rel}(n) = \frac{C(n)}{C(n=10^7)}$$

with $C(n)$ being $(C_{11}(n) + C_{22}(n) + C_{33}(n))/3$ and $n$ the number of Monte Carlo steps.

![Figure 4.4: Relative difference between actual $(C_{11}+C_{22}+C_{33})/3$ and the same value after $10^7$ MC steps. Solid lines delimiting shaded areas were calculated with Eq. (3-34) (stresses and strains), the other lines with Eq. (3-29) (strains alone), $T^* = 0.31$, 32 atoms](image)
After an initial run of $10^6$ steps to equilibrate the structure and to find a good starting value for $\Delta h_{\text{max}}$, the elastic constants were calculated from runs of $10^7$ steps assuming finite stresses. It can be clearly seen that there is hardly any difference between simulations with an acceptance rate of 5-10% and 45-50%, whereas higher acceptance rates clearly deteriorate the speed of convergence. This is mainly due to the smaller and smaller $\Delta h_{\text{max}}$ values (Table 4-6), which reduce the speed with which the system explores its phase space.

<table>
<thead>
<tr>
<th>$p_{\text{acc min}}$</th>
<th>$p_{\text{acc max}}$</th>
<th>$\Delta h_{\text{max}}$ [red. units]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.10</td>
<td>0.0245</td>
</tr>
<tr>
<td>0.45</td>
<td>0.50</td>
<td>0.0096</td>
</tr>
<tr>
<td>0.90</td>
<td>0.95</td>
<td>0.0012</td>
</tr>
</tbody>
</table>

For all subsequent simulations, acceptance rates of 12.5-17.5% or 45-50% were chosen. No influence of the acceptance rates on converged values of the elastic constants could be observed.

### 4.1.5.2 Elastic Constants at Very Low Temperatures

As shown in Table 4-3, MC simulations of a 108-atom cell were done at $T^* = 0.01, 0.02,$ and $0.05$. These results are of interest, because at such low temperatures, the anharmonic effects are small and the stress-strain correlation should converge very fast. At $T^* = 0.01$, this is indeed the case, as the above figure shows:
After a few steps, the elastic constants computed with the finite stress-strain fluctuation formula are to within a few percent of the final values, which themselves differ by less than a tenth of a percent from the static values. The roughly 19 (6 accepted) steps the stress-strain correlation needs to reduce its relative error down to about 10% are necessary to find an average cell shape, from which the strain can be calculated. The same level of accuracy is reached with the strain fluctuation method only after more than $10^8$ steps.

The complete matrix of the elastic constants at $T^* = 0.01$ and a table comparing the symmetry equivalent elastic constants at $T^* = 0.01, 0.02, and 0.05$ are given in Tables 4-7 and 4-8. Table 4-8: Reduced symmetry-equivalent elastic constants at $T^* = 0.01, 0.02, and 0.05$, strain (PR) and stress-strain fluctuation (GZS) formula. The reduced units have to be multiplied by 0.300 ($T^* = 0.01$), 0.598 ($T^* = 0.02$), and 1.487 MPa to obtain SI units

As is obvious from Table 4-8, there is a relation between the elastic constants of a crystal, if its lattice particles occupy centers of symmetry and interact
with central forces. This so-called Cauchy relation\textsuperscript{a} BornHuang54, Quesne93a can be expressed as\textsuperscript{a} Gusev96a

\[
\frac{2C_{44}}{(C_{11} - C_{12})} = 2 \quad C_{12} = C_{44}.
\] (4-22)

In Fig. 4.6, the ratio $2C_{44}/(C_{11} - C_{12})$ is plotted as a function of the temperature for the strain and the stress-strain fluctuation method. For both methods, this ratio approaches 2.0 at infinitely small temperature, with larger and larger deviations as the temperature rises and anharmonic effects come into play. These effects can be thought of as deflections of the individual atoms from the center of symmetry by thermal fluctuations. It can be further observed that the stress-strain fluctuation approach leads to a smoother form of the temperature dependence of the anisotropy ratio. Its error bars\textsuperscript{a} are especially at low temperatures.

\[4.6\]

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.6.png}
\caption{Cauchy relation of a 108-atom nearest-neighbour Lennard-Jones solid as a function of the reduced temperature}
\end{figure}

\textsuperscript{a} The standard deviations $dC_{11}$, $dC_{12}$ and $dC_{44}$ of the elastic constants $C_{11}$, $C_{12}$ and $C_{44}$ were calculated from the scattering of the corresponding symmetry-equivalent elastic constants $\{C_{11}, C_{22}, C_{33}\}$, $\{C_{12}, C_{13}, C_{23}\}$, and $\{C_{44}, C_{55}, C_{66}\}$ The total derivative

\[
d\alpha = d\left( \frac{2C_{44}}{(C_{11} - C_{12})} \right) = \frac{\partial \alpha}{\partial C_{11}} dC_{11} + \frac{\partial \alpha}{\partial C_{12}} dC_{12} + \frac{\partial \alpha}{\partial C_{44}} dC_{44}
\]

\[= \frac{2C_{44}}{(C_{11} - C_{12})^2} dC_{11} + \frac{2C_{44}}{(C_{11} - C_{12})^2} dC_{12} + \frac{2}{C_{11} - C_{12}} dC_{44}
\]

of $\alpha$ was used to calculate the error propagation.
atures, but even at $T^* = 0.225$ and 0.3 - smaller, which is a further indication that the stress-strain fluctuation approach takes advantage of the quasi-harmonic form of the effective potential.

### 4.1.5.3 Elastic Constants at Intermediate Temperatures

In Tables 4-2 and 4-3 on page 87, it can be seen that a particularly large number of simulations with various cell sizes have been performed at $T^* = 0.125$. Before the influence of the cell size on the resulting elastic constants is examined, the difference between working with linear and with finite stress in the stress-strain fluctuation method will be quantified by looking at the 108-atom cell at $T^* = 0.125$, 0.225, and 0.3. After sufficient equilibration ($\mathcal{O}(10^8$ steps)), variable-shape MC simulations of $10^8$ steps were done. The elastic constants calculated from these runs are listed in Table 4-9.

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$\langle \eta \sigma_{ij} \rangle / \langle \eta \eta \eta \eta \rangle^{-1}$</th>
<th>$\langle \eta \eta \eta \eta \rangle / \langle \eta \eta \eta \eta \rangle^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125 (3.658 MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>495.46 ± 0.14</td>
<td>496.92 ± 0.17</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>237.57 ± 0.12</td>
<td>241.03 ± 0.09</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>251.41 ± 0.06</td>
<td>250.35 ± 0.12</td>
</tr>
<tr>
<td>$2C_{44}/(C_{11}-C_{12})$</td>
<td>1.950 ± 0.002</td>
<td>1.957 ± 0.003</td>
</tr>
<tr>
<td>0.225 (6.431 MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>237.65 ± 0.18</td>
<td>239.00 ± 0.20</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>109.27 ± 0.15</td>
<td>112.58 ± 0.04</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>122.46 ± 0.10</td>
<td>121.32 ± 0.12</td>
</tr>
<tr>
<td>$2C_{44}/(C_{11}-C_{12})$</td>
<td>1.907 ± 0.006</td>
<td>1.919 ± 0.006</td>
</tr>
<tr>
<td>0.3 (8.405 MPa)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>157.27 ± 0.06</td>
<td>158.30 ± 0.35</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>69.62 ± 0.08</td>
<td>72.48 ± 0.12</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>82.10 ± 0.06</td>
<td>81.09 ± 0.07</td>
</tr>
<tr>
<td>$2C_{44}/(C_{11}-C_{12})$</td>
<td>1.873 ± 0.004</td>
<td>1.890 ± 0.011</td>
</tr>
</tbody>
</table>

The following tendencies can be observed: The $C_{11}$ and $C_{12}$ values are consistently higher if finite stresses were included, whereas the $C_{44}$ component is somewhat smaller. Thus the ratio $2C_{44}/(C_{11}-C_{12})$ is always closer to the theoretical value of 2. In general, the scattering of the finite stress data is a bit larger, especially at higher temperature. Obviously the switching from linear to finite
stresses brings a measurable although not dramatic effect.

The influence of the size of the simulation cell on the elastic constants (i.e. finite size effect) was investigated by a series of simulations at $T^* = 0.3$. Cells of 32, 108, 256, and 2048 atoms were run for $10^6$ to $10^8$ steps, depending on the size; i.e. the computing time was roughly the same for all systems. Since the very small 32-atom cell was used as well, all calculations were done with the finite-stress formalism. In Table 4-10, the results of elastic constant calculations using stress-strain correlations are given. There is no clear size dependence, except for the very small 32 atom system, which has somewhat lower values than the rest. A correction proposed by Cowley\textsuperscript{83a} was used for all results presented in this chapter, which normalizes the vibrational contributions by $N^{-1}$ instead of $N$. At $T^* = 0.5$, the same conclusions can be drawn, as Table 4-12 shows.

Similar calculations with linear stress-strain correlations have been made at $T^* = 0.31$. Table 4-11 gives the values of the various simulations. Again, the averages do not differ substantially, but the standard deviations clearly indicate that the smaller the simulation cell is the more precise the elastic constants can be determined. The average values of the finite stress calculations of Table 4-10, however, do suggest that the optimum system size seems to be the 108 atom system, offering the best trade-off between rate of convergence and self stabili-

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
$N$ [atoms] & MC steps & $\langle C_{11}, C_{22}, C_{33} \rangle^*$ & $\langle C_{12}, C_{23}, C_{13} \rangle^*$ & $\langle C_{44}, C_{55}, C_{66} \rangle^*$ \\
\hline
32 & $10^8$ & 155.46 \pm 0.16 & 72.05 \pm 0.02 & 80.03 \pm 0.12 \\
108 & $10^8$ & 158.38 \pm 0.22 & 72.57 \pm 0.10 & 81.14 \pm 0.07 \\
256 & $10^7$ & 158.09 \pm 0.55 & 72.48 \pm 0.17 & 80.74 \pm 0.05 \\
2048 & $2 \times 10^6$ & 159.42 \pm 1.98 & 73.44 \pm 1.32 & 80.81 \pm 0.67 \\
\hline
\end{tabular}
\caption{Comparison of the elastic constants of different cell sizes at $T^* = 0.3$, finite stresses}
\end{table}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|}
\hline
$N$ [atoms] & MC steps & $\langle C_{11}, C_{22}, C_{33} \rangle^*$ & $\langle C_{12}, C_{23}, C_{13} \rangle^*$ & $\langle C_{44}, C_{55}, C_{66} \rangle^*$ \\
\hline
32 & $10^8$ & 146.74 \pm 0.19 & 65.39 \pm 0.19 & 77.02 \pm 0.14 \\
256 & $10^7$ & 148.45 \pm 0.49 & 63.87 \pm 0.27 & 78.53 \pm 0.51 \\
2048 & $2 \times 10^6$ & 148.38 \pm 1.46 & 65.16 \pm 0.69 & 77.83 \pm 0.46 \\
\hline
\end{tabular}
\caption{Comparison of different cell sizes at $T^* = 0.31$, linear stresses}
\end{table}
4.1.5 Results

Table 4-12: Symmetry equivalent elastic constants at $T^* = 0.5$ for samples of 32, 108, 256, and 2048 atoms, finite stresses, stress-strain fluctuations

<table>
<thead>
<tr>
<th>$N$ [atoms]</th>
<th>MC steps</th>
<th>$(C_{11},C_{22},C_{33})^*$</th>
<th>$(C_{12},C_{23},C_{13})^*$</th>
<th>$(C_{44},C_{55},C_{66})^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>$10^8$</td>
<td>54.67 ± 0.18</td>
<td>22.35 ± 0.02</td>
<td>29.65 ± 0.10</td>
</tr>
<tr>
<td>108</td>
<td>$10^8$</td>
<td>60.20 ± 0.22</td>
<td>24.45 ± 0.13</td>
<td>32.04 ± 0.05</td>
</tr>
<tr>
<td>256</td>
<td>$10^7$</td>
<td>62.02 ± 0.22</td>
<td>25.73 ± 0.12</td>
<td>32.36 ± 0.09</td>
</tr>
<tr>
<td>2048</td>
<td>$2 \cdot 10^8$</td>
<td>60.13 ± 1.72</td>
<td>23.86 ± 1.03</td>
<td>31.36 ± 0.92</td>
</tr>
</tbody>
</table>

It is therefore advisable to use as small a system as possible while taking into account that a minimum cell size is required to provide mechanical stability against the thermal vibrations. If collective motions contribute significantly to the mechanical spectrum, it must be avoided to have cells or cutoffs that are too small to include these effects. The first limitation (mechanical stability) is of particular importance for crystalline systems, whereas the second one applies mainly to amorphous cells.

4.1.5.4 Elastic Constants at High Temperatures

As listed in Table 4-3, the elastic constants of cells of 32, 108, 256, and 2048 atoms have been determined by simulations carried out at $T^* = 0.5$. This temperature is the upper limit of the existence of literature data and most probably the upper limit for stable Lennard-Jones crystals. The melting temperature of argon is -189.3 °C (83.9 K, $T^* = 0.7$). Due to the absence of the long-range attractive force, the melting temperature of the nearest-neighbour Lennard-Jones solid is closer to $T^* = 0.5$ (Cowley83a, Rutledge94b). At this temperature, anharmonic effects become important and reduce the efficiency of the stress-strain fluctuation method. At the same time, the crystal is able to sample its phase space more efficiently. This improves the convergence of the strain-strain fluctuation method. As a consequence, the behaviour of the two methods should become more and more equal as the temperature raises. To quantify this statement, the convergence behaviour of the 32-atom system is shown in Fig. 4.7 and a list of the elastic constants of all simulations is given in Table 4-12.

Two conclusions can be drawn from the above table: First, the average values of the elastic constants increase with increasing cell size from 32 to 256 atoms, indicating that especially the 32- and to some extent the 108-atom cell is too small for the large thermal fluctuations close to the melting point of the structure. Second, the standard deviations are smaller for the smaller cell sizes, con-
firming Cowley’s statement\textsuperscript{83a}, that ‘the modulus, which depends on averages of fluctuations, seems to require a fixed number of configurations \textit{per atom} for a given uncertainty’. The 2048-atom cell in particular has not reasonably converged in roughly the same amount of CPU time.

4.1.5.5 Molecular Dynamics Calculations

Table 4-13 presents the results of various MD and MC calculations, which can be grouped in the following way:

In the first two lines, elastic constants from MC calculations with cutoffs, but without splines are listed. As described in Table 4-4, the cutoff was fixed to a value of 5.35 Å (1.4 in reduced units), a distance just between the first and the second nearest-neighbour shell. The difference between these values and the reference computations is quite small (2 - 4%) but nevertheless significant. The introduction of a cutoff (even at a position where the probability of finding an atom is minimal) already has an effect on the elastic constants, which can not be neglected.

As the following lines in the table show, the use of a spline does not improve the situation - on the contrary, the elastic constants are getting less and less accurate with increasing spline width. But it is of minor importance, whether MC or MD algorithms are used, as long as both are canonical. And with MD, there is neither a clear advantage of the stress-strain fluctuation approach over the strain fluctuations. It is not possible to make more comments on that, since the evaluation of the stresses was done by Discover 94 entirely and there is no exact information how this is done.
Table 4-13: ToN-MD and variable-shape MC results with nearest neighbors (nn) or with cutoffs with and without splines; symmetry equivalent elastic constants computed with the strain and the (linear) stress-strain fluctuation method; the shading of the cells is proportional to the difference between the actual value and the reference values listed at the bottom.

<table>
<thead>
<tr>
<th>Method</th>
<th>Spline</th>
<th>Fluctuations</th>
<th>( \langle C_{11}, C_{22}, C_{33} \rangle^* )</th>
<th>( \langle C_{12}, C_{23}, C_{13} \rangle^* )</th>
<th>( \langle C_{44}, C_{55}, C_{66} \rangle^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC</td>
<td>no</td>
<td>( \langle \eta_{ik} \eta_{lm} \rangle^{-1} )</td>
<td>160.63 ± 1.60</td>
<td>73.02 ± 0.58</td>
<td>84.10 ± 0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \langle \eta_{ik} \sigma_{n} \rangle \langle \eta_{n} \eta_{lm} \rangle^{-1} )</td>
<td>159.49 ± 0.38</td>
<td>71.45 ± 0.27</td>
<td>83.30 ± 0.23</td>
</tr>
<tr>
<td>MC</td>
<td>yes (0.4Å)</td>
<td>( \langle \eta_{ik} \eta_{lm} \rangle^{-1} )</td>
<td>173.80 ± 0.97</td>
<td>84.80 ± 0.61</td>
<td>90.50 ± 0.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \langle \eta_{ik} \sigma_{n} \rangle \langle \eta_{n} \eta_{lm} \rangle^{-1} )</td>
<td>167.12 ± 0.52</td>
<td>78.23 ± 0.28</td>
<td>86.32 ± 0.23</td>
</tr>
<tr>
<td>MD</td>
<td>yes (0.4Å)</td>
<td>( \langle \eta_{ik} \eta_{lm} \rangle^{-1} )</td>
<td>164.86 ± 1.10</td>
<td>76.20 ± 0.42</td>
<td>89.14 ± 0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \langle \eta_{ik} \sigma_{n} \rangle \langle \eta_{n} \eta_{lm} \rangle^{-1} )</td>
<td>176.40 ± 0.62</td>
<td>87.87 ± 0.51</td>
<td>90.10 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>yes (1.2Å)</td>
<td>( \langle \eta_{ik} \eta_{lm} \rangle^{-1} )</td>
<td>182.09 ± 0.26</td>
<td>88.71 ± 0.23</td>
<td>102.18 ± 0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \langle \eta_{ik} \sigma_{n} \rangle \langle \eta_{n} \eta_{lm} \rangle^{-1} )</td>
<td>200.17 ± 0.09</td>
<td>104.78 ± 0.02</td>
<td>104.16 ± 0.04</td>
</tr>
<tr>
<td>MC (10⁶ steps)</td>
<td>no (nn)</td>
<td>( \langle \eta_{ik} \eta_{lm} \rangle^{-1} )</td>
<td>157.36 ± 0.13</td>
<td>69.87 ± 0.24</td>
<td>81.97 ± 0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \langle \eta_{ik} \sigma_{n} \rangle \langle \eta_{n} \eta_{lm} \rangle^{-1} )</td>
<td>157.27 ± 0.06</td>
<td>69.62 ± 0.08</td>
<td>82.10 ± 0.06</td>
</tr>
<tr>
<td>Reference</td>
<td></td>
<td></td>
<td>( \langle C_{11}, C_{22}, C_{33} \rangle^* )</td>
<td>( \langle C_{12}, C_{23}, C_{13} \rangle^* )</td>
<td>( \langle C_{44}, C_{55}, C_{66} \rangle^* )</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>157.1 ± 1.0</td>
<td>69.3 ± 0.9</td>
<td>82.2 ± 0.2</td>
</tr>
</tbody>
</table>

4.1.5.6 Hybrid Monte Carlo Simulations

The results of a variable shape \( \langle \mathcal{E} \rangle \)-MD simulation run with relatively large time-steps at \( T^* = 0.3 \) are reported and compared with the 'standard' MC simulation in the following table:

Table 4-14: Symmetry equivalent elastic constants resulting from a 25'000 steps HMC run with 50 \( \mathcal{E} \)-MD steps each, 108 atoms

<table>
<thead>
<tr>
<th>Method</th>
<th>( \langle C_{11}, C_{22}, C_{33} \rangle^* )</th>
<th>( \langle C_{12}, C_{23}, C_{13} \rangle^* )</th>
<th>( \langle C_{44}, C_{55}, C_{66} \rangle^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \langle \eta_{ik} \eta_{lm} \rangle^{-1} )</td>
<td>150.48 ± 2.55</td>
<td>63.30 ± 1.42</td>
<td>82.23 ± 3.03</td>
</tr>
<tr>
<td>( \langle \eta_{ik} \sigma_{n} \rangle \langle \eta_{n} \eta_{lm} \rangle^{-1} )</td>
<td>182.80 ± 2.49</td>
<td>94.96 ± 1.18</td>
<td>90.47 ± 0.85</td>
</tr>
<tr>
<td>MC (10⁶ steps)</td>
<td>157.31 ± 0.11</td>
<td>69.74 ± 0.22</td>
<td>82.03 ± 0.13</td>
</tr>
</tbody>
</table>

The above numbers are averages over 25'000 steps, with each step consisting of a short MD simulation of 50 steps (90.36 fs step width, 5.4 Å cutoff, 0.4 Å spline). With this combination of number of steps and stepwidth, the acceptance ratio was 0.564. At the end of each MD trajectory, a modified Boltzmann weight decided whether a step was accepted or not. If yes, the new configuration served - with new velocities - as the starting point of the next simulation.
Otherwise, the old configuration initiated the next MD run. The accuracy is considering the effort - not spectacularly good, as indicated by the difference between the strain and the stress-strain fluctuations and the scattering between symmetry equivalent elastic constants.

The HMC using a self-written code, which is mentioned at the end of chapter 4.1.3.3 yielded the following results (Table 4-15):

Table 4-15: Symmetry equivalent elastic constants from the finite stress-strain fluctuations, nearest-neighbours, \( T^* = 0.3 \), hybrid Monte Carlo moves with varying order of deformation and EhN-MD

<table>
<thead>
<tr>
<th></th>
<th>( \langle C_{11}, C_{22}, C_{33} \rangle^* )</th>
<th>( \langle C_{12}, C_{23}, C_{13} \rangle^* )</th>
<th>( \langle C_{44}, C_{55}, C_{66} \rangle^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deformation</td>
<td>156.51 ± 0.19</td>
<td>68.69 ± 0.24</td>
<td>82.25 ± 0.31</td>
</tr>
<tr>
<td>Deformation-MD</td>
<td>166.30 ± 0.07</td>
<td>74.99 ± 0.05</td>
<td>86.43 ± 0.04</td>
</tr>
<tr>
<td>MD-Deformation</td>
<td>166.63 ± 0.11</td>
<td>75.49 ± 0.08</td>
<td>86.70 ± 0.10</td>
</tr>
</tbody>
</table>

The pure deformation, which was performed to test the code, agreed quite well with the standard values from variable-shape MC. The results of the moves that combined random deformation and EhN-MD are obviously independent on the sequence of MD and deformation, but both deviate considerably from the pure deformation MC. The reasons for this are not exactly known, since there is a large number of error sources ranging from simple programming errors to methodological deficiencies.

4.1.6 Discussion

4.1.6.1 Estimation of the Precision of the Elastic Constants

The convergence criterion (Eq. (3-37) or (3-38)) provides a useful check of whether a simulation has reached at least a stationary state or whether some relaxations still occur. In this section, the accuracy of selected calculations will be examined more closely in order to quantify the possible uncertainties. In the next section, these values will be compared with those obtained from the literature.

The selected calculations are those with the firmest theoretical basis and the longest trajectories. The canonical variable-shape MC algorithm described in chapter 4.1.3.1 is a simple and well established algorithm and the use of finite stresses allows to rigorously calculate the necessary fluctuation terms. The 108-atom cell is a balanced compromise between computational efficiency and stability, permitting to perform about \( 10^8 \) steps. This is enough to completely equilibrate the structure, since the possible relaxations of the simple fcc crystal are
The following figure (Fig. 4.8) shows the convergence of the elastic constants at $T^* = 0.125$. Both the strain and the finite stress-strain fluctuations deliver elastic constants which have converged very well after $10^8$ steps as the figure and Table 4-16 show. The finite stress-strain fluctuations, however, lead to a significantly faster convergence, as already pointed out.

Several methods can be used now to estimate the precision of the elastic constants:

The first, and maybe most important check is the difference between the
strain and the finite stress-strain results, as expressed in Eq. (3-37). The relevant stress-strain correlation matrix is given below and indicates that the difference between the two methods is in the order of 0.2 - 0.4%. It is therefore not necessary to continue the simulation, since the thermodynamical equilibrium has been approached quite well.

The second, quite obvious way to estimate the reliability of the calculation offer those elements in the matrix of the elastic constants that should be zero due to the symmetry of the problem. In the above example, these elements are -0.07 ± 0.73 reduced units for the strain fluctuations and -0.01 ± 0.23 for the stress-strain fluctuations.

The third indicator, which is related to the above one, is the deviation between symmetry equivalent elastic constants. In the case of the cubic symmetry of the fcc crystal, \{C_{11}, C_{22}, C_{33}\}, \{C_{12}, C_{13}, C_{23}\}, and \{C_{44}, C_{55}, C_{66}\} form such groups of equivalent elastic constants. The deviation within such a group is in the range of 0.3 - 0.5 reduced units for the strain fluctuations and 0.1 - 0.2 for the stress-strain fluctuations.

The forth possibility to estimate the convergence offer the symmetry of the matrix of the elastic constants or the stress-strain correlation matrix. Using the stress-strain fluctuations, the matrix of the elastic constants is not symmetric, although - as described in chapter 1.3.2 - it should be so. In the above example, the symmetric elements - zero and nonzero - differ by about 0.2 ± 0.15 reduced units.

Putting everything together, a reasonable estimate of the precision of a simulation would be the strain fluctuation formula to yield an error of ± 0.6 and the stress-strain fluctuation formula one of ± 0.2 reduced units. Since this does not contradict the precision indicated by the scattering between the symmetry equivalent elastic constants, these values are presented in the next tables.

The final - and in case of amorphous structures most important - method is the simulation of more than one structure and the comparison of the final results.

Table 4-17: The stress-strain correlation matrix at $T^* = 0.125$

| $\frac{1}{kT} \langle \eta_{ik} \eta_{jn} \rangle$ |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0.996           | 0.003           | 0.008           | 0.004           | 0.001           | -0.003          |
| 0.006           | 0.998           | 0.003           | 0.000           | -0.005          | 0.002           |
| -0.009          | 0.001           | 0.998           | -0.001          | -0.003          | -0.005          |
| 0.004           | 0.000           | -0.002          | -0.992          | 0.003           | 0.003           |
| 0.002           | -0.001          | -0.002          | 0.003           | 0.992           | 0.000           |
| -0.003          | 0.004           | -0.003          | 0.004           | -0.001          | 0.998           |
This has been done in the case of the 108-atom structures, for which two simulation runs of $10^8$ steps have been executed.

Table 4-18: Average elastic constants obtained from two runs of $10^8$ MC steps at the temperatures indicated, finite stress-strain fluctuation formula

<table>
<thead>
<tr>
<th>$T$</th>
<th>Run</th>
<th>$(C_{11}, C_{22}, C_{33})^*$</th>
<th>$(C_{12}, C_{23}, C_{13})^*$</th>
<th>$(C_{44}, C_{55}, C_{66})^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.125</td>
<td>1</td>
<td>496.92 ± 0.17</td>
<td>241.03 ± 0.09</td>
<td>250.35 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>496.63 ± 0.21</td>
<td>240.89 ± 0.18</td>
<td>250.35 ± 0.06</td>
</tr>
<tr>
<td>0.225</td>
<td>1</td>
<td>239.00 ± 0.20</td>
<td>112.58 ± 0.04</td>
<td>121.32 ± 0.12</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>238.46 ± 0.17</td>
<td>112.13 ± 0.07</td>
<td>121.36 ± 0.05</td>
</tr>
<tr>
<td>0.3</td>
<td>1</td>
<td>158.30 ± 0.35</td>
<td>72.48 ± 0.12</td>
<td>81.09 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>158.38 ± 0.22</td>
<td>72.57 ± 0.10</td>
<td>81.14 ± 0.07</td>
</tr>
</tbody>
</table>

4.1.6.2 Static Minimum Energy Calculations

In principle, it is possible to use Eq. (1-52),

$$C_{ijkl}^T = \left( \frac{\partial t_{ij}}{\partial n_{kl}} \right) = \rho_0 \left( \frac{\partial^2 A}{\partial n_{ij} \partial n_{kl}} \right)_T,$$

(1-52)

to get the elastic constants of a material by performing a series of deformations and minimizations. In practice, however, it is not possible to determine the free energy $A$ directly. Instead of that, it is often assumed that the entropic contributions can be neglected and therefore the potential energy $U$ can be used instead. The validity of this approximation is discussed in Refs [Theodorou86a] and [RutledgeSuter91a].

The 108-atom cell was minimized with a Newton-Raphson algorithm down to a maximum gradient of $10^{-4}$ kcal-mol$^{-1}$-Å$^{-1}$. The cell shape was included into this minimization and then deformed by a specific strain.

Since a general minimization scheme, which was used for crystalline and amorphous polymers, was applied, a detailed description is now given: In order to compute all elements of the matrix of the elastic constants, 25 deformations were carried out for each off-diagonal element ($C_{ik}$, $i > k$). These finite deformations consisted of all possible combinations of $\eta_i$ and $\eta_k$ in $\{-2\eta_0, -\eta_0, 0, \eta_0, 2\eta_0\}$ with $\eta_0$ being typically 0.001. After each deformation, the cell's potential energy $U_{pot}$ was again minimized down to $10^{-4}$ kcal-mol$^{-1}$-Å$^{-1}$ with the cell parameters held fixed. A function

$$U_{pot}(\eta_i, \eta_k) = a_0 + a_1 \eta_i + a_2 \eta_k + a_3 \eta_i \eta_k + a_4 \eta_i^2 + a_5 \eta_k^2$$

(4-23)
was fitted to these 25 minimum values using a singular value decomposition algorithm\textsuperscript{Pressetal92} obtained from Netlib\textsuperscript{a}.

The \(a_3\) value of the above function is directly proportional to \(C_{ik}\), whereas \(2a_4\) is proportional to \(C_{ij}\) and \(2a_5\) to \(C_{kk}\). It was therefore not necessary to compute the diagonal terms of the elasticity matrix explicitly. The goodness of fit was estimated via a \(\chi^2\) and a gamma formalism.\textsuperscript{Pressetal92} In all cases, the fit was excellent (i.e. no anharmonic effects at such small deformations).

The results of these calculations are given in the next table:

![Table 4-19: Elastic constants of a 108 atom Lennard-Jones solid](image)

These zero-temperature elastic constants have been converted to reduced units, assuming a low temperature of 1.198 K, and compared with MC values reproduced from Table 4-8. At this low temperature, the fluctuation approach and the static minimum energy results agree perfectly.

### 4.1.6.3 Comparison with Literature Values

It is not sensible to compare the isothermal elastic constants of the nearest-neighbour Lennard-Jones solid with the experimental (adiabatic) ones of a rare gas solid like argon (\(C_{11} = 4.1\) GPa, \(C_{12} = 2.4\) GPa, \(C_{44} = 2.3\) GPa, extrapolated to \(T = 0\) K or \(T = 0\) K, because - as pointed out in chapter 4.1.1 - they differ considerably in their interactions. So only model calculations using the same nearest-neighbour Lennard-Jones solid will be taken as reference. The first calculation of isothermal elastic constants was performed by Squire et al.\textsuperscript{Squire69a} in 1968. The authors simulated a 108-atom system with corrections for the finite cutoff applied, which leads to somewhat higher elastic constants than nearest-neighbour interactions alone: \(C_{11} = 2.84\) GPa, \(C_{12} = 1.61\) GPa and \(C_{44} = 1.69\) GPa at \(T = 40\) K. The elastic constants were calculated by using a combination of fluctuation, Born, and kinetic terms obtained from a derivation of the partition function. Cowley\textsuperscript{Cowley83a} used the same approach to make very accurate MC simula-

---

\textsuperscript{a} http://tonic.physics.sunysb.edu/docs/num_meth.html or ftp://ftp.zib-berlin.de/netlib
tions of $10^6 - 10^7$ steps at various temperatures. Sprik et al.\textsuperscript{Sprik84a} did some $HTN$-MD of $4 \cdot 10^4 - 10^5$ steps at $T^* = 0.31$, but the accuracy of their results is suffering from the shortness of the simulation runs. In 1988, Ray published an comprehensive overview including fluctuation formula for the $ErN$, $ThN$, $HTN$, and $ThN$ ensemble.\textsuperscript{Ray88a} Computations of isothermal elastic constants computed in the $ErN$ and $ThN$ ensemble were published previously.\textsuperscript{Ray85a} The adiabatic and isothermal elastic constants obtained from theses publications are given in the next table (4-20):

Table 4-20: Overview over elastic constants calculations; Cowley: MC, $2.16 \cdot 10^6, T^* = 0.3$, 108 atoms; Sprik et al.: $HTN$-MD, $10^5$ steps, 108 atoms, $T^* = 0.307, 8.6$ fs time step; Ray et al.: $ThN$-MD, $2 \cdot 10^4$ steps, 500 atoms, $T = 0.3, 10$ fs time step

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
$C_{ik}$ & Cowley\textsuperscript{Cowley83a} & Sprik et al.\textsuperscript{Sprik84a} & Ray et al.\textsuperscript{Ray88a} \\
\hline
\text{adiabatic} & $C_{11}$ & $182.0 \pm 0.5$ & $170 \pm 9$ & $185.1 \pm 1.9$ \\
& $C_{12}$ & $94.1 \pm 0.5$ & $84 \pm 8$ & $95.7 \pm 1.4$ \\
& $C_{44}$ & $82.2 \pm 0.2$ & $81.7 \pm 0.3$ & $81.6 \pm 1.6$ \\
\hline
\text{isothermal} & $C_{11}$ & $157.1 \pm 1.0$ & - & $165.6 \pm 4.9$ \\
& $C_{12}$ & $69.3 \pm 0.9$ & - & $76.3 \pm 4.5$ \\
& $C_{44}$ & $82.2 \pm 0.2$ & - & $81.6 \pm 1.6$ \\
\hline
\end{tabular}
\end{table}

Since Cowley's values are most accurate and serve as a reference in Sprik's and Ray's publications, we use the values in the shaded cells for comparison with our own results. Cowley did not only give the elastic constants at $T^* = 0.3$, but also at $T^* = 0.125$ and $T^* = 0.225$ and at higher temperatures.

Comparing these numbers with those from chapter 4.1.6.1, the final Table 4-21 can be established:

4.1.6.4 Conclusions

In the limit of thermodynamic equilibrium, the new stress-strain fluctuation formula (Eq. (3-35)) is equivalent to the well-established strain fluctuation formula of Parrinello and Rahman (Eq. (3-29)). Simple systems like the 108-atom nearest-neighbour Lennard-Jones solid allow very long simulations of up to $10^8$ MC steps. The absence of complicated intra- and intermolecular interactions leads to a fast equilibration of the structures. It is therefore possible to approach the thermodynamic equilibrium very closely and to check for the validity of the above statement: the theoretical equivalence could be proved practically.
Table 4-21: Comparison of elastic constants results from strain and stress-strain fluctuations at $T^* = 0.125, 0.225,$ and $0.3$ with results from Ref. [Cowley83a]

<table>
<thead>
<tr>
<th>$T^*$</th>
<th>$C_{ik}$</th>
<th>Eq. (3-29)</th>
<th>Eq. (3-35)</th>
<th>Cowley</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.125</td>
<td>$C_{11}$</td>
<td>496.12 ± 0.70</td>
<td>496.77 ± 0.24</td>
<td>494.0 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>$C_{12}$</td>
<td>238.00 ± 0.35</td>
<td>240.96 ± 0.16</td>
<td>237.8 ± 1.1</td>
</tr>
<tr>
<td></td>
<td>$C_{44}$</td>
<td>251.36 ± 0.75</td>
<td>250.35 ± 0.09</td>
<td>250.0 ± 0.2</td>
</tr>
<tr>
<td>0.225</td>
<td>$C_{11}$</td>
<td>237.73 ± 0.72</td>
<td>238.73 ± 0.33</td>
<td>237.0 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>$C_{12}$</td>
<td>109.68 ± 0.58</td>
<td>112.35 ± 0.23</td>
<td>108.2 ± 0.8</td>
</tr>
<tr>
<td></td>
<td>$C_{44}$</td>
<td>122.27 ± 0.21</td>
<td>121.34 ± 0.09</td>
<td>121.9 ± 0.2</td>
</tr>
<tr>
<td>0.3</td>
<td>$C_{11}$</td>
<td>157.03 ± 0.36</td>
<td>158.34 ± 0.28</td>
<td>157.1 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>$C_{12}$</td>
<td>69.51 ± 0.19</td>
<td>72.52 ± 0.11</td>
<td>69.3 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>$C_{44}$</td>
<td>81.84 ± 0.29</td>
<td>81.11 ± 0.07</td>
<td>82.2 ± 0.2</td>
</tr>
</tbody>
</table>

In the case of finite simulation runs, the convergence of the elastic constants is markedly improved by the new algorithm, especially at very low temperatures, where sampling of the phase space is slow. Here the elastic constants obtained by the new formula converge orders of magnitude faster. In the limit of zero temperature the results match those from the static minimum energy approach. Even at intermediate or high temperatures close to the melting point, the stress-strain fluctuation method is converging at least as fast as the strain fluctuation formula.

It is possible to use MC, MD, or Hybrid-MC methods to sample the configurational phase space of a structure. It is extremely important to do this canonically. For MC, a slight dependence of the rate of convergence, but not of the final results, on the acceptance ratio could be observed. If cutoffs and splines are used, e.g. in the MD simulations, the elastic constants depend strongly on the choice of these parameters.

The precision of the elastic constants is extremely high. It is possible to determine them with an accuracy of a few tenths of a percent. In order to achieve this, $10^6$ to $10^8$ steps are necessary even for a quite small 108-atom system. It seems that a certain number of configurations per atoms is necessary to obtain a given precision. Since it was not possible to observe significant size effects, the smallest stable crystal cell should be used. Delocalized thermal motions are obviously not significantly contributing to the elastic constants, as can also be deduced from Ref. [Cowley83a].
4.2 Polyethylene - Planar Zig-Zag Chains

4.2.1 Introduction

Polyethylene (PE) is a partially crystalline thermoplastic\textsuperscript{Franck88}, which is used in huge quantities. The mechanical properties - especially the elastic constants - are those of a typical amorphous material (i.e. 1 - 3 GPa\textsuperscript{Ward83}). In the last decade, however, a methodology was developed to produce polyethylene with highly oriented chains.\textsuperscript{Smith86a}. Commercially available are now filaments with a modulus of more than 100 GPa. Thus the formerly theoretical question of the ultimate modulus of a perfectly oriented PE crystal has become more and more of practical interest. It is very difficult to determine this number by experiment, because the stress that is transferred by the amorphous matrix to the crystallites is not known exactly, but depends on the morphology and the phase boundary. Therefore, the experimental values at room temperature - furthermore depending on the methodology - are scattering widely between 196 and 329 GPa\textsuperscript{Nakamae91a, Rutledge94a}.

It is not surprising that there were many trials to obtain estimates through theoretical calculations. Some examples will be briefly discussed while comparing the results of the present work with literature values (chapter 4.2.6.1), but it can already be stated that the theoretical results differ even more from each other than the experimental ones, spanning a range from 160 to more than 400 GPa (mostly at \(T = 0\text{ K}\))\textsuperscript{Nakamae91a}.

In the following chapter a model of monocrystalline PE will be generated and its elastic constants will be computed using the strain and the linear stress-strain fluctuation approaches.

4.2.2 Description and Cell Generation

Linear polyethylene crystallizes in an orthorhombic unit cell (space group 62: \(Pnma\))\textsuperscript{XrayTable83} with lattice constants of \(a=7.417\ \text{Å}, b = 4.945\ \text{Å},\) and \(c = 2.547\ \text{Å}^{Bunn39a}\). The two 'all-trans' chains in this cell, which is shown in Fig. 4.9, lead to a density of 0.997 g cm\(^{-3}\), being in agreement with the experimental density of PE crystals, which is 1.007 ± 0.008 g cm\(^{-3}\)\textsuperscript{Tadokoro90}. Two different cells were generated with the 'Crystal Cell' package\textsuperscript{MSIPolymer1} of 'InsightII':

The small simulation box consisted of \(3 \times 4 \times 8\) unit cells which totaled a minimized cell size of 21.651 × 19.608 × 20.569 Å with 1152 atoms. In order to prevent modelling just C\(_{16}\)H\(_{34}\)-chains, so-called bonds-across-boundaries were used, which connect one end of the chain in one periodic box with the other end.
of its own image in a neighboring box. The chains created by this procedure do not have any ends or special points, but they are not infinite with respect to their vibrational behavior. Due to the periodic continuations conditions, collective motions along the chains will be amplified rather than damped.

As will be seen later, the stability of the relatively small cell was rather poor, so a large, thermally more stable cell was generated. This cell comprised 4 × 6 × 12 unit cells and had a minimized size of 28.869 × 29.412 × 30.854 Å. It contained 3456 atoms in 48 chains of 24 CH₂-groups.

The setup of these cells involved the following steps:

• Generation of a helical repeat unit and a crystal asymmetric unit (CAU) according to the ‘Crystal Cell User Guide’.

• Conversion of the CAU into a Cartesian coordinate (.car) and molecular data file (.mdf) by the ‘hlx2pbc’ macro provided by MSI. The number of repeat units in the chain direction was also set by this program. Manual check of the bonds across boundaries in the .mdf file.

• Assembly of several such cells in the other two dimensions in order to form an approximately cubic shape.

For the subsequent molecular mechanics and dynamics simulations, the pcff91 and the scaled_pcff forcefields were used. They differ by about 3 % in the σ values of the Lennard-Jones interaction parameters of carbon and hydrogen atoms. This reduction was made, because the densities of hydrocarbon compounds are generally somewhat too low (a more detailed discussion of this problem is given in chapter 4.5.2.2).
4.2.3 Simulation Procedure

4.2.3.1 Small Cell Equilibration

The small crystal cell was equilibrated at 300 K using $T\sigma N$-MD for 230 ps. The $pcff91$-forcefield and a cutoff of 8.5 Å (spline: 0.5 Å) made it necessary to use a tail-correction pressure of 1417 bar. A Parrinello-Rahman pressure control with a cell mass of 20 a.m.u. was used to keep the average pressure at this level. The timestep was set to 0.5 fs, because of the Nosé-Hoover thermostat. The final density (averaged over the last 10 ps) was 0.958 g·cm$^{-3}$.

In dynamics, it turned out that the size of this cell was too small, as Fig. 4.10 shows:

![Figure 4.10: The cell angles of the small PE crystal as a function of the MD-time; the cell after 230 ps](image)

The cell angles, especially $\alpha$ and $\beta$ undergo sudden, sometimes simultaneous, jumps of 6 to 7 degrees. This phenomenon becomes more clear when the final structure is examined: The thermal fluctuations, which are very large for such a small structure (about 5 %), led to a rearrangement of some chains in the structure. These chains were simultaneously shifted by one crystal repeat unit. This process occurred several times during the simulation. A second, closely related process is the diffusion of individual chains along their axes, as a result of the low friction along the chain direction.

There are several possibilities to circumvent the above problem: One is to use the $7hN$-ensemble where the cell shape is fixed, another - similar - solution
seems to be the increase of the cell mass $W$ (Eq. (2-67)). But this last change does actually not reduce the amplitude but the frequency of the thermal fluctuations. The method chosen in this work is the enlargement of the simulation cell, since this reduces the absolute (and therefore even more the relative) fluctuations of the cell, as described in chapter 3.2.3. The diffusion of the chains along their axes is also hindered, which could not be achieved by switching to the $ThN$-ensemble.

4.2.3.2 Large Cell Equilibration

Generating a large cell, performance and stability have to be balanced to achieve a reasonable compromise. The cell parameters of the large simulation box have been given in chapter 4.2.2. After the generation and an initial minimization, a $ToN$-simulation over 150 ps in 0.5 fs steps was started. The standard cutoff and spline of 8.5 and 0.5 Å and Parrinello-Rahman and Nosé-Hoover control algorithms were applied to keep the temperature at 300 K and the pressure at a net value of 1 bar. The scaled_pcff forcefield demanded a somewhat reduced correction pressure of 1281 bars. The cell remained stable during the simulation, as Fig. 4.11 reveals:

![Cell angles](image)

Figure 4.11: The cell angles of the large PE cell as a function of the MD time (with same scale as in Fig. 4.10 for better comparison); the large PE cell after 150 ps

No collective transformations and hardly any chain diffusion could be observed. The average density during this simulation was $0.995 \pm 0.008 \text{ g cm}^{-3}$, which is much closer to the experimental value of $1.007 \text{ g cm}^{-3}$, justifying the use of the scaled_pcff forcefield.
4.2.4 Results

4.2.4.1 Effect of the Cell Mass on the Mechanical Relaxation Spectrum

Despite its deficiencies, the small cell was used for a short investigation of the influence of the cell mass on the spectrum of the mechanical relaxation. The mechanical relaxation spectrum (MRS) is the Fourier transform of the time-autocorrelation function of a mechanically relevant quantity. In the case of PE, the length of the cell vector parallel to the chain direction was used as the relevant degree of freedom.

There are two ways of weighting the amplitudes of the frequencies to obtain the contributions to the total fluctuation (the compliance) of the polymer\textsuperscript{Landau86c}. They both use the fluctuation-dissipation theorem:

The first one is a classical approximation that holds, if \( kT \gg \hbar \omega / 2\pi \), which is the case if \( \omega / 2\pi \ll 6.25 \times 10^{12} \) Hz:

\[
\langle x^2 \rangle = \frac{2kT}{\pi} \int_{0}^{\infty} \frac{\alpha''(\omega)}{\omega} d\omega 
\]

(4-24)

\( \alpha''(\omega) \) is the imaginary part of the Fourier transform of the fluctuating quantity \( x(t) \). So this approximation is obviously not valid for most of the frequencies appearing in our calculations.

According to the above considerations, it would be more appropriate to use the quantum mechanical formula.

\[
\langle x^2 \rangle = \frac{\hbar}{2\pi^2} \int_{0}^{\infty} \alpha''(\omega) \coth \left( \frac{\hbar \omega}{4\pi kT} \right) d\omega 
\]

(3-24)

The problem with this approach is that the system that produces the fluctuations is a completely classical one.

Besides these transformations, both the classical and the quantum mechanically weighted spectra were numerical integrated in order to estimate the contribution of individual processes to the total compliance.

A set of simulations was performed at 300 K with the familiar \textit{T}\textit{oN}-MD algorithm and the \textit{scaled_pcf} forcefield. A small box was used to perform 200 ps, with each 0.5 fs step being recorded to the disk for later evaluation. From these \( 4 \times 10^5 \) steps, the last 262'144 (2\textsuperscript{18}) were taken for the computation of the time-autocorrelation function of the cell edge length \( c \). The first half of this autocorrelation function was transformed using a fast Fourier (Cooley-Tukey FFT) algorithm and weighted according to Eqs (4-24) and (3-24). The cell masses \( W \) were
set to 1, 10, 100 and 1000 a.m.u., respectively.

Figure 4.12 makes the comparison between the classical and the quantum mechanical weighting of the fluctuations of a cell with a pressure control mass $W = 1$. There are relatively large contributions at the low-frequency end of the spectrum, where the statistical uncertainty is largest. So this part is not very meaningful. The peaks at $3 \times 10^{13}$ and $10^{14}$ Hz, however, are significant and their contribution to the mechanical relaxation spectrum depends on whether a classical or a quantum mechanical approach is made. The peak at $10^{14}$ Hz can be attributed to bond length and the one at $3 \times 10^{13}$ Hz to bond angle fluctuations.

With heavier cell masses, the peaks shift to lower frequencies and their relative contributions change such that the peak at originally at $10^{14}$ Hz becomes more and more dominant, as Fig. 4.12 shows. The shift in the frequencies is proportional to the square root of the cell mass. The classical and the quantum mechanical approach yield almost identical curves.

### 4.2.4.2 Elastic Constants of Orthorhombic PE

As the small crystal cell could not be used for the calculation of the elastic constants, the MD simulation of the large PE cell was taken for this purpose. The elastic constants were determined from the last 100 ps from information stored in 'table' files. In these table files, the cell parameters ($a$, $b$, $c$, $\alpha$, $\beta$, and $\gamma$) and the six components of the stress tensor ($\sigma_{xx}$, $\sigma_{yy}$, $\sigma_{zz}$, $\sigma_{yz}$, $\sigma_{xz}$, and $\sigma_{xy}$) have been recorded during the simulation at an interval of 1 fs.
The program 'ElastFluct.f' reads these table files and computes the elastic constants using both the strain and the linear stress-strain fluctuation formula. Besides this, the stress-strain correlation and the eigenvalues of the matrices of the elastic constants are printed. Figure 4.14 displays the convergence of the elastic constants. The final value of the $C_{33}$-component is almost the same, whereas the convergence of the stress-strain fluctuations is much smoother than
that of the strain fluctuations. In contrast to that, the $C_{12}$ and $C_{13}$ components computed from the stress-strain fluctuations exhibit a strange peak at about 8 ps which seems to be related to instabilities of the $C_{33}$-values. The precise nature of these spikes is not known.

The temporal evolution of the elements of the stress-strain correlation matrix is plotted in Fig. 4.15. This matrix should converge towards an identity matrix in the limit of thermodynamic equilibrium.

Finally, the matrices of the elastic constants are listed below:

Table 4-22: Elastic constants averaged over the last 100 ps of a 150 ps TσN-MD simulation. Components that should be non-zero according to the symmetry of the crystal (chapter 1.3.4) are bold faced.

<table>
<thead>
<tr>
<th>$\frac{kT}{\langle \sigma \rangle \langle \eta_{ik} \eta_{im} \rangle^{-1}}$ [GPa]</th>
<th>$\langle \eta_{ij} \sigma_{ij} \rangle \langle \eta_{nj} \eta_{nm} \rangle^{-1}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.25 3.11 4.29 0.06 0.02 0.36</td>
<td>5.81 3.67 3.70 -0.09 0.02 0.65</td>
</tr>
<tr>
<td>3.11 5.36 5.83 -0.03 -0.06 0.37</td>
<td>3.94 6.41 5.98 0.04 -0.05 0.49</td>
</tr>
<tr>
<td>4.29 5.83 223.29 0.12 0.03 -0.60</td>
<td>4.20 5.73 221.72 0.13 0.03 -0.62</td>
</tr>
<tr>
<td>0.06 -0.03 0.12 2.31 0.17 0.02</td>
<td>-0.05 -0.02 0.36 2.11 0.10 0.03</td>
</tr>
<tr>
<td>0.02 -0.06 0.03 0.17 1.81 0.06</td>
<td>0.04 -0.03 -0.02 0.08 1.67 0.05</td>
</tr>
<tr>
<td>0.06 0.37 -0.60 0.02 0.06 2.14</td>
<td>0.64 0.38 -1.51 0.06 0.06 2.32</td>
</tr>
</tbody>
</table>

All Eigenvalues of the above matrices are positive, guaranteeing the mechanical stability of the structure.
4.2.4.3 Static Minimum Energy Calculation

The same minimization procedure as in chapter 4.1.6.2 was used to compute the matrix of the elastic constants at 0 K. Using a unit cell and the scaled_pcf forcefield, the numbers in Table 4-22 were obtained.

Table 4-23: Elastic constants of PE: static minimum energy (left) and stress-strain fluctuation approach at 300 K (right).

<table>
<thead>
<tr>
<th>$\frac{1}{V_0} \left( \frac{\partial^2 U_{pot}}{\partial n_i \partial n_j} \right)_T$ [GPa]</th>
<th>$\langle \eta_{ik} \sigma_n \rangle \langle \eta_{nj} \sigma_{lm} \rangle^{-1}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.89 5.02 1.81 0.0 0.0 0.0</td>
<td>5.81 3.67 3.70 -0.09 0.02 0.65</td>
</tr>
<tr>
<td>5.02 8.19 3.03 0.0 0.0 0.0</td>
<td>3.94 6.41 5.98 0.04 -0.05 0.49</td>
</tr>
<tr>
<td>1.81 3.03 251.49 0.0 0.0 0.0</td>
<td>4.20 5.73 221.72 0.13 0.03 -0.62</td>
</tr>
<tr>
<td>0.0 0.0 0.0 3.52 0.0 0.0</td>
<td>-0.05 -0.02 0.36 2.11 0.10 0.03</td>
</tr>
<tr>
<td>0.0 0.0 0.0 0.0 2.03 0.0</td>
<td>0.04 -0.03 -0.02 0.08 1.67 0.05</td>
</tr>
<tr>
<td>0.0 0.0 0.0 0.0 0.0 4.07</td>
<td>0.64 0.38 -1.51 0.06 0.06 2.32</td>
</tr>
</tbody>
</table>

A comparison with the fluctuation results at 300 K shows that the influence of temperature can not be neglected, especially for the off-diagonal elements. The only exception is $C_{33}$: this value is not very much affected by temperature and does not change by more than 1%, if the strains were chosen to be ten times smaller or the maximum gradient for the minimization was allowed to be ten times larger).

4.2.5 Interlude: Amorphous Polyethylene

4.2.5.1 Structure Generation

PE, as mentioned in the introduction, is a semi-crystalline material and its elastic behaviour depends on both the elastic properties of the crystalline and the amorphous part. To determine the latter, the standard simulation routine for amorphous structures was used:

- To obtain a cubic structure of approx. 25 Å size, a chain of 600 CH2 groups was generated and terminated with hydrogens at both ends. To avoid problems in the subsequent packing, the chain was randomized (without cutoffs) by 5 ps at 500 K and 3 ps at 300 K.
- Using this chain, 5 simulation cells were generated with 'Amorphous Cell' at 300 K and a density of 0.95 g-cm$^{-3}$. After minimization (5000 steps down to 0.001 kcal-mol$^{-1}$-Å$^{-1}$), the three structures with the lowest energies were used in the following dynamics runs.
- Each of the three structures was first held for 50 ps in a $T_hN$-ensemble and then for 25 ps in an $T_\sigma N$-ensemble. For the second ensemble, an automatic
van-der-Waals tail correction was used, which yielded an average correction pressure of 1005, 1007, and 998 bars and an reduction of the average density down to 0.83 g cm\(^{-3}\). This reduction is partly explainable by the use of the \emph{pcff91-forcefield}, which is known to overestimate the van-der-Waals radii and/or the C-H bondlength.

- The production run for each structure consisted in 1 ns of \emph{T\sigma N-MD} at 300 K with a correction pressure of 1005 bars.

\textbf{4.2.5.2 Simulation Results}

These production runs, however, have been stopped after a few hundred picoseconds, because of cell instabilities:

![Cell angle fluctuations of the first structure of amorphous PE at 300 K.](image)

All simulation cells made large fluctuations in the cell angles, such as those of the first structure shown in Fig. 4.16. The state of the cells could be described as 'melt-like' and the shear moduli would tend to zero for infinitely long trajectories. It was therefore not possible to compute the elastic constants. To do so, larger cells are required and it might be necessary to sample the stress-fluctuations in a \emph{T\sigma N-ensemble}.

\textbf{4.2.6 Discussion}

\textbf{4.2.6.1 Comparison with Literature Values}

It is quite difficult to compare the \(C_{33}\) value of about 220 GPa obtained by the fluctuation formula with data from the literature. The first uncertainty is the
convergence of the calculation, which can roughly be estimated by the using the
same techniques as in chapter 4.1.6.1. Based on the stress-strain correlations,
for example, the uncertainty is found to be in the range of 10 - 15% (Fig. 4.15).
The other possible checks (crystal symmetry restrictions, and symmetry of the
matrix of the elastic constants) lead to more conservative estimates. It would
therefore be desirable to perform a more extended sampling of the phase space
by either a longer MD trajectory or a specialized MC algorithm. With the large
cell necessary for thermal stability, however, 1 fs of MD takes about 6 CPU sec-
onds on a workstation.

The second - and in this case even larger - uncertainty is the scattering of
the experimental and theoretical values. They range from 160 to more than
400 GPa, with the ‘observed' values concentrating between 220 and
230 GPaHakamae91a and quantum mechanical and semi-empirical results ranging
from 276 to 420 GPaHeren96a. It might be interesting to comment on some
experimental and theoretical work:

Matrices of the elastic constants have been calculated by Odajima and
MaedaOda'ima66a, AnandAnand67a, Sorensen et al.Boyd88a and many others. Not
only the $C_{33}$ element varies from 242 to 341 GPa but also $C_{11}$ is between 4.8
and 14.3 GPa and $C_{22}$ between 2.9 and 12.2 GPa.

Often, it is not clearly indicated at which temperature these values were
measured or calculated. Experiments from Barham et al.Barham79a show a strong
dependence of the modulus of PE fibres ranging from 262 GPa (288 GPa, if cor-
rected) at 77 K down to about 140 GPa at room temperature. Part of this reduc-
tion seems to originate from morphological changes so only a small part can be
attributed to a reduction of the crystal modulus.

A more recent theoretical analysis by Lacks and RutledgeRutledge94a esti-
mates that the zero temperature $C_{33}$ value is 316 GPa and the one at room tem-
perature 290 GPa ($C_{11}$ and $C_{22}$ are both 8.8 GPa). This fits quite well into the
extrapolations made by Irvine and SmithSmith86a, where experimental results are
well fitted by assuming an axial modulus of 300 GPa. The value of 349 GPa
obtained by MeierMeier93a was corrected by himself to 333 GPa for the single
chain and 299 GPa for the crystal as a whole (at 0 K)Meier96a. The same
299 GPa are also supported in a discussion of quantum mechanical and
semiempirical calculations made by Crist and Herrera.Heren96a A most recent ab
initio MD calculation from Hageman et al.Hagen*97a yields an ultimate Young
modulus of 334 GPa.
4.2.6.2 Conclusions

It is not the purpose of this work to defend the 220 GPa obtained from the fluctuation approach heavily, because the fluctuations have not fully converged. Furthermore, this number depends largely on the forcefield (in particular on the C-C bond stretching and angle bending parameters). The static minimum energy result of about 250 GPa yields a temperature dependence consistent with other results but seems to be too low by about 50 GPa with respect to the zero-temperature values obtained from quantum-mechanical and semi-empirical calculations and extrapolations of experimental results. These (and the necessity to scale van-der-Waals parameters to compensate for long C-H bonds\(^3\)) are strong indications that the scaled_pcf force field is not perfectly adequate for the simulation of hydrocarbons.

Irrespective of the force field used, the intermolecular interactions between individual PE chains are very weak, both in crystals and in the amorphous phase. This makes it necessary to use relatively large simulation cells, which in turn reduce the effectiveness of the fluctuation formula, demanding long simulation runs.

Despite this restriction, the fluctuation approaches seem to be capable of reproducing the temperature dependence of the elastic constants. The \(C_{33}\) value obtained from the new stress-strain fluctuation method converges considerably faster than the one from the strain fluctuation approach. The combination of the two methods - the stress-strain correlation matrix - allows for a quantitative estimation of the degree of convergence.

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a. E. Leontidis, private communication (1997)
4.3 Polypropylene - Helical Chains

4.3.1 Introduction

Similar to polyethylene, polypropylene (PP) is also a technologically important thermoplastic with poorly understood mechanical properties. The experimental values of the crystal modulus of isotactic PP (it-PP), for example, range from 18 to 80 GPa.\textsuperscript{Hong90a} This quite low value - less than a third of that of PE - has its origin in the lower density of chains (2.9 chains-nm\textsuperscript{-2} vs. 5.5 chains-nm\textsuperscript{-2}) and in the helical structure of the chains in the crystal. Elongations of the crystal do result not only in bond and angle but also in torsion deformations, which tend to 'unwind' the helix.

4.3.2 Crystal Modifications and Cell Generation

4.3.2.1 Crystal Modifications

There are several crystal modifications of it-PP\textsuperscript{Tadokoro90,Corradini83a}: the monoclinic \(\alpha\)-form, the most stable one, which was simulated in this work, the hexagonal \(\beta\)- and the trigonal \(\gamma\)-form. Another monoclinic \(\gamma\)-form is reported, too.\textsuperscript{Ferro92a} The \(\alpha\)-modification was first described by Natta and Corradini\textsuperscript{Natta60a}: they reported a monoclinic structure with \(a = 6.65 \pm 0.05 \text{ Å}\), \(b = 20.96 \pm 0.15 \text{ Å}\), \(c = 6.5 \pm 0.05 \text{ Å}\), and \(\beta = 99.20^\circ \pm 1^\circ\).

The detailed structure of the it-PP crystal is quite complicated, since the individual chains form 3/1 helices, which can be either left(L)- or right(R)-handed. In addition to that, the methyl groups, which are directed outwards of the helix, can point up (\(\uparrow\)) or down (\(\downarrow\)), resulting in four different possible conformations. The most regular structure is the one shown schematically in Fig. 4.18 c) with the four possible helix conformations distributed on a regular grid. However, it was found\textsuperscript{Tadokoro92a} that this 'ordered' crystal lattice only appears after annealing at higher temperature. In 'native' PP crystals, the distribution of left- and right-handed chains is the same, but the methyl groups point up or down randomly (Fig. 4.18 b)). The disordered structure shown in Fig. 4.18 a) and d) and used for most of the following calculations, is therefore
4.3 Polypropylene - Helical Chains

4.3.2.2 Structure Generation

A simulation cell containing $3 \times 1 \times 3$ unit cells and $9 \cdot 108 = 972$ atoms was built, using the 'Crystal Cell' module in the 'Insight' modelling environment. In order to do this, helical repeat units of the four different helix conformations had to be generated and placed into the crystal asymmetric unit (CAU). The values of the fractional positions, the setting angle, and the vertical offset are given in Table 4-24:

Using periodic continuation conditions, the fractional coordinates and the vertical offset are only meaningful relative to each other. In the structure used for almost all simulations, the last helix in the above table was an RI instead of a Rl helix.
This CAU was converted into a cartesian coordinate file and surrounded by the appropriate number of unit cells, which were merged into one simulation box of approximately cubic shape with an edge length of about 20 Å. As in the case of PE, 'bonds across boundaries' were applied to connect the chain ends of neighbouring cells. The pcf91 forcefield was able to reproduce the experimental cell shape sufficiently well, as is shown in the next table:

Table 4-25: Cell shape at 300 K (average taken from 530 to 930 ps (20'000 frames) of a TσN-MD run, Comparison with corresponding experimental values (from ref. Natta60a)

<table>
<thead>
<tr>
<th></th>
<th>( a ) [Å]</th>
<th>( b ) [Å]</th>
<th>( c ) [Å]</th>
<th>( \alpha ) [°]</th>
<th>( \beta ) [°]</th>
<th>( \gamma ) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation</td>
<td>19.70</td>
<td>21.06</td>
<td>19.95</td>
<td>89.5</td>
<td>98.5</td>
<td>89.3</td>
</tr>
<tr>
<td>Experiment</td>
<td>19.95</td>
<td>20.96</td>
<td>19.50</td>
<td>90.0</td>
<td>99.3</td>
<td>90.0</td>
</tr>
</tbody>
</table>

4.3.3 Simulation Procedure

4.3.3.1 MD Simulations

The cell generated with the above methodology and setting parameters was first minimized in order to remove the largest energy terms. A short minimization of a few hundred steepest-descent or conjugate gradient steps should always be done after the generation of a structure, because the geometry of the repeat units and groups used to build it is only adapted for a particular force field (cvff in the case of the MSI/Discover software) and needs to be changed if another force field is applied.

The elastic constants of it-PP were calculated at three different temperatures, 300 K (25°C), 335 K (60°C), and 375 K (100°C). In the TσN-ensemble, the strain-strain and the stress-strain fluctuation formula were used. In addition to these calculations, simulations in the \( T\h N \)-ensemble were started to compute the Born and the stress-fluctuation terms (details are given in the next chapter).

Table 4-26: Overview of the MD simulations performed with it-PP crystals

<table>
<thead>
<tr>
<th>Temperature</th>
<th>TσN</th>
<th>Born-( T\h N )</th>
<th>Fluct-( T\h N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300 K (25°C)</td>
<td>1000 ps</td>
<td>50 config.</td>
<td>250 ps</td>
</tr>
<tr>
<td>335 K (60°C)</td>
<td>580 ps</td>
<td>50 config.</td>
<td>250 ps</td>
</tr>
<tr>
<td>375 K (100°C)</td>
<td>1000 ps</td>
<td>50 config.</td>
<td>250 ps</td>
</tr>
</tbody>
</table>

Table 4-26 lists the MD simulations performed in the two ensembles. The configurations necessary for the Born term were taken at intervals of 20 fs from a 1 ps
The cell shape used in the \( T_{\text{hN}} \)-ensemble was the average cell shape of the \( T_{\text{oN}} \)-simulation.

The temperature was kept constant in all simulations by a Nosé-Hoover thermostat, which in turn limited the stepsize to 0.5 fs. The default coupling constant \( Q \) (see chapter 2.5.2.3) and a cell mass \( W = 20 \) were applied. Regardless of the density, all constant-stress calculations were performed by using a tailcorrection pressure of 1417 bar.

### 4.3.3.2 Elasticity from Stress Fluctuations in the \( T_{\text{hN}} \)-Ensemble

Elastic constants can not only be computed from strain fluctuations in the \( T_{\text{oN}} \)-ensemble but also from stress-fluctuations in the \( T_{\text{hN}} \)-ensemble.\(^{Ray88a}\)

There are three terms that add up to the elastic constants:

The *Born term*, which is represents the elastic constants at 0 K, is computed similar to the static minimum energy elasticity by deforming an instantaneous frame and measuring the change of the internal stresses at 0 K:

\[
C_{ik}^{\text{Born}} = \frac{\partial \sigma_i}{\partial e_k}
\]

The *kinetic energy term*, which is the bulk modulus (compressibility) of an ideal gas at the simulation temperature, compensates the neglect of temperature in the Born term:

\[
C_{ik}^{\text{Kinetic}} = -\frac{NkT}{V}.
\]

The last term - the *stress fluctuation term* - takes into account that the atoms in the crystal do not form a monoatomic Bravais lattice and that there are other deviations from the ideal behaviour:

\[
C_{ik}^{\text{Fluctuation}} = \frac{V}{kT} \langle \sigma_i \sigma_k \rangle.
\]

The stress \( \sigma \) is the actual stress minus the average stress, since it is assumed that the cell is in a stress-free state (should be checked!).

### 4.3.4 Results

#### 4.3.4.1 Static Minimum Energy Calculations

The procedure described in chapter 4.1.6.2 was applied to compute the elastic constants using the *pcff91 forcefield*. The results of the static minimum energy approach are listed in Table 4-28.
Table 4-27: Static minimum energy elastic constants (left) compared with results from stress-strain fluctuations at 300 K (right).

<table>
<thead>
<tr>
<th>$\frac{1}{V_0} \left( \frac{\partial^2 U_{pot}}{\partial \eta_{ij} \partial \eta_{kl}} \right)$ [GPa]</th>
<th>$\langle \eta_{ik} \sigma_{jkl} \rangle / \langle \eta_{ij} \eta_{lm} \rangle^{-1}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.11 5.80 8.43 0.0 0.41 0.0</td>
<td>8.79 3.96 7.33 0.12 0.43 0.35</td>
</tr>
<tr>
<td>5.80 10.82 4.84 0.0 0.20 0.0</td>
<td>4.00 7.24 3.83 0.24 0.42 0.04</td>
</tr>
<tr>
<td>8.43 4.84 62.58 0.0 5.45 0.0</td>
<td>7.78 4.02 58.84 0.87 7.56 0.26</td>
</tr>
<tr>
<td>0.0 0.0 0.0 3.12 0.0 0.20</td>
<td>0.19 0.26 0.84 2.57 0.18 0.63</td>
</tr>
<tr>
<td>-0.41 -0.20 -5.45 0.0 6.24 0.0</td>
<td>-0.40 -0.70 -2.98 0.13 5.26 0.48</td>
</tr>
<tr>
<td>0.0 0.0 0.0 0.20 0.0 4.53</td>
<td>-0.11 0.03 0.01 -0.27 -0.49 2.02</td>
</tr>
</tbody>
</table>

4.3.4.2 MD Simulations

The results of the MD simulations are given in the next few tables. The first table (Table 4-28) shows the average of the cell shape taken from the last Table 4-28: Average it-PP cell parameters, obtained from the last 500 ps of Ta/N-MD

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$\langle a \rangle$ [Å]</th>
<th>$\langle b \rangle$ [Å]</th>
<th>$\langle c \rangle$ [Å]</th>
<th>$\langle \alpha \rangle$ [°]</th>
<th>$\langle \beta \rangle$ [°]</th>
<th>$\langle \gamma \rangle$ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>19.700</td>
<td>21.053</td>
<td>19.954</td>
<td>89.52</td>
<td>98.51</td>
<td>89.32</td>
</tr>
<tr>
<td>335</td>
<td>19.755</td>
<td>21.173</td>
<td>19.958</td>
<td>89.56</td>
<td>98.52</td>
<td>89.37</td>
</tr>
<tr>
<td>375</td>
<td>19.811</td>
<td>21.313</td>
<td>19.962</td>
<td>89.59</td>
<td>98.58</td>
<td>89.38</td>
</tr>
</tbody>
</table>

$10^6$ MD steps (500 ps). From this information, it is possible to estimate the thermal expansion coefficient in the $a$-, $b$-, and $c$-direction. The corresponding table (4-29) compares the expansion coefficients obtained from the above simulation at 300 K with experimental values and with simulation results from Lacks and Rutledge.\Rutledge95a The thermal expansion in the $a$- and $b$- directions is quite well reproduced, but in the $c$-direction a small expansion is predicted instead of the observed contraction. The difference between experimental and simulated values is small, allowing minor effects to come into play.

Table 4-29: Thermal expansion coefficients from Table 4-28, from experiment and from Lacks and Rutledge\Rutledge95a

<table>
<thead>
<tr>
<th>$[10^{-5} \text{K}^{-1}]$</th>
<th>this work</th>
<th>experiment</th>
<th>Lacks and Rutledge</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_a$</td>
<td>8.0</td>
<td>6.2</td>
<td>8.2</td>
</tr>
<tr>
<td>$\alpha_b$</td>
<td>16.2</td>
<td>15</td>
<td>8.7</td>
</tr>
<tr>
<td>$\alpha_c$</td>
<td>0.57</td>
<td>-1.0, -0.45</td>
<td>-0.84</td>
</tr>
</tbody>
</table>

-0.48
The average normal stresses lower with temperature from ~1300 bars to ~1270 bars, whereas the shear stresses are hardly affected by temperature and remain in the range of 2-4 bars. The average normal stresses differ from the applied correction pressure of 1417 bars by more than 100 bars, due to the finite step size (0.5 fs) of the simulation.

The next three tables, Table 4-30 to 4-33, list the matrices of the elastic constants obtained from strain and stress-strain fluctuations. The convergence of the individual matrix elements (from stress-strain fluctuations) at 300 K is shown in Fig. 4.19. A detailed discussion of these values will follow in chapter 4.3.5. Despite the large negative number found for the $C_{35}$ component, all eigenvalues of all matrices are positive, guaranteeing mechanical stability.

<table>
<thead>
<tr>
<th>$\frac{K}{V} \langle \eta_{ik} \eta_{lm} \rangle^{-1}$ [GPa]</th>
<th>$\langle \eta_{ik} \sigma_{ij} \rangle \langle \eta_{ij} \eta_{lm} \rangle^{-1}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>8.33 3.73 7.22 -0.02 0.28 -0.22</td>
<td>8.79 3.96 7.33 0.12 0.43 -0.35</td>
</tr>
<tr>
<td>3.73 6.95 3.63 0.22 -0.73 0.05</td>
<td>4.00 7.24 3.83 0.24 -0.62 0.04</td>
</tr>
<tr>
<td>7.22 3.63 54.76 0.86 -6.26 -0.32</td>
<td>7.78 4.02 58.84 0.87 -7.56 -0.26</td>
</tr>
<tr>
<td>0.28 -0.73 -6.26 0.05 5.82 -0.53</td>
<td>-0.40 -0.70 -2.98 0.13 5.26 -0.48</td>
</tr>
<tr>
<td>-0.22 0.05 -0.32 -0.46 -0.53 2.11</td>
<td>-0.11 0.03 0.01 -0.27 -0.49 2.02</td>
</tr>
</tbody>
</table>

Figure 4.19: Convergence of the elastic constants of it-PP (stress-strain fluctuations, diagonal elements as heavy lines; $C_{12}$, $C_{13}$, and $C_{23}$ in heavy grey lines), simulation at $T = 300$ K
### Table 4-31: Elastic constants averaged over the last 500 ps of a 580 ps TiN-MD simulation at 335 K. Non-zero components are bold faced.

<table>
<thead>
<tr>
<th>$\frac{kT}{\langle \mathbf{V} \rangle} \langle \eta_{ik} \eta_{jm} \rangle^{-1}$ [GPa]</th>
<th>$\langle \eta_{ik} \sigma_{nj} \rangle \langle \eta_{nj} \eta_{im} \rangle^{-1}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.93 3.62 7.12 0.10 -0.54 -0.13</td>
<td>8.23 3.75 7.68 0.09 0.27 -0.21</td>
</tr>
<tr>
<td>3.62 6.61 3.53 0.14 -0.65 0.04</td>
<td>3.91 7.02 4.05 0.14 -0.92 0.12</td>
</tr>
<tr>
<td>7.12 3.53 55.96 0.76 -6.50 -0.28</td>
<td>7.31 3.72 58.16 0.77 -7.57 -0.22</td>
</tr>
<tr>
<td>0.10 0.14 0.76 2.51 0.01 -0.49</td>
<td>0.18 0.25 0.89 2.55 0.16 -0.67</td>
</tr>
<tr>
<td>-0.54 -0.65 -6.50 0.01 5.44 -0.41</td>
<td>-0.58 -0.70 -2.68 0.11 5.02 -0.41</td>
</tr>
<tr>
<td>-0.13 0.43 -0.28 -0.49 -0.41 1.90</td>
<td>-0.13 0.03 -0.22 -0.27 -0.39 1.87</td>
</tr>
</tbody>
</table>

### Table 4-32: Elastic constants averaged over the last 500 ps of a 1000 ps TiN-MD simulation at 375 K. Non-zero components are bold faced.

<table>
<thead>
<tr>
<th>$\frac{kT}{\langle \mathbf{V} \rangle} \langle \eta_{ik} \eta_{jm} \rangle^{-1}$ [GPa]</th>
<th>$\langle \eta_{ik} \sigma_{nj} \rangle \langle \eta_{nj} \eta_{im} \rangle^{-1}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.67 3.24 7.18 0.05 -0.42 -0.17</td>
<td>8.12 3.53 7.68 0.11 0.18 -0.30</td>
</tr>
<tr>
<td>3.24 6.30 3.84 0.14 -0.71 0.09</td>
<td>3.70 6.62 4.21 0.17 -0.74 0.11</td>
</tr>
<tr>
<td>7.18 3.84 56.29 0.57 -6.74 -0.21</td>
<td>7.17 3.85 56.61 0.58 -7.34 -0.17</td>
</tr>
<tr>
<td>0.05 0.14 0.57 2.23 -0.04 -0.48</td>
<td>0.11 0.16 0.30 2.33 0.19 -0.64</td>
</tr>
<tr>
<td>-0.42 -0.71 -6.74 -0.04 5.39 -0.33</td>
<td>-0.43 -0.67 -2.59 0.04 4.99 -0.33</td>
</tr>
<tr>
<td>-0.17 0.09 -0.21 -0.48 -0.33 1.79</td>
<td>-0.19 0.14 -0.19 -0.31 -0.35 1.71</td>
</tr>
</tbody>
</table>

The matrix of the elastic constants of the ordered structure of Fig. 4.18 c) is given in Appendix F.

### 4.3.4.3 Elastic Constants from Constant-Shape MD simulations

Table 4-33 lists selected elements of the matrix of the elastic constants, that were computed in the ThN-ensemble. At 300 K, the Born, the kinetic energy, and the stress fluctuation term as well as the sum of these three contributions were given. At 335 and 375 K, only the sums, i.e. the effective elastic constants, were listed. In general, the results obtained in this ensemble do not seem to be very consistent. The $C_{33}$ and $C_{66}$ values agree quite well with other calculations, but especially $C_{44}$ and $C_{55}$ are much too high, whereas the $C_{11}$ and $C_{22}$ components at 375 K are even negative! The convergence of the stress fluctuations seems to be so slow that an equilibration could not be achieved in the 250 ps of the simulation. It was therefore not possible to verify Ray’s statement that the elastic constants converge much faster in the ThN-ensemble than in the TiN-ensemble. Ray88a
Table 4-33: Elastic constants from ThN-simulations of it-PP at 300 K, 335 K, and 375 K, all values in GPa

<table>
<thead>
<tr>
<th>Born</th>
<th>Kinetic</th>
<th>Fluct</th>
<th>300 K</th>
<th>335 K</th>
<th>375 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}$</td>
<td>221.27</td>
<td>-0.48</td>
<td>-209.63</td>
<td>11.16</td>
<td>13.89</td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>230.48</td>
<td>-0.48</td>
<td>-222.14</td>
<td>7.86</td>
<td>9.78</td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>248.32</td>
<td>-0.48</td>
<td>-191.43</td>
<td>56.41</td>
<td>57.97</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>103.00</td>
<td>0</td>
<td>-79.19</td>
<td>23.81</td>
<td>25.41</td>
</tr>
<tr>
<td>$C_{55}$</td>
<td>112.55</td>
<td>0</td>
<td>-84.47</td>
<td>28.08</td>
<td>25.89</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>97.21</td>
<td>0</td>
<td>-94.27</td>
<td>2.94</td>
<td>1.44</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>45.78</td>
<td>0</td>
<td>-40.78</td>
<td>5.00</td>
<td>5.12</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>32.70</td>
<td>0</td>
<td>-21.43</td>
<td>11.27</td>
<td>10.91</td>
</tr>
<tr>
<td>$C_{23}$</td>
<td>23.51</td>
<td>0</td>
<td>-20.04</td>
<td>3.47</td>
<td>4.36</td>
</tr>
<tr>
<td>$C_{35}$</td>
<td>-3.87</td>
<td>0</td>
<td>1.55</td>
<td>-2.32</td>
<td>2.09</td>
</tr>
</tbody>
</table>

4.3.5 Discussion

4.3.5.1 Rotation of the Matrix of the Elastic Constants

In contrast to PE, the chains in the it-PP simulation box are not parallel to the $x_3$-axis of the external frame of reference. In order to be able to estimate the modulus in the fiber direction, it is first necessary to rotate this external coordinate frame until its $x_3$-axis is aligned with the PP-chains. A procedure was written that performs such a rotation (using Eq. 1-50) by minimizing a penalty function. This function was proportional to the sum of the squares of those elements that should be zero by symmetry minus the square of the $C_{33}$ value (i.e. $C_{33}$ was maximized and a monoclinic symmetry was favoured). The resulting matrices are given in the next table (Table 4-35). The experimentally accessible

Table 4-34: Matrices of table 4-30, rotated successively by $1^\circ$ around the $x_1$-axis, $8^\circ$ around the $x_2$-axis and $3.3^\circ$ around the $x_3$-axis

$$\begin{array}{cccccc}
\frac{kT}{\langle V \rangle} \langle n_{ik} n_{lm} \rangle^{-1} [\text{GPa}] & & & & & \\
8.91 & 3.47 & 5.97 & 0.14 & 1.46 & -0.31 \\
3.47 & 6.96 & 3.83 & 0.09 & -0.78 & 0.13 \\
5.97 & 3.83 & 56.79 & -0.02 & -0.76 & 0.06 \\
0.14 & 0.09 & -0.02 & 2.61 & 0.34 & -0.42 \\
1.46 & -0.78 & -0.76 & 0.34 & 4.52 & -0.40 \\
-0.31 & 0.13 & 0.06 & -0.42 & -0.40 & 1.96 \\
\end{array}$$

$$\begin{array}{cccccc}
\langle n_{ik} \sigma_{nj} \rangle \langle n_{nj} n_{lm} \rangle^{-1} [\text{GPa}] & & & & & \\
9.18 & 3.70 & 7.03 & 0.28 & 1.52 & -0.39 \\
3.78 & 7.25 & 4.03 & 0.14 & -0.68 & 0.12 \\
6.46 & 4.21 & 60.15 & -0.12 & -1.50 & 0.10 \\
0.33 & 0.11 & 0.04 & 2.71 & 0.42 & -0.56 \\
0.68 & -0.73 & 3.07 & 0.31 & 4.41 & -0.35 \\
-0.13 & 0.10 & 0.35 & -0.20 & -0.33 & 1.88 \\
\end{array}$$
modulus, and the linear compressibility along the chain axis, $E_3$ and $\beta_3$, were calculated from the compliance matrix $S_{ik} (=C_{ik}^{-1})$ using Tadokoro92a

$$E_3 = \frac{1}{S_{33}} \quad \text{and} \quad \beta_3 = S_{31} + S_{23} + S_{33}. \quad (4-28)$$

For the strain fluctuations $E_3 = 51.9$ GPa and $\beta_3 = 0.31 \cdot 10^{-2}$ GPa$^{-1}$, whereas the stress-strain fluctuations yield $E_3 = 56.3$ GPa and $\beta_3 = 0.26 \cdot 10^{-2}$ GPa$^{-1}$.

4.3.5.2 Comparison with Literature Values

One of the earliest values of Young's modulus in the chain direction is 28 GPa from Miyazawa which was opposed to an observed 32 GPa from Sakurada et al. Tadokoro90 In the more recent work of Tashiro et al. Tadokoro92a, experimental $E_3$ values of 35 to 43 GPa - depending on the methodology - and a $\beta_3$ of 0.4-10$^{-2}$ GPa$^{-1}$ are reported. As mentioned in the introduction, Hong et al. Hong90a quote Young's moduli between 18 and 80 GPa.

Theoretical three-dimensional matrices were computed by Tashiro et al. Tadokoro92a and by Lacks and Rutledge Rutledge95a. In Tadokoro's work, the reference axes are as follows: $x(1)$-axis = $a \cdot \sin \beta$, $y(2)$-axis = $b$, and $z(3)$-axis = $c$. This is identical with the rotated matrices of Table 4-30. Lacks and Rutledge do not specify the relation between external cartesian and crystal coordinate system explicitly, but it is assumed that it is the same. A comparison with these literature values and the numbers obtained in this work is given in Table 4-35. Almost all values fit perfectly in the range spanned by the previous calculations, except for the $C_{44}$ value, which is a bit lower, and the $C_{35}$ value from the stress-strain fluctuations. As was seen in the process of rotating the elasticity matrix, this component is extremely dependent on the orientation (only 1 or 2° would suffice to change the sign without involving considerable changes in the other components).

4.3.5.3 Conclusions

At 300 K, the elastic constants obtained from the strain and the stress-strain fluctuations agree very well with experimental and other theoretical results. Young's modulus in the chain direction (51.9 GPa from the strain and 56.3 GPa from the stress-strain fluctuations) is higher than the experimental values of 35 - 43 GPa. Looking at Fig. 4.19, it can be seen that at least the stress-strain calculation has not yet converged and that a further drop by a few GPa can be anticipated. This would bring the stress-strain value closer to the one obtained from strain fluctuations and reasonably close to the experimental val-
Table 4-35: Comparison between the elastic constants [in GPa] and the linear compressibility in the chain direction [in $10^{-2}$ GPa$^{-1}$] obtained in theoretical calculations at 300 K from Tashiro et al., Lacks and Rutledge, and the strain and the stress-strain fluctuation formula of this work. Off-diagonal elements in the last column are averages of the two symmetry-equivalent numbers. SLKB* and KDG* denote modifications of force fields by Sorensen, Liau, Kesner, and Boyd and Karasawa, Dasgupta, and Goddard, which are used in Ref. [Rutledge95a].

<table>
<thead>
<tr>
<th></th>
<th>Tashiro et al</th>
<th>Lacks &amp; Rutledge</th>
<th>this work</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SLKB*</td>
<td>KDG*</td>
<td>$\eta_{ik}$</td>
</tr>
<tr>
<td>$C_{11}$</td>
<td>7.78</td>
<td>9.9</td>
<td>9.1</td>
</tr>
<tr>
<td>$C_{22}$</td>
<td>11.55</td>
<td>10.8</td>
<td>8.6</td>
</tr>
<tr>
<td>$C_{33}$</td>
<td>42.44</td>
<td>55.1</td>
<td>64.5</td>
</tr>
<tr>
<td>$C_{44}$</td>
<td>4.02</td>
<td>4.0</td>
<td>4.3</td>
</tr>
<tr>
<td>$C_{55}$</td>
<td>3.10</td>
<td>4.9</td>
<td>4.7</td>
</tr>
<tr>
<td>$C_{66}$</td>
<td>2.99</td>
<td>1.7</td>
<td>3.5</td>
</tr>
<tr>
<td>$C_{12}$</td>
<td>3.91</td>
<td>3.4</td>
<td>3.6</td>
</tr>
<tr>
<td>$C_{13}$</td>
<td>3.72</td>
<td>7.1</td>
<td>7.2</td>
</tr>
<tr>
<td>$C_{23}$</td>
<td>3.99</td>
<td>4.4</td>
<td>4.3</td>
</tr>
<tr>
<td>$C_{15}$</td>
<td>0.90</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$C_{25}$</td>
<td>-0.36</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$C_{35}$</td>
<td>-0.57</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$C_{46}$</td>
<td>-0.12</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>$E_3$</td>
<td>40.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>0.97</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The thermal expansivity of it-PP is quite well reproduced, with the exception of the small contraction in the chain direction, which must be attributed to...
4.3.5 Discussion

Figure 4.20: Convergence of the $C_{33}$-component of the elasticity matrix at 300, 335, and 375 K; the table gives the temperature dependence of the $C_{33}^{\text{rot}}$-component [in GPa] calculated with strain and stress-strain fluctuations

deficiencies in the pcff91-forcefield.
4.4 Cellulose-\(\beta\) - Chains with Hydrogen Bonds

4.4.1 Introduction

Cellulose is the most abundant natural polymer on earth; there exist about \(800 \times 10^9\) t\textsuperscript{Woodwell}\textsuperscript{78a} primarily in the cell walls of higher plants but also in some algae, fungi, protists, bacteria, and tunicata. The annual production rate of approx. \(70 \times 10^9\) t exceeds that of synthetic, man-made polymers by a factor of \(10^3\). In nature, highly crystalline cellulose fibers act as reinforcements in composite materials, like the lignin/cellulose complex in the reticulum of trees. These cellulose composites are responsible for the mechanical stability of the higher plants.\textsuperscript{Kraessig92}

In industrial applications, cellulose is mainly used in the form of its derivatives in the production of paper and of textile yarns like cotton and viscose. Further applications are wood-like materials made up from wooden filler particles and polymer matrices. Examples are plywoods, resinbonded boards or extrudable panels. In total, cellulose in its various forms constitutes about 50% of the polymer utilized in the industry worldwide.\textsuperscript{Maldas93a}

The reinforcing abilities of individual cellulose fibers are becoming of interest in order to increase the elastic moduli of synthetic polymers and rubbers. The experimental results reveal substantial effects even of comparatively small amounts of cellulose whiskers in rubbery materials.\textsuperscript{Chanzy95a} To make full use of the capabilities of such systems, it is important to establish a connection between the morphology of a reinforced two-phase matrix-whisker polymer, the elastic behaviour of its constituents, and the overall elastic properties.

With the knowledge of the complete matrix of the elastic constants of the polymer matrix and the reinforcing particles, it is possible to compute the elastic behaviour of the composite system. Assuming isotropy of the rubberous part, its elastic constants can readily be determined by tensile and shear experiments. The elastic constants of the anisotropic, crystalline cellulose whiskers are not accessible through experimental methods as stated in chapter 4.2.1.

It is therefore of theoretical and practical interest to compute the full matrix of the elastic constants of cellulose. The results of the structure generation and the simulation runs will be presented after a short discussion about the various modifications of crystalline cellulose.
4.4.2 Crystal Modifications and Cell Generation

4.4.2.1 Crystal Modifications

Despite repeated efforts in the last 70 years, the crystalline structures of native and of chemically modified cellulose still are disputed. At present, there is evidence for at least four major modifications of crystalline cellulose:\textsuperscript{Kraessig92}: cellulose-I is the form in which native cellulose appears; after its treatment with strong alkaline solutions or after precipitation from solution in suitable solvents, the cellulose-II modification is observed. Cellulose-III is formed by the decomposition of the reaction product of native cellulose and liquid ammonia, whereas cellulose-IV is obtained by treating regenerated cellulose-II fibers in hot baths under stretch. Although the existence of cellulose-I and cellulose-II is well established - in contrast to the latter two modifications\textsuperscript{Atalla74a} - not only the actual arrangement of the chains in the unit cell but also the size and shape of the unit cells still are subject to ongoing research.

Recent studies\textsuperscript{Atalla84a, Sugiyama90a, Chanzy91a} give indication that crystals of native cellulose-I are composed of two crystalline phases: a monoclinic, two chain \(\text{I}_\beta\)-phase which is dominant in ramie, cotton and tunicin and a triclinic \(\text{I}_\alpha\)-phase occurring in \textit{Valonia ventricosa} and bacterial cellulose. The fraction of the \(\text{I}_\alpha\)-phase depends on the origin of the cellulose and amounts to 65\% in \textit{Valonia} samples. This phase, however, is only metastable and can be converted by hydrothermal annealing into the thermodynamically stable \(\text{I}_\beta\)-phase.

While the cell parameters of cellulose-\(\text{I}_\alpha\) are still under discussion, it is generally accepted that the \(\text{I}_\beta\)-phase is monoclinic and contains two cellulose chains at the twofold screw axes, one at the corner and another one in the center of the unit cell. Unresolved is the question, whether the two chains are parallel or antiparallel. In one of the first proposals, still widely in use, from Meyer, Mark and Misch\textsuperscript{Meyer37a}, the two chains were in antiparallel position. Later, Gardner and Blackwell\textsuperscript{Gardner74a} and Woodcock and Sarko\textsuperscript{Woodcock80a} suggested models in which there was a parallel arrangement of the chains. In the present work, the model structure of Woodcock and Sarko was used for the calculation of the elastic constants. The latest reports, however, support an antiparallel alignment of the chains in cellulose-II,\textsuperscript{Chanzy95b} which in turn makes an antiparallel setup of the chains in cellulose-\(\text{I}_\beta\) more likely. MD calculations made by Kroon-Batenburg \textit{et al.}\textsuperscript{Kroon96a} favour, on the other hand, parallel chains according to the Woodcock/Sarko structure.

The cellulose-\(\text{I}\) structure suggested by Woodcock and Sarko is monoclinic, with unit cell parameters given in Table 4-36. The arrangement of the cellulose
Table 4-36: Unit cell dimensions and helical setting parameters of Cellulose-Iβ and Cellulose-II

<table>
<thead>
<tr>
<th>Property</th>
<th>Cellulose-Iβ</th>
<th>Cellulose-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>a [Å]</td>
<td>7.78</td>
<td>8.00</td>
</tr>
<tr>
<td>b [Å]</td>
<td>8.20</td>
<td>9.05</td>
</tr>
<tr>
<td>c [Å]</td>
<td>10.34</td>
<td>10.38</td>
</tr>
<tr>
<td>$\gamma$ [°]</td>
<td>96.5</td>
<td>116.8</td>
</tr>
<tr>
<td>Chain 1 Position/Orientation</td>
<td>[0,0] / 'up'</td>
<td>[0,0] / 'up'</td>
</tr>
<tr>
<td>Setting angle [°]</td>
<td>-42.0</td>
<td>28.0</td>
</tr>
<tr>
<td>Vert. offset [Å]</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Chain 2 Position/Orientation</td>
<td>$[{\frac{1}{2}},{{\frac{1}{2}}}]$ / 'up'</td>
<td>$[{\frac{1}{2}},{{\frac{1}{2}}}]$ / 'down'</td>
</tr>
<tr>
<td>Setting angle [°]</td>
<td>-42.0</td>
<td>18.0</td>
</tr>
<tr>
<td>Vert. offset [Å]</td>
<td>-2.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

chains in the cell is shown in Figure 4.21. The various intra- and intermolecular hydrogen bonds are not shown in order not to cluster the picture too much. The intramolecular hydrogen bonds are depicted in Fig. 4.24, the intermolecular hydrogen bonds act mainly between neighbouring sheets in the $b$-direction.

Based on experimental data and the comparison with chemically similar molecules, Chanzy et al. suggested a crystal structure of cellulose-II whose unit cell parameters are listed in Table 4-36, too.

Figure 4.21: Unit cell projections of the parallel-chain structure of cellulose-Iβ. The center chain is drawn gray-shaded, the corner chains are solid black.
4.4.2.2 Structure Generation

The commercial Insight/Discover\textsuperscript{MSIDiscover1} program package was used for the setup and minimization of the crystalline simulation cell and for the computation of the molecular dynamics (MD) trajectory. Note: In the Discover simulations, the cartesian coordinate frame was set such that the a-edge of the simulation cell was parallel to the $x_1$-direction and the b-edge was in the $x_1$-$x_2$-plane. This is in contrast to the orientation of the coordinate frame used in the literature and in this work, in which the chains and thus the c-direction are parallel to the $x_3$-axis and the b-axis is in the $x_2$-$x_3$-plane (in the case of monoclinic symmetry parallel to the $x_2$-axis).

After the building and minimization of a chemical repeat unit of cellulose, a short oligomer with a degree of polymerization (DP) = 3 was generated in order to extract the helical repeat unit. Two such helical repeat units were placed in a box of the size of the Woodcock and Sarko crystal cell, one at a corner (0,0) and one in the center ($\frac{1}{2}, \frac{1}{2}$) with an offset in the c-direction of -2.6 Å. The setting angle for both chains was -42° (cf. Table 4-36). In the refinement process, different force-fields were used to find the most suitable one for cellulose. This refinement procedure consisted in a systematic change of the cell parameters, the setting locations, and the setting angles of the chains followed by an energy minimization to find the most stable crystal conformation. MSIPolymer\textsuperscript{1} The amber, cvff and pcfP force-fields were tested, and it turned out that the most sensitive cell parameter was the $\gamma$ angle. The amber force-field gave a correct estimate of 96.5°, but lacked some parameters necessary for dynamic simulations. Of the remaining two force-fields, cvff seemed to be more suitable than pcfP (as Table 4-37 shows) and was thus used for the further computations.

<table>
<thead>
<tr>
<th></th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>$\alpha$ [°]</th>
<th>$\beta$ [°]</th>
<th>$\gamma$ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pcfP</td>
<td>7.89</td>
<td>8.38</td>
<td>10.63</td>
<td>93.25</td>
<td>89.05</td>
<td>99.05</td>
</tr>
<tr>
<td>cvff</td>
<td>7.77</td>
<td>8.14</td>
<td>10.68</td>
<td>90.73</td>
<td>89.79</td>
<td>97.34</td>
</tr>
<tr>
<td>exp.</td>
<td>7.78</td>
<td>8.20</td>
<td>10.34</td>
<td>90</td>
<td>90</td>
<td>96.5</td>
</tr>
</tbody>
</table>

The results will show, the $\gamma$ angle was quite close to the experimental value. The cvff is an all-atom force field with flexible bond lengths, bond angles and torsional degrees of freedom. MSIDiscover\textsuperscript{1} No Morse bond potentials, no out-of-plane and no cross terms were used. There are no explicit
terms for the hydrogen bonds, but large partial charges invoke similar effects.

To reduce the effects of the small unit cells, a super cell of $2 \times 2 \times 2$ unit cells with periodic boundary conditions was generated. The images of the cellulose chains were connected to their parent chains by 'bonds across boundaries' in order to mimic infinitely long molecules. This super cell contained 672 atoms in 8 chains.

### 4.4.3 Simulation Procedure

The MD simulation was carried out in the familiar $T\sigma N$-ensemble, where the pressure was controlled by a Parrinello-Rahman manostat and the temperature by a Nosé-Hoover algorithm. The coupling constant $W$ between the internal stress fluctuations and the velocity of the cell shape changes was again set to 20 a.m.u. The fictitious mass $Q$ of the Nosé-Hoover thermostat was chosen as 7.33·10$^6$ kcal·mol$^{-1}$·fs$^{-2}$ at 325 K. Again, the dynamic properties, i.e. the temperature fluctuations, depend on $Q$, whereas static quantities, such as the average temperature, are not influenced by the choice of this variable, but rather by the stepwidth of the simulation.\textsuperscript{Nose91a} The smaller the timestep, the closer the average temperature approaches the target temperature. A canonical ensemble of the correct temperature will only be created by using infinitely small timesteps. Having, e.g., 325 K as the target temperature, a timestep of 0.5 fs leads to an average temperature of 318.3 K (cf. chapter 2.5.2.3).

The long-range Lennard-Jones interactions were taken into account by applying an external pressure of 180 MPa (1800 bar). The Coulombic interactions were treated with a conventional splined cutoff (switching from full interactions at 7.5 Å down to no interactions at 8.5 Å) and with Ewald terms that were summed up to an accuracy of 0.0025 kcal·mol$^{-1}$.

Calculations were performed at 325 K (for the sake of comparison with Ref. [Chanzy95a]), 150, and 400 K, which allows the calculation of the temperature dependence of the density (thermal expansion coefficients) and of the elastic constants of cellulose. Splined cutoffs made it possible to perform 2·10$^6$ MD steps of 0.5 fs, totalling 1 ns, whereas the computationally more expensive Ewald summation reduced the simulation length to 0.5·10$^5$ steps or 250 ps. These values correspond to roughly 1 month of CPU time on a workstation per simulation run and are the limit of feasibility.

In addition to the simulation of cellulose-Iβ, the cellulose-II structure of Ref. [Chanzy95b] was generated with the same methodology as described above using the parameters of Table 4-36, chain 2 being antiparallel to chain 1. Just like for cellulose-Iβ, the application of the \textit{cvff} force-field led to the best agree-
ment of the simulation structure with the experimental values. For this structure, a \( \text{ToN-MD} \) simulation was made for \( 0.5 \times 10^6 \) steps of 0.5 fs (250 ps). Again, Ewald summation of the coulombic interaction terms was used.

### 4.4.4 Results

#### 4.4.4.1 Cell Shape and Thermal Expansion

In this subchapter, only results from calculations with Ewald summation of the charged interactions are presented.

An example of the thermal fluctuations of the lengths of the vectors spanning up the cellulose-\( \alpha \) simulation cell is given in Figure 4.22. The averages of

![Figure 4.22: Fluctuations of the vector lengths \( a \), \( b \), and \( c \) of the cellulose-\( \alpha \) simulation cell at 325 K (Ewald summation)](image)

the cell parameters \( \{a, b, c, \alpha, \beta, \gamma\} \) taken at any subtrajectory are not significantly different from those of the whole trajectory, indicating that the cell is fluctuating around a quasi-equilibrium point at 150 and at 325 K. At 400 K, however, a transition occurred after approx. 130 ps, in which \( b \) increased by about 0.4 Å (Fig. 4.26) and the \( \alpha \) and \( \gamma \) values by about 2°. The reason for this transition is most probably the small cell size in combination with the elevated temperature, which creates considerable fluctuations. In order to have some indication of the material’s behaviour at 400 K, relatively stable parts of the trajectory were taken for further investigation.

In Figure 4.22, visual inspection already allows to estimate the elastic constants in the \( c \)-direction (along the chains) being higher and in the \( a \)-direction being lower than in the \( b \)-direction, because the fluctuations are smaller in the
Cellulose-Iβ-Chains with Hydrogen Bonds

...direction and larger in the a-direction. This is supported by the apparently higher frequency of the oscillations of the c-value than of the a-value. So the c-direction, which is parallel to the chains, is a 'hard' direction, whereas the a-direction, where only weak Lennard-Jones forces act perpendicular to the hydrogen-bonded sheets, is a 'soft' one. These rough estimates will be confirmed by the following standard deviations of the cell parameters and by numerical analysis in chapter 4.4.4.2.

Table 4-38: Summary of simulation cell parameters of minimized cellulose-Iβ, at 150, 325, and 400 K. Averages were taken from 2.5·10^5 frames at 150 and 325 K and from 1.2·10^5 frames at 400 K. The time interval between the frames was 1 fs (2 MD steps)

<table>
<thead>
<tr>
<th>T [K]</th>
<th>a [Å]</th>
<th>b [Å]</th>
<th>c [Å]</th>
<th>α [°]</th>
<th>β [°]</th>
<th>γ [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>15.53</td>
<td>16.27</td>
<td>21.37</td>
<td>90.2</td>
<td>89.9</td>
<td>97.5</td>
</tr>
<tr>
<td>150</td>
<td>15.70</td>
<td>16.29</td>
<td>21.38</td>
<td>90.0</td>
<td>90.0</td>
<td>97.5</td>
</tr>
<tr>
<td>± 0.08</td>
<td>± 0.07</td>
<td>± 0.03</td>
<td>± 0.4</td>
<td>± 0.6</td>
<td>± 0.4</td>
<td></td>
</tr>
<tr>
<td>325</td>
<td>15.85</td>
<td>16.40</td>
<td>21.39</td>
<td>90.0</td>
<td>90.0</td>
<td>97.5</td>
</tr>
<tr>
<td>± 0.13</td>
<td>± 0.10</td>
<td>± 0.05</td>
<td>± 0.7</td>
<td>± 1.1</td>
<td>± 0.8</td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>15.96</td>
<td>16.46</td>
<td>21.40</td>
<td>90.0</td>
<td>89.9</td>
<td>97.8</td>
</tr>
<tr>
<td>± 0.14</td>
<td>± 0.10</td>
<td>± 0.05</td>
<td>± 0.9</td>
<td>± 1.3</td>
<td>± 1.0</td>
<td></td>
</tr>
</tbody>
</table>

The average values and the standard deviations of the cell parameters at 150, 300 and 400 K are given in Table 4-38. Linear regressions of these parameters show that there is virtually no drift of the cell shape with time, i.e. that there are no significant relaxations in the timescale of the simulation. Only at 400 K, the reduced stability of the cell becomes manifest in higher values of the slope of the regression line (cf. Fig. 4.26).

From Table 4-38, it is possible to compute the matrix of the thermal expansion coefficients. Assuming no change in the cell symmetry (i.e. shape), the thermal expansion coefficients at 325 K can be estimated as \( \alpha_1 = 7 \pm 2 \times 10^{-5} \), \( \alpha_2 = 5 \pm 1 \times 10^{-5} \), and \( \alpha_3 = 5 \pm 1 \times 10^{-6} \) K\(^{-1}\). As with PP, these values are in accord with experimental measurements of the \( \alpha_1 \) and \( \alpha_2 \) coefficients, but are not able to reproduce the contraction effect along the chains of \(-4.5 \times 10^{-5} \) K\(^{-1}\) Godovsky92.

The cellulose II structure was not completely stable, as the next figure shows. Especially the b and γ values exhibit drifts, that are of the same or a larger magnitude than the thermal fluctuations, making it impossible to evaluate the elastic constants properly.
4.4.4.2 Elastic Constants

The strain and the stress-strain fluctuation formalisms of Eqs. (3-29) and (3-36) were used to compute the elastic constants of cellulose-1\(\beta\) at 150, 325, and 400 K. At first, the results using a splined cutoff and an Ewald summation for the coulombic interactions at 325 K are compared:

The matrices of the elastic constants (in the Discover coordinate system) obtained from interactions with a splined cutoff, given in Table 4-39, differ dramatically from those that used an Ewald summation for the charged interactions (Table 4-41).

The comparison with literature values (chapter 4.4.5.1) shows that the simulations which involve an Ewald summation of the far-reaching coulombic inter-
Table 4-40: Elastic constants averaged over a 250 ps TαN-MD simulation at 325 K, cutoff = 8.5 Å, spline = 1 Å, Ewald summation for the coulombic interactions. Non-zero components are bold faced.

<table>
<thead>
<tr>
<th>$kT$</th>
<th>$\langle \eta_{ik}\eta_{lm} \rangle^{-1}$ [GPa]</th>
<th>$\langle \eta_{ik}\sigma_{nj}\eta_{lj}\eta_{im} \rangle^{-1}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.2</td>
<td>12.9</td>
<td>6.8 -0.1</td>
</tr>
<tr>
<td>12.9</td>
<td>34.3</td>
<td>14.7 0.1</td>
</tr>
<tr>
<td>6.8</td>
<td>14.7</td>
<td>162.0 0.1</td>
</tr>
<tr>
<td>-0.1</td>
<td>0.1</td>
<td>0.1 5.0 -0.2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0</td>
<td>0.0 -0.2</td>
</tr>
<tr>
<td>-0.5</td>
<td>-0.5</td>
<td>0.9 -0.1</td>
</tr>
<tr>
<td>17.3</td>
<td>13.2</td>
<td>6.9 -0.1</td>
</tr>
<tr>
<td>11.9</td>
<td>31.6</td>
<td>10.7 0.1</td>
</tr>
<tr>
<td>6.4</td>
<td>13.5</td>
<td>160.8 0.1</td>
</tr>
<tr>
<td>0.0</td>
<td>0.2</td>
<td>0.6 4.9 -0.2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2</td>
<td>0.0 0.0</td>
</tr>
<tr>
<td>-0.7</td>
<td>-1.5</td>
<td>1.5 -0.1</td>
</tr>
</tbody>
</table>

actions are much more reliable than those from calculations with splined cutoffs. The reason for this can be seen in Figs. 4.24 and 2.5. Figure 4.24 shows a structural repeat unit of cellulose I

![Partial charges](image)

Figure 4.24: Partial charges of a structural repeat unit of cellulose I

...
was less pronounced for the PE and it-PP crystals because the partial charges were much smaller ($\mathcal{O}(0.05-0.15)$) and the neutral groups less extended.

In order to obtain reliable results for the elastic constants of cellulose, the charged interactions must be treated using an Ewald summation or an equivalent technique.

The elastic constants at 150 K, computed with Ewald summation, are given in Table 4-42, and the convergence of the $C_{11}$, $C_{22}$, and $C_{33}$ component is shown in Fig. 4.25.

Table 4-41: Elastic constants averaged over a 250 ps TσN-MD simulation at 150 K, cutoff = 8.5 Å, spline = 1 Å, Ewald summation for the coulombic interactions. Non-zero components are bold faced.

<table>
<thead>
<tr>
<th>$\frac{kT}{\langle V \rangle}$</th>
<th>$\langle \eta_{ik} \eta_{lm} \rangle^{-1}$ [GPa]</th>
<th>$\langle \eta_{ik} \sigma_{ij} \rangle \langle \eta_{ij} \eta_{lm} \rangle^{-1}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.4 15.2 6.8 0.2 -0.1 -1.2</td>
<td>21.7 17.0 7.6 0.2 -0.1 -1.4</td>
<td></td>
</tr>
<tr>
<td>15.2 37.0 14.3 -0.4 0.2 -0.3</td>
<td>12.4 30.1 11.7 -0.3 0.1 -0.3</td>
<td></td>
</tr>
<tr>
<td>6.8 14.3 158.3 0.0 0.1 0.9</td>
<td>6.7 14.1 156.0 0.0 0.1 0.9</td>
<td></td>
</tr>
<tr>
<td>0.2 -0.4 0.0 7.2 -0.4 0.0</td>
<td>0.1 -0.4 0.0 6.8 -0.4 0.0</td>
<td></td>
</tr>
<tr>
<td>-0.1 0.2 0.1 -0.4 2.1 -0.2</td>
<td>-0.1 0.2 0.1 -0.4 2.2 -0.2</td>
<td></td>
</tr>
<tr>
<td>-1.2 -0.3 0.9 0.0 -0.2 4.4</td>
<td>-1.3 -0.3 0.9 0.0 -0.2 4.6</td>
<td></td>
</tr>
</tbody>
</table>

At a temperature of 400 K, the cellulose cell became slightly unstable, as is manifest from Fig. 4.26. Actually, it is not possible to evaluate the elastic constants from this trajectory at all, since the system is not in equilibrium. In order to have an approximate idea of the elasticity matrix, the first and the last 100 ps (from 0 to 100 and from 150 to 250 ps) were used to compute the matrix of the
elastique constants. The elastique constants of the last 100 ps are also listed in

Figure 4.27: Convergence of the \( C_{11}, C_{22}, \) and \( C_{33} \) components of the matrix of the elastique constants of cellulose-\( \beta \) at 400 K. Averages obtained from two intervals between 0 - 100 and 150 - 250 ps.

Table 4-43. The difference between the two matrices is relatively large, because of the short trajectory used for their evaluation. The diagonal elements of the stress-strain correlation matrix range from 0.94 to 1.02 \( kT \), whereas the off-diagonal elements vary between -0.2 and 0.2 \( kT \).

A short simulation run was started at 450 K to check the thermal stability of the cellulose-\( \beta \) cell. After approximately 70 ps, the structure started 'melting', i.e.
Table 4-42: Elastic constants averaged over the last 100 ps of a 250 ps ToN-MD simulation at 400 K, cutoff = 8.5 Å, spline = 1 Å, Ewald summation for the coulombic interactions. Non-zero components are bold faced.

<table>
<thead>
<tr>
<th>(\frac{k_T}{V}\langle \eta_{ik}\eta_{im}\rangle^{-1}) [GPa]</th>
<th>(\langle \eta_{ik}\sigma_{nj}\rangle\langle \eta_{nj}\eta_{im}\rangle^{-1}) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.6 8.8 6.4 0.1 0.3</td>
<td>14.8 9.6 7.0 0.1 0.3</td>
</tr>
<tr>
<td>8.8 30.1 9.2 -0.7 0.4</td>
<td>7.2 24.9 7.6 -0.6 0.4</td>
</tr>
<tr>
<td>6.4 9.2 155.6 -4.1 -1.5 -1.9</td>
<td>6.1 8.7 148.2 -3.9 -1.5 -1.8</td>
</tr>
<tr>
<td>0.1 -0.7 -4.1 1.2 0.5</td>
<td>0.1 -0.6 -3.7 1.1 0.5</td>
</tr>
<tr>
<td>0.3 0.4 -1.5 -0.5 2.8</td>
<td>0.3 0.5 -1.7 -0.6 2.9</td>
</tr>
<tr>
<td>0.3 -2.6 -1.9 0.2</td>
<td>0.3 -2.6 -1.9</td>
</tr>
</tbody>
</table>

the cell angles preformed large jumps of several degrees. It is therefore quite probable that the instabilities observed at 400 K are due to the large thermal fluctuations of the small cellulose 1\beta cell. There is of course no melting of cellulosic materials at this temperature, this is only an effect of the finite-size of the simulation box. 'Infinite' cellulose crystals do not melt, but start decomposing at 480 - 550 K Brandrup. 89

4.4.4.3 Mechanical Relaxation Spectra

To obtain the relaxation spectra of the three cell edges, their time-autocorrelation functions were computed and then Fourier transformed. The resulting spectra are plotted in Fig. 4.28. The contributions to the mechanical loss spec-

![Figure 4.28](image-url)
trum along the chains (c-direction) have been calculated for the classical and the quantum mechanical case using the formulae of chapter 4.2.4.1. There is hardly any difference between the quantum mechanical and the classical integral. In contrast to the corresponding Fourier transforms of polyethylene and polypropylene crystals, there exists a variety of peaks belonging to different processes being responsible for the fluctuations. The long range interactions between the charged groups (hydrogen bonds) couple different fluctuation modes in neighbouring chains. These undirected forces are responsible for the broadening of the peaks.

4.4.4.4 Static Minimum Energy Calculation of the Elastic Constants

According to the methodology presented in chapter 4.1.6.2, the elastic constants at 0 K were evaluated for cellulose-\(\beta\) using the cvff-forcefield and an Ewald summation of the Coulombic interactions.

<table>
<thead>
<tr>
<th>(\frac{1}{V_0} \frac{\delta^2 U_{pot}}{\delta n_j \delta n_k} ) [GPa]</th>
<th>(\langle \eta_{ik} \sigma_{nj} \rangle \langle \eta_{nj} \eta_{im} \rangle^{-1} ) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.5 15.1 7.2 0.2 -0.5 -0.8</td>
<td>21.7 17.0 7.6 -0.2 -0.1 -1.4</td>
</tr>
<tr>
<td>15.1 38.6 14.0 -0.3 -0.2 0.1</td>
<td>12.4 30.1 11.7 -0.3 0.1 -0.3</td>
</tr>
<tr>
<td>7.2 14.0 168.6 -1.3 0.1 1.6</td>
<td>6.7 14.1 156.0 0.0 0.1 0.9</td>
</tr>
<tr>
<td>0.2 -0.3 -1.3 7.1 -0.5 -0.7</td>
<td>0.1 -0.4 0.0 6.8 -0.4 0.0</td>
</tr>
<tr>
<td>-0.5 -0.2 0.1 -0.5 1.8 0.1</td>
<td>-0.1 0.2 0.1 -0.4 2.2 -0.2</td>
</tr>
<tr>
<td>-0.8 0.1 1.6 -0.7 0.1 4.5</td>
<td>-1.3 -0.3 0.9 0.0 0.2 4.6</td>
</tr>
</tbody>
</table>

In contrast to the previous calculations (PE and PP), the static minimum energy results of cellulose are subject to a considerable uncertainty. Since several calculations for the diagonal elements are made, their standard deviation can be estimated to be in the range of 0.5 GPa. A similar conclusion can be drawn from those elements that should be zero due to the symmetry of the crystal. The origin of this behaviour is the use of the Ewald summation technique. Although relatively small deformations (± 0.2%, as for PE and PP) were used, the coulombic interactions with their 'infinite' range had a substantial influence in the subsequent minimizations. Application of deformations, that were 10 times smaller (max. 0.02%) did not improve the situation, but led to larger errors due to problems with the precision of the minimization.
4.4.5 Discussion

4.4.5.1 Comparison with Literature Values

There is a number of reports on the elastic constants of cellulose I in the literature, most of them dealing with Young's modulus in the chain direction. Nishino\textsuperscript{95a} Most experimental and theoretical $E_3$ values are between 78 and 180 GPa. Experimental X-ray studies from Nishino \textit{et al.}\textsuperscript{95b} and from Matsuo \textit{et al.}\textsuperscript{90a} yielded $E_3$ values of 138 and 120 - 135 GPa. There are theoretical calculations of parts of the matrix of the elastic constants from Gillis\textsuperscript{69a} and of the full matrix from Tashiro and Kobayashi\textsuperscript{88a} which are given in Table 4-44. Of these two, only Tashiro and Kobayashi's values seem to be reasonably close to the experimental findings and the theoretical $E_3$ estimations.

Comparing Young's moduli in the chain direction of this work (Table 4-45)

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$\eta$-Fluct. [GPa]</th>
<th>$\sigma$-$\eta$-Fluct. [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>151.4</td>
<td>150.2</td>
</tr>
<tr>
<td>325</td>
<td>155.2</td>
<td>150.4</td>
</tr>
<tr>
<td>400</td>
<td>133.1</td>
<td>126.1</td>
</tr>
</tbody>
</table>

with the literature values, it can be stated that they are more or less between the experimental and the theoretical results. It is difficult to compare the matrix from Tashiro \textit{et al.} with the present calculations, but considering the fact that there were no temperature effects taken into account, the agreement between the
Young’s moduli is quite good. Larger discrepancies occur for the $C_{12}$, $C_{13}$, and $C_{23}$ values, where the far reaching undirected Coulombic interactions might enhance the coupling between the orthogonal stress and strain states.

4.4.5.2 Conclusions

The elastic moduli of cellulose along the chain direction - determined by the strain and the stress-strain fluctuations - are in the range of 150 - 155 GPa. This is in reasonable agreement with both experimental and theoretical results.

It is, however, extremely important to treat the Coulombic interactions properly by using e.g. an Ewald summation technique, because the regular structure of the crystal and highly charged atoms deny the use of a cutoff.

These strong Coulombic interactions are also responsible for the excellent elastic properties of cellulose-Iβ. The elastic modulus in the chain direction is not as high as for PE, but in the directions perpendicular to the chains, the elastic moduli are several times higher, due to the intermolecular hydrogen bonds (which are modeled by large partial charges in the cvff forcefield). This explains why nature is using such huge quantities of this material in all kinds of structural elements.
4.5 Polyamide-6 - Monoclinic Crystals

4.5.1 Introduction

Excellent mechanical, dynamical and chemical properties like high tensile and impact strength, low coefficient of friction, good hardness and high resistance against organic solvents are the main features of polyamides that make them technologically so important. They are used as engineering materials in bearings, gears, cams etc., for tubes, jackets of electrical wires, casings and for the production of fibers and yarns.\textsuperscript{Billmeyer84,Franck88}

Polyamide (PA)-6 (\(\text{R}_1\text{-CO[-NH-(CH}_2\text{)_5-CO]}\text{n-NH-R}_2\)) is produced within minutes by fast anionic polymerization from waterfree \(\varepsilon\)-caprolactam. The resulting material is composed of spherulites of crystalline lamellae embedded in an amorphous matrix.\textsuperscript{Puffr91} The crystalline parts are not always perfectly ordered - mesomorphous\textsuperscript{Puffr67a} - for the degree of crystallinity not only depends on the processing history but also on the method of measurement and varies between 20\% and 60\%.\textsuperscript{Puffr91,Bhat89a} In order to understand the behaviour and the properties of Polyamide-6 and related materials, the semicrystalline morphology of these materials needs to be considered in detail, as performed in a recent investigation\textsuperscript{Hsia95a}. In this work, the elastic constants of both amorphous and crystalline domains were determined by fitting the behaviour of a finite-element representation of the morphology to experimental data.

In the present work, the inverse approach is made. Starting from a force field, the elastic properties of amorphous and crystalline PA-6 will be computed, which may serve as an input for a finite-element calculation. This chapter reports the fine-tuning of the \textit{pcff91} force field and the subsequent calculation of the elastic constants of the \(\alpha\)-crystal of PA-6.

4.5.2 Crystal Modifications and Cell Generation

4.5.2.1 Crystal Modifications

Polyamide-6 crystals can exist in two major forms: a monoclinic \(\alpha\)- and a monoclinic \(\gamma\)-form, although the existence of other structures has also been reported. The two forms usually coexist in the bulk material. The \(\alpha\)-phase can be converted to the \(\gamma\)-phase by iodine treatment, and the \(\gamma\)-phase can be converted to the \(\alpha\)-phase by phenol treatment and by stretching. The \(\alpha\)-phase has been found to be the most stable structure of PA-6 crystals.\textsuperscript{Lin92a} A schematic representation of the unit cell is given in Fig. 4.29 and the cell parameters are listed in Table 4-46.
4.5 Polyamide-6 - Monoclinic Crystals

Figure 4.29: Front and top view of: a) $\alpha$ - Form of monoclinic PA-6, b) $\gamma$ - Form of monoclinic PA-6 (hydrogen atoms are omitted for clarity)

Table 4-46: Experimental cell parameters of $\alpha$ - and $\gamma$ - PA-6 $^\text{Tadokoro90}$, average of the last $2 \cdot 10^5$ T$\sigma$N-MD steps at 300 K in the middle column (scaled force field)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$\alpha$ - PA-6</th>
<th>$\alpha$ - PA-6 (MD)</th>
<th>$\gamma$ - PA-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ [Å]</td>
<td>9.56</td>
<td>9.64</td>
<td>9.33</td>
</tr>
<tr>
<td>$b$ [Å]</td>
<td>8.01</td>
<td>8.03</td>
<td>9.56</td>
</tr>
<tr>
<td>$c$ [Å]</td>
<td>17.24</td>
<td>17.38</td>
<td>16.88</td>
</tr>
<tr>
<td>$\alpha$ [$^\circ$]</td>
<td>90</td>
<td>90.0</td>
<td>90</td>
</tr>
<tr>
<td>$\beta$ [$^\circ$]</td>
<td>90</td>
<td>90.0</td>
<td>90</td>
</tr>
<tr>
<td>$\gamma$ [$^\circ$]</td>
<td>67.5</td>
<td>69.0</td>
<td>121</td>
</tr>
</tbody>
</table>

4.5.2.2 Structure Generation and Forcefield Modification

At first, it was necessary to redefine the PA-6 repeat unit. The default repeat unit, provided with the 'Insight' package and the redefined unit are shown in Fig. 4.30. The grouping of the default repeat unit was adjusted to the cvff forcefield, while the changes inferred by the scaled_pcff forcefield made it nec-
4.5.2 Crystal Modifications and Cell Generation

**Figure 4.30:** Polyamide-6: a) default repeat unit, b) modified repeat unit with neutral groups.

A macrocell of 3x3x2 units cells of α-monoclinic PA-6, containing 36 chains of 4 repeat units (2736 atoms in total) was built using the 'Crystal Cell' tools of the 'Insight' modeling package. As for all polymer crystals, bonds across boundaries were applied in order to mimic infinite chains. While simulating the cell, it was realized that the density of the crystal was about 2-3% too low. In order to correct for this, two of the nonbonded parameters of the pcff forcefield were reduced by 3%. The table below shows the difference between

<table>
<thead>
<tr>
<th>pcff</th>
<th>scaled_pcff</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sigma^c) [Å]</td>
<td>4.0100</td>
</tr>
<tr>
<td>(\sigma^h) [Å]</td>
<td>2.9950</td>
</tr>
<tr>
<td>(\sigma^c) [Å]</td>
<td>3.8897</td>
</tr>
<tr>
<td>(\sigma^h) [Å]</td>
<td>2.9052</td>
</tr>
</tbody>
</table>

The scaled_pcff forcefield was therefore used for all subsequent simulations of Polyamides (PA-6 and PA-12).

Although there are considerable charges in the PA-6 repeat unit, the Coulombic interactions were computed using a cutoff, because the Ewald summation would have slowed down the whole process too much. (A short test run required 47 seconds/step on an Indigo II workstation, i.e. approx. \(\frac{1}{2}\) day/ps.)
results of the simulations of the crystal should be interpreted with this limitation in mind. But since all charged groups are neutral and small - most of them consist of CH₂-groups, and the largest group, HN-CH₂, is less than 3 Å in diameter - the effect should be much smaller than for cellulose. The amorphous cell computations are even less sensitive to the problem of large partial charges because they lack long-range order.

4.5.3 Simulation Procedure

After the setting up of the crystal structure, the cell was minimized down to an energy of -2.902 kcal/(mol-atom), followed by a TaN-MD simulation of 3·10⁵ steps (150 ps), conducted at 300 K. The long-range Lennard-Jones interactions were taken into account by a correction pressure of 1630 bar. As usual, a Parrinello-Rahman pressure control and a Nosé-Hoover thermostat algorithm were used to keep stress and temperature approximately constant (the effective pressure was 1514 bar and the effective temperature 293 K).

After some initial fluctuations, the simulation cell was stable in dynamics, as can be verified from Fig. 4.31. In the last 100 ps, the cell parameters and the components of the actual stress were stored every fs, totalling 10⁶ samples. From these samples, the elastic constants were calculated using Eqs. (3-29) and (3-36). The results of this procedure are reported in the next chapter.

![Figure 4.31: Cell parameters of crystalline PA-6 (TaN-MD at 300 K)](image-url)
4.5.4 Results

4.5.4.1 Elastic Constants from Fluctuation Approaches

Table 4-49 lists the values of the elastic constants averaged over the last 100 ps of a 150 ps Tor-N-MD simulation at 300 K. Non-zero components are bold faced.

Table 4-49: Elastic constants of PA-6 averaged over the last 100 ps of a 150 ps Tor-N-MD simulation at 300 K. Non-zero components are bold faced.

<table>
<thead>
<tr>
<th>( \frac{\kappa^T}{\langle V \rangle} \langle \eta_{ik} \eta_{lm} \rangle^{-1} ) [GPa]</th>
<th>( \langle \eta_{ik} \sigma_{nj} \rangle \langle \eta_{nj} \eta_{lm} \rangle^{-1} ) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.67 2.75 0.36 0.06 -0.06 -1.08</td>
<td>21.15 2.18 0.29 0.04 -0.05 -0.85</td>
</tr>
<tr>
<td>2.75 8.13 9.79 0.00 -0.04 0.33</td>
<td>4.30 12.73 15.34 0.00 -0.07 0.51</td>
</tr>
<tr>
<td>0.36 9.79 191.0 -0.07 0.61 0.84</td>
<td>0.36 9.58 186.8 -0.07 0.60 0.82</td>
</tr>
<tr>
<td>0.06 0.00 -0.07 1.21 -0.32 -0.01</td>
<td>0.06 0.00 -0.08 1.37 -0.36 -0.01</td>
</tr>
<tr>
<td>-0.06 -0.04 0.61 -0.32 3.31 0.09</td>
<td>-0.04 -0.03 0.45 -0.24 2.43 0.07</td>
</tr>
<tr>
<td>-1.08 0.33 0.84 -0.01 0.09 1.31</td>
<td>-0.92 0.28 0.72 -0.01 0.08 1.12</td>
</tr>
</tbody>
</table>

100 ps of the MD-trajectory and Fig. 4.32 shows the convergence of the diagonal elements of the elasticity matrix with averaging time.

![Figure 4.32: Convergence behaviour of the diagonal elements (and \( C_{12}, C_{13}, \) and \( C_{23} \)) of the elasticity matrix form the strain (dotted lines) and the stress-strain fluctuations (solid lines)](image)

4.5.5 Discussion

4.5.5.1 Relationship Between Structure and Elastic Constants

The calculation of the Eigenvalues of the strain fluctuation matrix of Table 4-49, as shown below, gives three orthogonal directions with largely differ-
4.5 Polyamide-6 - Monoclinic Crystals

Table 4-50: Eigenvectors and Eigenvectors of the elasticity matrix (strain fluctuations)

<table>
<thead>
<tr>
<th>Eigenvalue [GPa]</th>
<th>Components of the Eigenvector (Voigt notation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>191.52</td>
<td>0.003 0.053 0.999 0.000 0.003 0.004</td>
</tr>
<tr>
<td>27.10</td>
<td>0.990 0.137 -0.010 0.002 -0.003 -0.040</td>
</tr>
<tr>
<td>7.25</td>
<td>-0.135 0.987 -0.053 0.001 -0.016 0.071</td>
</tr>
<tr>
<td>3.36</td>
<td>0.003 0.013 -0.004 -0.148 0.988 0.041</td>
</tr>
<tr>
<td>1.23</td>
<td>0.049 -0.065 -0.001 0.101 -0.027 0.991</td>
</tr>
<tr>
<td>1.17</td>
<td>-0.007 0.008 0.000 0.984 0.151 -0.095</td>
</tr>
</tbody>
</table>

ent elastic constants. The highest value is of course along the $x_3$-(c)-direction, parallel to the chains. Still a relatively high value of 27 GPa can be found along the $x_1$-(a)-direction. Comparison with Fig. 4.29 shows that this is more or less parallel to the hydrogen bridges between carbonyl and amine groups. The value of 7.25 GPa in the $x_2$-(b)-direction is typical of Lennard-Jones interactions. Almost identical results can be obtained using the stress-strain fluctuations.

4.5.5.2 Comparison With Literature Values

Again, the available experimental and theoretical data are so widely scattered that hardly any precise conclusions are possible. Experimental results range from 165 to 175 GPa, whereas computational results span a range from 190 to 312 GPa, as the next table summarizes.

Table 4-51: Experimental and theoretical estimations of the ultimate Young’s modulus in the chain direction of PA-6

<table>
<thead>
<tr>
<th>Reference</th>
<th>$E_3$ [GPa]</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manley et al.</td>
<td>244 - 263</td>
<td>energy balance</td>
</tr>
<tr>
<td>Tashiro et al.</td>
<td>312</td>
<td>general matrix</td>
</tr>
<tr>
<td>Sakurada et al.</td>
<td>165</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Kaji et al.</td>
<td>183</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>Lewis et al.</td>
<td>164.8</td>
<td>macroscopic &amp; Takayangi model</td>
</tr>
<tr>
<td>Matsuo et al.</td>
<td>173 - 175</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>

The results of this work (179 GPa from the strain-, and 174 GPa from the stress-strain-fluctuations) compare very well with the most recent experimental data from Matsuo et al. They are, however, lower than Young’s modulus
obtained from theoretical calculations. No comparison is made here for the whole matrix of the elastic constants, since the only one published in the literature from Tashiro et al. has quite an unrealistic $C_{33}$-value of more than 300 GPa.

Concerning the transverse moduli $E_1$ and $E_2$, experimental results of 11.4 - 12 GPa and 7.7 - 9 GPa can be found\textsuperscript{Matsuo94a}, which for the $E_1$ modulus are considerably lower than the values of this work (19.5 - 23.6 GPa and 7.2 - 11.3 GPa, respectively). The difference of almost a factor 2 can be rationalized by the sensitivity of this value to the partial charges used to model the hydrogen bonds and by the difficulties to properly sum up these coulombic interactions.

4.5.5.3 Conclusions

A reduction of the atom radii of carbon and hydrogen atoms in the \textit{pcff} forcefield was made by 3\% to match the experimental and calculated density of $\alpha$-PA-6. The crystal cell was large enough to remain stable in dynamics at 300 K, so the elastic constants could be calculated from the strain and the stress-strain fluctuations. Young's modulus in the chain direction was found to be 174 and 179 GPa, which compares well with recent experimental data, but which is lower than most other theoretical calculations. The transverse modulus along the direction of the hydrogen bonds is considerably higher than experimental data. This fact can be explained by the difficulties arising from the modeling of hydrogen bonds with partial charges. The favourable Ewald summation could not be performed on these large cells without slowing down the calculations too much. The transverse modulus perpendicular to the hydrogen bonds is in complete agreement with experimental numbers.
4.6 Polyamide-6 - Amorphous Cells

4.6.1 Introduction

As already pointed out in chapter 4.5.1, polyamide-6 is a semicrystalline material composed of mesomorphic crystalline (30 - 40 %) Kawasaki64a, Inoue76a and amorphous parts. The very good mechanical properties do not depend on the morphology only, but also on the amount of water absorbed from the moisture of the air. The equilibrium content of water in the polymer depends on the activity of water in the air (relative humidity) Puffr67a, Asada63b, Inoue76a, the concentration of NH-CO-groups Son990a, and the degree of crystallinity. The crystalline phase exhibits insignificant solubility for water molecules, so that the amorphous phase is responsible for the observed effects Puffr67a, Song90a, Starkweather59a, Kawasaki64a, Prevorsek71b. These comprise the mechanical relaxations, called γ, β and α, which take place in PA-6 at approx. -120°C, -40°C and +50 to +90°C Prevorsek71b, Kettle77a, Khanna95a, respectively. The γ relaxation is attributed to the motion of methyl groups and is hardly affected by the presence of water, while the β relaxation, which is caused by water molecules bonded to amide groups via hydrogen bonds, naturally is highly sensitive to the water content and disappears in thoroughly dried nylon. The α relaxation - the glass transition - is assigned to the motion of large chain segments in the range of 15 repeat units. Prevorsek71b, Boyd59a

There exists a variety of experimental curves for the dependence of the glass transition temperature \( T_g \) on the water content: In one measurement, \( T_g \) decreases with increasing water content in several stages: A fast drop of \( T_g \) is found between 0 and 2 wt% of water, while between 2 and 4 wt% the dependence is less pronounced, followed again by a further reduction at water concentrations higher than 4 wt%. Kettle77a In other experiments, however, \( T_g \) declines fast with increasing water content up to 3 wt% and then reduces more slowly beyond this level. Prevorsek71b, Khanna95a, Reimschuessel78a

From these and other effects like anisotropic swelling of oriented samples Kaimin73a, sorption isotherms Hernandez94a and changes in Raman spectra Stuart94a, a 3-stage model has been proposed Puffr67a (Figure 4.33): At first, water forms a double hydrogen bond between two adjacent carbonyl groups (Site 1 in Figure 4.33). In this step a large amount of energy is released and the molecules are referred to as firmly bound. The second stage is the extension of the already existing hydrogen bonds between carbonyl and amide groups by bridging water molecules, which are classified as loosely bound water (Site 2). These first 2-3% of absorbed water strongly affect the glass transition due to the change in the interchain distance and the creation of voids in the
Figure 4.33: Model of adsorption of water in nylon. Site 1: firmly bound water, 2: loosely bound water, 3: sites for capillary condensed water structure. In the third stage, further water is attached to the already absorbed water molecules and forms clusters in capillary sites (Site 3).

The effect of relatively large water concentrations (10 wt%, corresponding to 100% relative humidity) on the storage modulus of PA-6 is depicted in Figure 4.34. The glass transition temperature is reduced by the presence of water from approx. 80°C close to 0°C. This is a consequence of the increased mobility of the chain segments by the widening of the hydrogen bonds by the bridging water molecules. At temperatures below the transition point, the
plasticizing effect of water is reversed into an antiplasticizing one, which is expressed by the higher modulus of wet PA-6.

In the following work it was investigated whether or not the above described influence of water on the elastic constants could be reproduced by using fluctuation approaches. To do this, several atomistically detailed microstructures of amorphous PA-6 with and without water molecules were generated and minimized. ToN-MD simulations of 1000 ps at 150, 300, and 450 K were performed to gather information about the temperature dependence of the mechanical behavior.

4.6.2 Cell Generation

4.6.2.1 Introduction

In contrast to polymer crystals, the conformation of a chain in an amorphous material is not specified and can vary to a large extent. The long relaxation times of dense polymeric systems forbid the generation of an amorphous cell from an ordered system by melting and subsequent equilibration. It is therefore necessary to build a representative chain conformation from the very beginning of the construction process.

This was done by using the 'Amorphous Cell' module in the 'Insight' modelling package. The method used therein can be briefly described as the stepwise RIS method of Theodorou and Suter, which is loosely based on the the scanning method of Meirovitch. After placing the first two backbone bonds in a random orientation in the center of an empty cell with periodic continuation conditions, the chain is built up in a bond-by-bond fashion. For each step, a number of random configurations is built with a couple of so-called lookahead bonds in order to estimate the partition function of this short segment and to avoid deadlocks. In the building process, either the RIS states and their corresponding weights are used or the minima of the backbone torsion potential define the possible states. If adjacent minima are separated by high barriers (e.g. double bonds), a bond is allowed only the state it was in in the initially - in vacuo - constructed molecule. To increase the flexibility of the chain, a number of substates around each state and a corresponding substate width can be specified. From these lookahead conformations, a dihedral angle $\phi_j$ is selected with the probability.
The term $\Delta U_j$ stands for the change in the nonbond energy if the entire lookahead were added.

The density of the final structure is determined by the size of the periodic box. For linear polymers without cyclic groups, it is possible to take the experimental density. If polymers with ring structures are used, it is necessary to specify a target density that is 20 to 30% below the experimental density. Otherwise, almost all structures will be rejected during the building process because of spearing or catenation.

### 4.6.2.2 Dry and Wet Samples

A single chain of 50 modified (chapter 4.5.2.2) repeat units with 952 atoms - including the two terminating hydrogen atoms - was generated by using the following parameters for the construction:

- Temperature: 300 K
- Density: 1.10 g/cm³
- Lookahead bonds: 5
- Number of substates: 1
- Substate width: 10
- Max. lookahead configurations: 50

If a water-saturated structure was to be generated, there were at first 35 water molecules (corresponding to 10 wt% in the amorphous phase and about 6 wt% in the semicrystalline material) being placed in the empty simulation cell before the chain was grown around them.

There were 3 'dry' and 'wet' structures each built.

### 4.6.3 Simulation Procedure

#### 4.6.3.1 Equilibration

To remove the largest overlaps, all structures were first minimized by 500 steps of steepest descent routines. The cutoff was set to 8.5 Å with a spline width of 1 Å.

After minimization, 250 ps of TpN-MD - i.e. the cell size was allowed to vary, but the cell shape was kept cubic - were conducted at 300 K. Since a Berendsen thermostat was used, it was possible to make steps of 1 fs. The pressure
was set to 1630 bar in order to compensate for the neglect of long-range Lennard-Jones interactions.

This was done because cells that were allowed to fluctuate in shape immediately after minimization were sometimes heavily distorted in the initial period of an MD run. The TpN-simulation allowed for the relaxation of the largest internal strains and for the setting of the density.

### 4.6.3.2 Sampling

The sampling runs of both wet and dry amorphous PA-6 were conducted according to the following scheme:

![Diagram](image)

i.e. after sampling the structure for 1 ns (2·10⁶ steps) at approx. 300 K, the temperature was raised to 450 or lowered to 150 K and another 2·10⁶ steps were performed at the new temperature. Again, an MD algorithm sampling the ToN-ensemble with a Nosé-Hoover thermostat and a Parrinello-Rahman manostat was used. A correction pressure of 1630 bar was applied, irrespective of the exact density.

### 4.6.4 Results

#### 4.6.4.1 Densities and Thermal Expansion

A good overview over the fluctuations in density and the stability of the simulations is given in Fig. 4.35. At all three temperatures, the density shows no substantial drifts. Furthermore, the increase in the fluctuation width with raising temperature can be well observed. Going from 300 K to higher or lower temperature, the equilibration period of the density seems to be rather short and in the range of 100 ps. If all six (3 'dry' and 3 'wet' structures) were plotted together, the following picture (Fig. 4.36) results: The antiplasticizing effect of water at low temperatures is manifest in an increase of the density, whereas at room temperature, water has no significant influence. At 450 K, the lower density of the 'wet' structures indicates a weakening of the nonbonded interactions by the presence of water molecules - a plastification takes place. Table 4-52 lists the average
Figure 4.35: Density of structure 1 of wet PA-6 as a function of time and temperature

Figure 4.36: Densities of all six structures during the second 500 ps of dynamics; black lines refer to 'wet' structures, whereas gray lines signify 'dry' structures.

Table 4-52: Average densities of dry and wet amorphous PA-6 cells

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>$\langle \rho_{\text{dry}} \rangle$ [g/cm$^3$]</th>
<th>$\langle \rho_{\text{wet}} \rangle$ [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>$1.1297 \pm 0.0052$</td>
<td>$1.1455 \pm 0.0007$</td>
</tr>
<tr>
<td>300</td>
<td>$1.0950 \pm 0.0051$</td>
<td>$1.0997 \pm 0.0027$</td>
</tr>
<tr>
<td>450</td>
<td>$1.0416 \pm 0.0040$</td>
<td>$1.0201 \pm 0.0030$</td>
</tr>
</tbody>
</table>

densities of dry and wet PA-6 as a function of the temperature. From these val-
ues, the thermal expansion coefficient $\alpha$ (for isotropic materials, the tensor of the thermal expansivity, $\eta_{ik} = \alpha_{ik} \Delta T$, reduces to $\alpha_{ik} = \alpha \delta_{ik}$, where $\delta_{ik}$ denotes the familiar Kronecker symbol) can be computed as

$$
\alpha = \frac{1}{2} \left[ \frac{V}{V_0} \right]^2 - 1 = \frac{1}{2} \left[ \frac{\rho_0}{\rho} \right]^2 - 1. \quad (4-30)
$$

The resulting thermal expansion coefficients are summarized below:

<table>
<thead>
<tr>
<th></th>
<th>Temperature</th>
<th>Thermal expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>150 $\rightarrow$ 300 K</td>
<td>7.0 $\times 10^{-5}$ K$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>300 $\rightarrow$ 450 K</td>
<td>11.3 $\times 10^{-5}$ K$^{-1}$</td>
</tr>
<tr>
<td>Wet</td>
<td>150 $\rightarrow$ 300 K</td>
<td>9.3 $\times 10^{-5}$ K$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>300 $\rightarrow$ 450 K</td>
<td>17.1 $\times 10^{-5}$ K$^{-1}$</td>
</tr>
</tbody>
</table>

The values of Table 4-53 agree well with experimental data$^{89}$ of $\alpha = 7-10.10^{-5}$ K$^{-1}$ at 20° and 10-14.10^{-5}$ K$^{-1}$ at 100°C. The experimental density at 20°C is 1.10 g/cm$^3$ (compare Tables 4-48 and 4-52).

### 4.6.4.2 Diffusion of Water

From coordinate files, which were saved every 10 ps, the mean square displacement $r^2$ of the water molecules of the wet structures could be calculated. The displacement of the center of mass of the water molecules was replaced by the displacement of the oxygen atoms without noticeable loss of precision. Assuming an Einstein diffusion (i.e. random walk mechanism), the diffusion constant $D$ is defined by

$$
\langle r^2 \rangle = 6Dt. \quad (4-31)
$$

Taking the logarithm on both sides yields

$$
\log \langle r^2 \rangle = \log (6Dt) = \log (6D) + \log (t) \quad (4-32)
$$

In a log($\langle r^2 \rangle$) vs. log($t$) plot, there should be a straight line with a slope of one and an intercept of $\log (6D)$. If the slope is different from one, there is no random walk, but another mechanism (e.g. constraint motion along specific paths, hopping between two neighbouring sites). In Fig. 4.37, the average mean square
displacement of the water molecules in PA-6 has been plotted as a function of time and temperature. The three straight lines with slopes of 1, $\frac{1}{2}$, and 0 are only guidelines for the eyes and do not represent any regression analysis. Only at 450 K, a random walk mechanism can be observed, whereas an anomalous diffusion is manifest at 300 K. At 150 K, the mobility of the water atoms is so low that no diffusion at all can be observed within the simulation time.

It is therefore only meaningful to compute the diffusion constant at 450 K, where the intercept of the straight line at 1000 ps yields a value of $D \approx 1.8 \times 10^{-5}$ cm$^2$/s. There is no experimental data at this temperature available, but an extrapolation from 20°, 60°, and 100°C to 177°C results in $D \approx 4.6 \times 10^{-5}$ cm$^2$/s. Since experimental diffusion constants are known to be subject to substantial uncertainties and the extrapolation spans more than 70 K, the calculated value is still plausible.

4.6.4.3 Clustering of Water Molecules

An attempt was made to quantify the distribution of the water molecules in the polyamide microstructures. In a first step, the microstructures were tessellated into Voronoi polyhedra, using a code of Peter Mott.

According to Figure 4.38, two water molecules were considered to belong to the same cluster, if any two of their atoms shared a common surface. In a second step, the number and size of the different water clusters in a polyamide structure were determined. Doing this for each coordinate frame, a ‘dynamics’ of the formation and disintegration of the water clusters could be established. A
short example of this process is given in Table 4-54. At the low temperature of 150 K, the cluster dynamics is rather slow, which allows to track the motion of individual water molecules quite well. At higher temperatures, the temporal resolution of 10 ps is sometimes too long to follow all changes. More detailed analyses at 300 and 450 K can be found in Appendix G-1.

From these tables and from more detailed examinations, the following conclusions can be drawn: It is not possible to observe a significant change in the average size of the clusters with time or with temperature. There seems to be nothing like Ostwald ripening, i.e. a growth of the large clusters at the expense of the small ones. Instead of this, there is a dynamic process of clustering and breaking apart of the water molecules. Some water molecules are quite fixed in the local structure - i.e. they remain isolated for the whole observation period or stay together for quite a while - whereas more mobile water molecules can form large clusters from time to time. These large clusters, however, only have a short lifetime (<10 ps) before they separate into two or more smaller units. This is an indication that the bridges connecting the different parts of the larger clusters are...
quite thin, whereas cores of more closely connected water molecules must also exist. (see Fig. 4.39).

Figure 4.39: Model of the cluster dynamics of water molecules in PA-6

The distribution of the different cluster sizes and the probability of finding a water molecule in a cluster of a given size are plotted in Fig. 4.40. Although the statistics is not excellent, it can be clearly seen that the increased mobility of the water molecules at elevated temperatures leads to a more or less uniform distribution of the cluster sizes, i.e. there is no preferred cluster size anymore. If the temperature is only 150 K, there are just a few clusters, which hardly change their size. The initial water distribution (from the previous run at 300 K) remains almost frozen for the rest of the simulation.
The exact orientation of the water molecules within the clusters was not studied in detail, but the following picture (Fig. 4.41) might provide an idea:

Cluster statistics:

<table>
<thead>
<tr>
<th>Cluster</th>
<th>Molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 4.41: Distribution of water in PA-6 (300 K, after 700 ps of ToN-MD)

There is no 'ice-like' structure, but there are complexes being formed of partly oriented water molecules, which was also observed in a recent study of Terzis et al.\textsuperscript{Terzis97a}.

4.6.4.4 Elastic Constants

There were in total 18 trajectories of 1000 ps from which the elastic constants were calculated: 3 microstructures of 'dry' and 'wet' PA-6 at 150, 300, and 450 K. From each trajectory, the first 500 ps were discharged for relaxation processes and only the last 500 ps contributed to the fluctuations from which the elastic constants were calculated. Since the cell parameters $a$, $b$, $c$, $\alpha$, $\beta$, and $\gamma$ and the stress tensor $\sigma$ were recorded with an interval of 10 fs, $5 \times 10^4$ frames were used for the computation of the elastic constants each. Both the strain fluctuation approach from Parrinello and Rahman, and the Gusev-Zehnder-Suter stress-strain fluctuation approach were applied. Appendix G-2 lists the results of the stress-strain fluctuation approach for all trajectories. From these trajectories, the two Lamé constants $\lambda$ and $\mu$ were fitted to the matrices of the elastic constants such, that the difference to a theoretical matrix of an isotropic material,
was minimal.

Averaged over the three microstructures, these Lamé constants are summarized in Table 4-55. As could be recognized immediately from the data and Table 4-55: Lamé constants of amorphous PA-6 as a function of the temperature and the water content

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>'Dry' [GPa]</th>
<th>'Wet' [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>$\lambda = 5.60 \pm 0.41$</td>
<td>$\lambda = 6.40 \pm 0.30$</td>
</tr>
<tr>
<td></td>
<td>$\mu = 2.07 \pm 0.21$</td>
<td>$\mu = 2.22 \pm 0.19$</td>
</tr>
<tr>
<td>300</td>
<td>$\lambda = 4.26 \pm 0.19$</td>
<td>$\lambda = 4.63 \pm 0.29$</td>
</tr>
<tr>
<td></td>
<td>$\mu = 1.05 \pm 0.15$</td>
<td>$\mu = 0.81 \pm 0.11$</td>
</tr>
<tr>
<td>450</td>
<td>$\lambda = 2.21 \pm 0.10$</td>
<td>$\lambda = 0.94 \pm 0.10$</td>
</tr>
<tr>
<td></td>
<td>$\mu = 0.25 \pm 0.04$</td>
<td>$\mu = 0.08 \pm 0.03$</td>
</tr>
</tbody>
</table>

also from Fig. 4.42, there is an stiffening effect of water at low temperatures,

Figure 4.42: The temperature dependence of the Lamé constants of dry and wet PA-6 (average values and standard deviations)
whereas at high temperatures, water acts as a plasticizer. At room temperature, the two effects almost balance, and the influence of water is only small. A comparison with experimental data will be given in the next chapter, where the results obtained from the simulations will be discussed.

4.6.5 Discussion

4.6.5.1 Comparison with Literature Values

For the density, the thermal expansion coefficient, and the water diffusion, experimental values from the 'Polymer Handbook'\textsuperscript{Brandrup89} have already been given. The computations all seem to be in reasonable agreement with experimental findings. This is a good validation of the model being used, although the simulation time at 300, and even more at 150 K, is too short to see a regular diffusion of the water molecules. The anomalous diffusion at 300 K is a well-known phenomenon, which occurs also in other systems (rare gases in BPA-PC), as the next plot (Fig. 4.43) shows: At relatively short times, the MD simulation is not able to propagate the diffusants far enough in order to establish a normal diffusion behaviour. Since water is considerably larger than helium, the curves in the above plot would be shifted to the right, so that no normal diffusion can be observed within the simulation period. The clustering behaviour of water in PA-6 was examined by Frank \textit{et al.}\textsuperscript{Frank96a} They found that clustering of water molecules starts at 6 wt\% and that at 10 wt\% on the average 2 - 3 water molecules are present in a cluster. In our simulations, the average number of molecules in a cluster is more than 5. The difference between the two numbers might originate from a different definition of a cluster. Hernandez and Gavara\textsuperscript{Hernandez94a} estimated that nearly 90 \% of the water molecules in PA-6 are moving freely. Ana-
lyzing the individual trajectories of water molecules (Fig. 4.44), it was not possible to make this distinction between 'adsorbed' or 'free' water. The 3-stage adsorption model presented in the introduction could therefore not be confirmed in this way.

One of the most important problems is to decide whether the simulation was long enough for the relevant mechanical relaxations to take place. Strictly speaking, it was not, since a complete relaxation of the chain would involve a self-diffusion in the order of the radius of gyration and the water molecules were not able to move sufficiently.

On the other hand, the finite size of the simulation box reduces the relaxation times considerably. (This argument is explained in more detail in chapter 4.8.2). An indication of this mechanism being active is the fast adaptation of the density after the sudden change in temperature after 1 ns. The density relaxed within 100 ps and remained fairly constant afterwards (Fig. 4.35). This in turn allows to determine the thermal expansion coefficient quite well.

The elastic constants - the main concern of this work - compare with experimental data\textsuperscript{Prevorsek71d} as follows:

As already mentioned, the general trend is reproduced, i.e. a stiffening effect of water below the glass transition and a plasticizing effect above the glass transition can be observed.

At 150 and also at 300 K, the computed values are consistently higher than the measured ones. This discrepancy (which is much smaller, if other sources of experimental values like Table 4-56 are considered) can be rationalized by the insufficient mobility of the water molecules, as became manifest in the diffusion
behaviour. They are more or less trapped in the locations they occupied at the end of the structure generation and are not able to diffuse to ‘better’ places. Therefore, the influence of water on the elastic constants is not as marked as in the experiment. Parallel to that, the polymer chain mobility is not sufficient to sample the whole phase space within the simulation time. The width of the fluctuations is therefore smaller and the elastic constants higher than in the case of a fully relaxed polymer. Another reason for the difference is the fact that in a semicrystalline material with 30 - 40% crystallinity and 10 wt% of water, the effective water content in the amorphous part is approx. 15 wt%. In our simulation, however, there were only 10 wt% water in the amorphous part.

At the high temperature of 450 K, the mobility of both the water molecules and the polymer chain is sufficient to explore most of the available phase space. The elastic constants are therefore quite close to the experimental curves. The convergence of the two curves at temperatures above 120° C is due to the fact that, above the boiling point, the water molecules diffuse out of the polyamide. It can thus be assumed that the calculated elastic constants reflect the plasticizing effect of water better.

Finally, Table 4-56 compares the values of the Young's and shear moduli of PA-6 found in the 'Polymer Handbook'\textsuperscript{89} with computed values. The experimental results at 100° C are compared with computed values at 450 K, because - as mentioned in the introduction - there is an $\alpha$-relaxation at 50 to 90° C, which would make a straight interpolation of the computed data question-
4.6.5 Discussion

Table 4-56: Young’s and shear moduli of semicrystalline experimental\textsuperscript{Brandrup89} and amorphous computed PA-6

<table>
<thead>
<tr>
<th>Modulus</th>
<th>$T$, state</th>
<th>exp. [MPa]</th>
<th>calc. [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$23^\circ$ C, dry</td>
<td>3000</td>
<td>2940 ± 400</td>
</tr>
<tr>
<td></td>
<td>$23^\circ$ C, moist</td>
<td>1500</td>
<td>2310 ± 310</td>
</tr>
<tr>
<td></td>
<td>$100^\circ$ C, dry</td>
<td>500</td>
<td>720 ± 110</td>
</tr>
<tr>
<td>$G$</td>
<td>$23^\circ$ C, dry</td>
<td>1100</td>
<td>1050 ± 150</td>
</tr>
<tr>
<td></td>
<td>$100^\circ$ C, dry</td>
<td>200</td>
<td>250 ± 40</td>
</tr>
</tbody>
</table>

A further problem, which makes a comparison difficult, is that the experimental morphology is semicrystalline, whereas the simulation was performed on a purely amorphous microstructure. Besides these limitations, the simulated data seem to be in better agreement with experiment than Figure 4.45 suggests. The missing details about the experimental setup prevent a straightforward decision about their reliability.

4.6.5.2 Conclusions/Summary

At low temperatures (150 K) there is virtually no diffusion; a limited amount of clustering/unclustering happens. At room temperature, only anomalous diffusion of water could be observed. The clusters rearrange quite quickly (approx. every 30 ps). The classical 3-stage model could not be reproduced. Instead of this, a dynamical model of clusters with mobile peripheral atoms and relatively lasting cores was presented. At 450 K, the diffusion obeys a normal, random walk law and the cluster dynamics is very fast. The calculated diffusion coefficient does not contradict experimental results.

At low temperatures, the antiplasticizing effect of water expresses itself in an increase of the density due to some attractive interactions between water molecules and the polymer matrix (hydrogen bonds). At room temperature, the thermal motion of water more and more balances these attractive forces. Hardly any effect on the density could therefore be seen. At higher temperatures, the mobilization of the water molecules reduces the density of the polyamide matrix.

The dependence of the elastic constants on the temperature and the water content could be reproduced qualitatively, which is somewhat astonishing, since the limited size and the short trajectory prevent the water from taking its equilibrium positions at low and medium temperatures. A large part of the quantitative discrepancy between simulated and experimental elastic modulus might be attributed to this fact.
4.7 Polyamide-12 - Amorphous Cells

4.7.1 Introduction

The physical properties of polyamides, especially the elastic constants, depend on the amount of absorbed water, as pointed out in the previous chapter. In many applications, it would be desirable to reduce this dependency since the relative humidity of the air and therefore the water content and finally the properties of the polymer are subject to climatic changes. A reduction of the concentration of the functional, water absorbing carbonyl and amide groups automatically reduces the number of possible absorption sites and limits thus the equilibrium water content. On the other hand, the hydrogen bridges between carbonyl and amide groups are essential for the outstanding mechanical properties of polyamides. With their concentration reducing, the material approaches the behavior of polyolefines. Polyamide-12 (PA-12) is a compromise between reduced water absorption and enhanced polyolefinic character.

The results of MD runs at various temperatures with ‘dry’ and ‘wet’ microstructures are reported and the relation between the concentration of carbonyl and amide groups and the sensitivity of - mainly elastic - properties towards the water content is discussed.

4.7.2 Cell Generation

4.7.2.1 Dry and Wet Samples

A repeat unit of PA-12 was generated according to Figure 4.46. Analogous to PA-6, there were charged groups in the original setup. Simulations with

![Figure 4.46: Repeat unit of PA-12 with (a) and without (b) charged groups](image)
4.7.2 Cell Generation

charged groups according to Fig. 4.46 a) and with neutral groups were carried out. Except where explicitly noted, only the results obtained from neutral charge groups will be presented.

The above repeat units were subject to a short run of 1000 ThN-MD steps to modify the torsion angles a bit. This modification away from an all-trans conformation eases the task of the 'Amorphous Cell' construction run.a

The degree of polymerization $n_{ru}$ as a function of the cell size $l$ is given by

$$n_{ru} = \frac{\rho [g/cm^3] \cdot l [\text{Å}]^3 \cdot 10^{-30} \cdot N_A}{m_w [g/mol]}$$

which can be shortened to

$$n_{ru} = (l [\text{Å}])^3 \cdot 0.00308247,$$

assuming an experimental density $\rho$ of 1.01 g/cm$^3$ (for amorphous mouldingsBrandrup89) and setting the mass of the repeat unit $W = 197.32$ g/mol. Together with the number of atoms per repeat unit (37 atoms), it can be estimated that 28 repeat units with 980 atoms yield a cell of approx. 21 Å size.

A single chain of the above size was polymerized with random angles between the repeat units. Again, a short ThN-MD run was started in order to further randomize the torsional degrees of freedom. Afterwards, an 'Amorphous Cell' construction run was started using the following parameters:

- Temperature: 300 K
- Density: 1.01 g/cm$^3$
- Number of Substates: 1
- Substate Width 5.0
- Lookahead 5
- Number of Lookahead Configurations: 50
- Bonds per Step: 5

If 'wet' cells were generated, 12 water molecules were placed in the simulation cell before the polyamide chain was grown around them. This number was estimated from water concentrations of 16 Pathmanathan95a and 25 mol%Varlet90a at saturation and a degree of crystallinity of about 30 %Varlet90a given in the literature. From these informations, a concentration of 40 mol%, corresponding to 3.7 wt% water in the amorphous phase was chosen, balancing between a statistically sufficient number of water molecules and a realistic water content that allows comparison with experimental findings. The nylon cell contains 28 poly-

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a. Andrew Tiller, MSI, private communication
mer repeat units to which \(0.428 = 11.2\) water molecules - which were rounded up to 12 - were added.

Of the 5 configurations that were each built, the 3 with the lowest energy after the initial minimization were chosen.

### 4.7.3 Simulation Procedure

To remove the largest overlaps, all structures were first minimized by 5000 steps of steepest descent and conjugate gradient routines. The cutoff was set to 8.5 Å with a spline width of 0.5 Å.

After minimization, 50 ps of TpN-MD were conducted at 300 K with a Nosé-Hoover thermostat and a stepsize of 0.5 fs. The pressure was set to 1110 bar to compensate for the neglect of long-range Lennard-Jones interactions.

The sampling runs of PA-12 were conducted according to the same scheme as for amorphous PA-6, i.e. after sampling the structure for 1 ns (2 \(10^6\) steps) at approx. 300 K, the temperature was raised to 450 or lowered to 150 K and another 2 \(10^6\) steps were performed at the new temperature. An MD algorithm sampling the \(T\sigma N\)-ensemble with a Nosé-Hoover thermostat and a Parrinello-Rahman manostat was used. A constant correction pressure of 1110 bar was applied again. The cell parameters and the stresses were saved to table files every 10 fs and the coordinates and velocities of all atoms were stored every 10 ps for further analysis.

### 4.7.4 Results

#### 4.7.4.1 Densities and Thermal Expansion

The mechanical relaxation at the three different temperatures (150, 300, and 450 K) of the 'wet' structure no. 2 is given as an overview in Figure 4.47.

![Figure 4.47: Density of structure 2 of wet PA-12 as a function of time and temperature](image-url)
After an initial densification period of a few hundred picoseconds, the structure reaches a 'quasi-equilibrium'. At 150 K, there is a slight drift to lower densities after an initial raise, whereas at 450 K, the average values of the fluctuations seem to be stable. Taking the second half of each trajectory and averaging over the three microstructures, the densities of Table 4-57 result. The density of 0.956 g/cm³ at 300 K is a bit lower than the experimental values of 0.99 g/cm³ and 1.01 g/cm³, but still acceptable. In general, the influence of water on the density is much smaller than it is for PA-6. The thermal expansion coefficient at 300 K is the same for both dry and wet microstructures and has a value of about 14·10⁻⁵ K⁻¹, which is in accord with the value of 11·10⁻⁵ K⁻¹ found in the 'Polymer Handbook'.

### 4.7.4.2 Diffusion of Water

The diffusion of the water molecules in the wet microstructures was assessed by the same analysis as in chapter 4.6.4.2. Figure 4.48 shows the

<table>
<thead>
<tr>
<th>T [K]</th>
<th>( \langle \rho_{\text{dry}} \rangle ) [g/cm³]</th>
<th>( \langle \rho_{\text{wet}} \rangle ) [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1.0055 ± 0.0112</td>
<td>1.0052 ± 0.0068</td>
</tr>
<tr>
<td>300</td>
<td>0.9549 ± 0.0162</td>
<td>0.9574 ± 0.0128</td>
</tr>
<tr>
<td>450</td>
<td>0.8904 ± 0.0164</td>
<td>0.8897 ± 0.0166</td>
</tr>
</tbody>
</table>

Figure 4.48: Average of the mean square displacement of the water molecules in PA-6 and PA-12, the dashed lines have slopes of exactly 0, 1/2, and 1 and are not the result of a regression analysis.
results of this analysis and makes a comparison with the corresponding values of PA-6. The absence of any diffusion at 150 K and the anomalous diffusion at room temperature found with PA-6 are confirmed with PA-12. In both polymers, the water molecules seem to behave very similarly; the differences can be attributed to the different statistics (a total of 105 water molecules in PA-6 vs. 36 in PA-12). This finding is supported by the very similar diffusion constants cited in the 'Polymer Handbook'\textsuperscript{Brandrup89} (55 vs. 85-10\textsuperscript{-8} cm\textsuperscript{2}/s at 100° C).

In the next chapter, the influence of water on the elastic constants of PA-12 will be examined.

### 4.7.4.3 Elastic Constants

The elastic constants of the 18 PA-12 trajectories (3 'dry' and 3 'wet' microstructures at 3 different temperatures) were computed analogous to those of PA-6. I.e. the cell parameters and stresses recorded during the last 500 ps of each trajectory were used to compute the strain and the stress-strain fluctuations. The detailed results of the stress-strain fluctuations are given in Appendix H, whereas the following tables refer to the results obtained from the

Table 4-58: Lamé constants of the three dry and three wet PA-12 microstructures, strain fluctuations only

<table>
<thead>
<tr>
<th>$T$ [K]</th>
<th>#</th>
<th>Dry PA-12</th>
<th>Wet PA-12</th>
</tr>
</thead>
</table>
| 150 | 1 | $\lambda = 3.78 \pm 0.20$
$\mu = 1.44 \pm 0.13$ | $\lambda = 4.51 \pm 0.15$
$\mu = 1.38 \pm 0.10$ |
|  | 2 | $\lambda = 4.48 \pm 0.22$
$\mu = 1.68 \pm 0.14$ | $\lambda = 4.16 \pm 0.20$
$\mu = 1.31 \pm 0.12$ |
|  | 3 | $\lambda = 4.40 \pm 0.13$
$\mu = 1.72 \pm 0.08$ | $\lambda = 4.01 \pm 0.16$
$\mu = 1.25 \pm 0.10$ |
| 300 | 1 | $\lambda = 2.47 \pm 0.09$
$\mu = 0.44 \pm 0.06$ | $\lambda = 2.88 \pm 0.10$
$\mu = 0.53 \pm 0.06$ |
|  | 2 | $\lambda = 2.68 \pm 0.09$
$\mu = 0.43 \pm 0.06$ | $\lambda = 2.78 \pm 0.10$
$\mu = 0.49 \pm 0.06$ |
|  | 3 | $\lambda = 2.85 \pm 0.10$
$\mu = 0.69 \pm 0.06$ | $\lambda = 2.64 \pm 0.08$
$\mu = 0.44 \pm 0.05$ |
| 450 | 1 | $\lambda = 1.09 \pm 0.03$
$\mu = 0.09 \pm 0.02$ | $\lambda = 0.35 \pm 0.03$
$\mu = 0.10 \pm 0.02$ |
|  | 2 | $\lambda = 1.21 \pm 0.02$
$\mu = 0.09 \pm 0.01$ | $\lambda = 1.01 \pm 0.05$
$\mu = 0.11 \pm 0.03$ |
|  | 3 | $\lambda = 0.50 \pm 0.03$
$\mu = 0.07 \pm 0.02$ | $\lambda = 0.72 \pm 0.04$
$\mu = 0.07 \pm 0.02$ |
strain fluctuations. Table 4-58 compares the Lamé constants of the individual dry and wet microstructures, whereas Table 4-59 illustrates the substantial influence of the charged groups of atoms on the elastic constants. Similar to cellulose-Iβ,

Table 4-59: Influence of the charged groups on the elastic constants of PA-12, strain fluctuations only, all values in GPa

<table>
<thead>
<tr>
<th>T [K]</th>
<th>Neutral groups</th>
<th>Charged groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ = 4.22 ± 0.36</td>
<td>λ = 6.42 ± 0.92</td>
</tr>
<tr>
<td></td>
<td>μ = 1.61 ± 0.17</td>
<td>μ = 3.11 ± 0.67</td>
</tr>
<tr>
<td>Dry</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>λ = 2.67 ± 0.18</td>
<td>λ = 3.73 ± 0.48</td>
</tr>
<tr>
<td></td>
<td>μ = 0.52 ± 0.13</td>
<td>μ = 1.16 ± 0.25</td>
</tr>
<tr>
<td>300</td>
<td>λ = 0.93 ± 0.31</td>
<td>λ = 2.59 ± 0.47</td>
</tr>
<tr>
<td></td>
<td>μ = 0.08 ± 0.02</td>
<td>μ = 0.65 ± 0.15</td>
</tr>
<tr>
<td>450</td>
<td>λ = 4.23 ± 0.27</td>
<td>λ = 6.06 ± 0.70</td>
</tr>
<tr>
<td></td>
<td>μ = 1.31 ± 0.12</td>
<td>μ = 3.25 ± 0.34</td>
</tr>
<tr>
<td>Wet</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>λ = 2.77 ± 0.14</td>
<td>λ = 4.05 ± 0.39</td>
</tr>
<tr>
<td></td>
<td>μ = 0.49 ± 0.07</td>
<td>μ = 1.63 ± 0.37</td>
</tr>
<tr>
<td>300</td>
<td>λ = 0.69 ± 0.27</td>
<td>λ = 2.06 ± 0.23</td>
</tr>
<tr>
<td></td>
<td>μ = 0.09 ± 0.03</td>
<td>μ = 0.31 ± 0.08</td>
</tr>
</tbody>
</table>

where the charged interactions were summed without and with Ewald summation, a mistake in the summation of the Coulombic interaction leads to an overestimation of the elastic constants. The artificial, additional interactions obviously make the simulation cell stiffer.

Figure 4.49: Temperature dependence of PA-12 (black) and PA-6 (gray), the dashed lines signify averages over the 'dry' and the solid lines averages over the 'wet' microstructures
In Figure 4.49, the Lamé constants $\lambda$ and $\mu$ of PA-12 are compared with those of PA-6. In contrast to the marked dependence particularly of the first Lamé constant $\lambda$ of PA-6 on the water content, $\lambda$ of PA-12 exhibits the antiplasticification/plastification transition only in much weaker form. The second Lamé constant $\mu$ changes with temperature almost independently of the water content.

4.7.5 Discussion

4.7.5.1 Comparison with Literature Values

Experimental Young's and shear moduli found in the 'Polymer Handbook'\textsuperscript{Brandrup89} are compared to calculated ones in Table 4-60. Note that the Table 4-60: Young's and shear moduli of semicrystalline experimental and amorphous computed PA-12

<table>
<thead>
<tr>
<th>Modulus</th>
<th>$T$, state</th>
<th>exp. [MPa]</th>
<th>calc. [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>$23^\circ$ C, dry</td>
<td>1400</td>
<td>1470 ± 360</td>
</tr>
<tr>
<td></td>
<td>$23^\circ$ C, moist</td>
<td>1200</td>
<td>1400 ± 190</td>
</tr>
<tr>
<td></td>
<td>$100^\circ$ C, dry</td>
<td>200</td>
<td>230 ± 60</td>
</tr>
<tr>
<td>$G$</td>
<td>$23^\circ$ C, dry</td>
<td>500</td>
<td>520 ± 130</td>
</tr>
<tr>
<td></td>
<td>$100^\circ$ C, dry</td>
<td>100</td>
<td>80 ± 20</td>
</tr>
</tbody>
</table>

computed values that are compared to the dry PA-12 at $100^\circ$ C are those at 450 K. There was no interpolation of the data between 300 and 450 K, because the $\alpha$-relaxation is located at about 340 K\textsuperscript{Pathmanathan92a}. Keeping the limitations (no direct comparison of experimental data at $100^\circ$ C, semicrystalline morphology for the experiments versus purely amorphous simulation cell) in mind, the agreement is very good and the effect of the presence of water at $23^\circ$ C is well reproduced.

4.7.5.2 Conclusions/Summary

The elastic constants of amorphous PA-12 are reproduced by atomistic simulations within the given error bars. These error bars originate from three different sources:

First, the simulation has not yet converged fully and the values are thus subject to a certain scatter. This scatter can be estimated by looking at the stress-strain correlation function (Eq. (3-38)). At 150 and 300 K, the deviation from the identity matrix is in the range of 1 to 3 %, but reaches 4 to 10 % at 450 K. This is also reflected by the temporal behaviour of the elastic constants.
At lower temperatures, they reach much faster more or less stable values than at 450 K.

Second, the individual microstructures exhibit, due to their smallness, a certain degree of anisotropy. This effect is - together with the first one - manifest in Table 4-58, where the uncertainties in the individual Lamé constants originate from a imperfect mapping to the actual matrices of the elastic constants.

The third effect, which is related to the second one, is the question of the representative volume element. Materials, which are on a global scale completely amorphous and isotropic, exhibit strong variations of their properties on a local scale. If small boxes are taken out of an amorphous material, they are anisotropic and differ in their average properties. With increasing box size, the anisotropy and the difference in the average properties diminish and disappear, if the representative volume size has been reached. Since the microstructures, that have been used for the simulations, are very small, it was necessary to use several of them to estimate the size of the representative volume element. As could be seen again from Table 4-58, the Lamé constants differ considerably (by about 20 %) between the three simulation boxes. The boxes are therefore smaller than the representative volume element and it was necessary to have a rudimentary statistics by running three of them.

Within the framework of the scaled_pccf force field and the MD sampling algorithm, the elastic constants in Table 4-60 reflect in their error bars all three sources of uncertainty mentioned above. The error bars are reasonably small, allowing to make useful statements about the elastic constants of PA-12 at different temperatures and water contents.

As expected, the Lamé constants of dry PA-6 are at all temperatures 30 % higher than those of PA-12. Since this difference vanishes completely for wet PA-6 at 450 K, it can be entirely attributed to the increased density of hydrogen bonds of PA-6 with respect to PA-12. The equilibrium water sorption, which is approximately three times smaller, supports the model of water molecules bridging between two neighbouring amide groups. Geometrical considerations would lead to a fourfold reduction of 'hydrogen bonds', if the density of amide groups is reduced by a factor of two. This explains, why PA-12 in experiments is so much less sensitive to the presence of water. The atomistic model that was used to compute the elastic constants is suitable to include the effects of temperature and water on the elastic constants.
4.8 Polycarbonate - Amorphous Cells

4.8.1 Introduction

Polycarbonate - or more precisely Bisphenol-A-polycarbonate (BPA-PC) - was the first polymer to be simulated in the course of this work in order to obtain its elastic constants. Polycarbonate is a purely amorphous polymer with excellent mechanical properties, especially with a very high fracture toughness, and good optical qualities. It is therefore used in large quantities for the production of CDs, sunglasses, etc. It is of great interest to elucidate the structure-property relationships by atomistic modelling. In the framework of a BMFT-Project with various groups from academia and industry, an attempt was made to compute the elastic constants of BPA-PC using atomistic modelling.

Pioneering work in the field of the atomistic modelling of BPA-PC was done by Hutnik et al., who defined a forcefield for BPA-PC, generated amorphous microstructures, modelled the chain dynamics, and computed the elastic and plastic response of these structures. Their results and methods were used as a basis and starting point for this work.

4.8.2 Cell Generation

The high density of 1.2 g/cm$^3$ and the high concentration of rings impose a challenge on the building of amorphous structures. It is not trivial to generate good microstructures of BPA-PC:

Modifying a method of Theodorou and Suter, Hutnik et al. used a model with fixed bond length and bond angles to build a dense structure according to the RIS scheme. The building process was quite complicated and involved many steps in which the interaction potentials were slowly increased to their full strength.

It was not possible to use a similar method from within the 'Amorphous Cell' module of 'InsightII', since on the one hand it was not possible to define RIS weights for rings, and on the other hand, the method described in chapter 4.6.2.1 was not able to generate structures at full density, because always a spearing or catenation occurred and the algorithm stopped. The highest density at which it became possible to produce some structures was 0.6 g/cm$^3$.

However, it was decided to follow a different path and to build the chains at the lowest possible initial density of 0.01 g/cm$^3$. Before that, the repeat unit of PBA-PC (Fig. 4.50) was constructed and a chain of 69 repeat units (2285 atoms, including two terminating CH$_3$-groups) was 'polymerized'. Due to the symmetry
of the BPA-PC repeat unit, the actual degree of polymerization was 138. The pcf91 force field was chosen to represent the energetic interactions, as it contained terms specially optimized for some polymers, among them polycarbonate. Three such chains were each grown in the usual stepwise fashion in a cubic cell of 138.6 Å size. After a short minimization of 50 steepest descent and 500 conjugate gradient steps to remove initial overlaps, a TpN-MD simulation of 25'000 steps of 1 fs was run to densify each cell. The compression was accelerated by applying a pressure of 1600 bar. This pressure corresponds to the tail correction pressure of BPA-PC at the experimental density of 1.2 g/cm³ Hutnik91b for the cutoff of 8.25 Å.

The densification process is shown in Figure 4.51. The densification was very fast: after the first 25 ps, the densities of the three cells lay between 1.172 and 1.178 g/cm³. This was sufficiently high to switch to a TσN-MD simulation
with a Nosé-Hoover thermostat and a Parrinello-Rahman pressure control. (If the simulations had been carried out from the beginning in a variable shape ensemble, very large deviations from a cubic shape would have occurred.) The duration of the \( \tau\sigma N \) simulations, the average densities during the last 50 ps of the MD simulation, and the final cell edge lengths are listed in Table 4-61. As it can already be seen, there is virtually no difference between the calculated densities and the experimental value of 1.2 g/cm\(^3\).

The very fast densification can be explained by the concept of diffusion of ‘free volume’ out of the cube. If a real body is getting more dense, ‘free volume’ (holes, cavities, and faults) is diffusing out of it, a process that takes place as well in a simulation box. In a random walk diffusion process, the time required to move a distance \( r \) away from the origin is given by Eq. (4-31), i.e. the time is proportional to the square of the distance. Comparing a macroscopic body of 1 cm and a simulation box of 20 Å size, the diffusion distances differ by a factor of \( 5 \times 10^6 \) and the diffusion times by \( 2.5 \times 10^{13} \), reducing the corresponding processes from minutes in the real body to picoseconds in the simulation box. This allows for a densification in a reasonable computer time.

The structures, nevertheless, are not ‘good’ representations of amorphous polycarbonates, since the individual chains were considerably compacted during the densification process. Their average end-to-end distance was only 32 and the radius of gyration only 16 Å, compared to RIS values of a chain of the same length, which are 135 and 56 Å. These findings were confirmed by a solubility parameter (square-root of the cohesive energy density) of only 14.5 (J/cm\(^3\))\(^{\frac{1}{2}}\), that opposed experimental findings\(^{191b} \) of 20.1 to 20.3 (J/cm\(^3\))\(^{\frac{1}{2}}\).

‘Good’ structures with reasonable end-to-end distances, radii of gyration, and cohesive energy densities were obtained from BAYER, where they had been generated in process involving several stages of minimization and MD simulation.\(^{93a} \) It was therefore possible to estimate the influence of the molecular geometry on the elastic constants of BPA-PC.

**Table 4-61: Total MD-simulation time at 300 K, densities averaged over the last 50 ps, and final cell edge lengths of BPA-PC**

<table>
<thead>
<tr>
<th>Cell #</th>
<th>( \tau\sigma N )-MD [ps]</th>
<th>( \langle \rho \rangle ) [g/cm(^3)]</th>
<th>( a ) [Å]</th>
<th>( b ) [Å]</th>
<th>( c ) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>450</td>
<td>1.205 ± 0.007</td>
<td>29.06</td>
<td>28.20</td>
<td>29.63</td>
</tr>
<tr>
<td>2</td>
<td>260</td>
<td>1.202 ± 0.007</td>
<td>28.01</td>
<td>29.95</td>
<td>28.72</td>
</tr>
<tr>
<td>3</td>
<td>460</td>
<td>1.194 ± 0.007</td>
<td>30.00</td>
<td>27.30</td>
<td>29.85</td>
</tr>
</tbody>
</table>
4.8.3 Simulation Procedure

4.8.3.1 Torsion angle distribution

The distribution of the torsion angles of the carbonate group (Fig. 4.52) was

![Trans (left) and cis (right) conformation of carbonate group.](image)

Figure 4.52: Trans (left) and cis (right) conformation of carbonate group. $\varphi_c = 0^\circ$ defines the trans state and $\varphi_c = \pm 180^\circ$ the cis-state

computed for simulation cells 1 and 3, since they were equilibrated best. For comparison, 15 small 18.44 Å-cubes from Hutnik and 2 larger 29.74 Å boxes from MSI were also included into the calculations.

4.8.3.2 Static Minimum Energy Elastic Constants

The static minimum energy elastic constants were computed by a random deformation process. First, the polycarbonate structure was minimized down to a gradient of 0.01 kcal/(molÅ). From thorough minimizations, it was found that this gradient guaranteed that the energy should not lower more than 0.001 kcal/mol if the minimization was continued to a gradient of $10^{-5}$ kcal/(molÅ). The cell was then subject to a total of 21 random deformations, with the elements of the strain matrix being limited to $\pm 0.05 \%$. The deformed cells were again minimized with their shape and size held fixed. The 21 unknown elastic constants could be calculated from 21 Equations of the form

$$\Delta U_{pot} = \sum_{i=1}^{b} \sum_{k>i}^{b} C_{ik} \varepsilon_i \varepsilon_k$$

(4-33)

by using linear algebra methods.

4.8.3.3 Fluctuation Approaches for the Elastic Constants

After the unsatisfactory results of the static minimum energy approach, which will be described in chapter 4.8.4.2, it became apparent that the thermal effects on the cell size and shape can not be neglected. Andrei Gusev independently derived a formula, that turned out to be identical to the strain fluctuation approach of Parrinello & Rahman. Applying this formula to very short TøN-MD
runs of only 10 ps yielded much better results than the static calculations, as can be seen in chapter 4.8.4.3.

However, the elastic constants obtained from this method were strongly dependent on the length of the simulation run. More extended simulations with detailed recording of the cell parameters and the pressure (in 1 fs steps) were performed after the initial densification, which lasted 160 ps and has been included into the total simulation time of Table 4-61. There were thus two runs of more than 250 and one run of 100 ps at 300 K. In order to check for the influence of temperature, the three structures were simulated in the $T_aN$-ensemble for 100 ps at 100 K. The starting structure was the one after 160 ps.

To improve the convergence, the idea came up to use the information of the actual pressure that had been printed out in the '.ext' files. The first trial was the computation of the bulk modulus from the slope of the $\Delta p$-$\Delta V$($V$)-plot (Fig. 4.57). As will be reported later, this trial delivered encouraging results, and a method was searched for to include the information of the full stress tensor to compute the whole matrix of the elastic constants.

The result of this effort was the familiar stress-strain fluctuation formula (Eq. (3-36)), which was applied to an already mentioned structure from BAYER, in order to compare the efficiency of the two fluctuation approaches and the influence of the generation process on the elastic constants. It was first necessary to equilibrate this structure by a minimization and a short (12 ps) $T_pN$-MD run. After that, an MD simulation of 200 ps in the $T_aN$-ensemble was performed. The last $10^5$ frames (recorded during the last 100 ps) contained the information necessary to evaluate the elastic constants using the strain and the stress-strain fluctuation approaches.

### 4.8.4 Results

#### 4.8.4.1 Torsion Angle Distribution

The distribution of the torsion angles of the carbonate group of BPA-PC microstructures that were generated with a variety of methods is shown in Figure 4.53. The fraction of cis angles (i.e. torsion angles between -90 and 90°) is virtually independent of the generation procedure - which included RIS and torsional potential builders with initial densities between 0.01 and 1.2 g/cm³ and combined minimization and dynamics equilibration - and lies between 25 and 30 %. This result is in marked contrast to recent $C^{13}$-NMR investigations of Tomaselli et al.\textsuperscript{97a}, which yield a cis-fraction of at most 10 %, but most probably less than 5 %.
This experimental finding is also in accord with the forcefield parameters of Hutnik et al.\cite{Hutnik91a} and of the pcff91 forcefield. These forcefields both have values of $\Delta E = E_{\text{cis}} - E_{\text{trans}}$ of 1.7 and even 3.45 kcal/mol (from diphenylcarbonate using a density functional starting geometry and a subsequent minimization down to $10^{-5}$ kcal/(mol\cdot Å)), which lead to cis-fractions,

$$[\text{cis}] = \frac{2\gamma}{1 + \gamma},$$

with $\gamma = \exp\left(\frac{\Delta E}{kT}\right)$, of 5\% or much less.

An MD simulation run on a polycarbonate chain of 5 repeat units was prepared to record the distribution of the torsion angles in dynamics to see whether MD might be responsible for the high fraction of cis-conformations. The vacuum simulation with a timestep of 1 fs and velocity rescaling to keep the temperature at 300 K lasted 25000 ps, during which a total of 5000 torsion angles were recorded: after 50ps roughly 30\% of the carbonyl groups were in a cis conformation and the distribution of the torsion angles remained stationary with the torsion angles changing between cis and trans every few picoseconds.

This result was not highly conclusive, since the polycarbonate chain was...
simulated \textit{in vacuo}. Trials were therefore made to simulate a solution of BPA-PC in a theta solvent (in this case chloroform), but the cell became so large that equilibration was not possible within a reasonable time.

4.8.4.2 Static Minimum Energy Approach

After 160 ps of dynamics, the static minimum energy elastic constants of the first and the second PC structure were computed according to chapter 4.8.3.2. As in dynamics, the nonbonded interactions were computed groupwise with a cutoff of 8.5 Å and a spline of 0.5 Å. The resulting matrices of the elastic constants and their Eigenvalues are given in Table 4-62. As can be seen immediately, there is a large difference between the actual matrices of the elastic constants and the one of a perfectly anisotropic material (Eq. (1-78) on page 25). Some Eigenvalues are even negative, indicating problems with the minimization algorithm. The Lamé constants are far away from the experimental values of \( \lambda = 4.27 - 5.55 \) GPa and \( \mu = 0.8 - 1.1 \) GPa\textsuperscript{Hutzik93a}.

Besides the technical problem to find the absolutely lowest point in a global minimum, a short T\textsuperscript{o}H\textsubscript{MD} simulation of the first PC structure sheds light on the principal problem. During 1 ps, the actual MD frame was dumped out every 100 fs and then minimized - including the cell parameters - down to a maximal gradient of \( 10^{-5} \) kcal/(mol-Å). The final energies and cell parameters are listed in Table 4-63: the all-atom \textit{pcff91} forcefield with bond and angle deformation terms leads to a high-dimensional energy hypersurface, where the minima are separated only by low energy barriers. A great number of such minima is accessible.

<table>
<thead>
<tr>
<th>1 \left( \frac{\partial^2 U_{pot}}{\partial \eta_{ij} \partial \eta_{kl} / T} \right) [GPa]</th>
<th>1 \left( \frac{\partial^2 U_{pot}}{\partial \eta_{ij} \partial \eta_{kl} / T} \right) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.45 9.15 11.78 0.60 0.30 0.14</td>
<td>8.06 6.37 8.89 -1.05 0.04 -0.70</td>
</tr>
<tr>
<td>9.15 8.44 9.44 0.21 0.99 -0.22</td>
<td>6.37 5.16 8.06 0.12 0.53 -1.16</td>
</tr>
<tr>
<td>11.78 9.44 8.91 0.52 0.62 -0.35</td>
<td>8.99 8.06 8.73 -1.75 1.33 -0.28</td>
</tr>
<tr>
<td>0.60 0.21 0.52 1.42 -0.18 0.12</td>
<td>-1.05 0.12 -1.75 2.29 0.65 0.61</td>
</tr>
<tr>
<td>0.30 0.99 0.62 -0.18 2.00 0.47</td>
<td>0.04 0.53 1.33 0.65 2.54 -0.44</td>
</tr>
<tr>
<td>0.14 -0.22 -0.35 0.12 0.47 1.84</td>
<td>-0.70 -1.16 -0.28 0.61 -0.44 2.21</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lamé constants</th>
<th>Eigenvalues ( \lambda_{6x6} )</th>
<th>Lamé constants</th>
<th>Eigenvalues ( \lambda_{6x6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda = 9.28 \pm 0.537 )</td>
<td>28.97, 2.44, 1.77</td>
<td>( \lambda = 6.92 \pm 0.694 )</td>
<td>23.38, 3.27, 2.57</td>
</tr>
<tr>
<td>( \mu = 0.08 \pm 0.340 )</td>
<td>1.18, -0.16, -0.31</td>
<td>( \mu = 0.63 \pm 0.439 )</td>
<td>1.77, 0.07, -2.10</td>
</tr>
</tbody>
</table>
for a molecule at finite temperature, since the energy barriers between them are of the same size as the kinetic energy. A picture (Fig. 4.54) might illustrate this:

![Figure 4.54: Model of a two-dimensional cut through the energy hypersurface of an amorphous material](image)

The determination of the curvature of a single minimum is in this case of no use in the determination of the elastic constants, which are determined by the size of the accessible phase space at a given temperature. Since this volume is increasing with temperature, the elastic constants of amorphous materials will always reduce if the temperature is rising.

### 4.8.4.3 Fluctuation Approaches

The strain fluctuation formula yielded very satisfactory results, as can be seen from Table 4-65 and Figure 4.55. Table 4-65 shows the results of the strain fluctuation formula averaging over the last 250 ps of \( T_oN \)-MD of the first and the third microstructure. The Lamé constants computed from such matrices are shown in Fig. 4.55 as a function of the averaging time. They reduce with increasing simulation time, as larger and larger volumes of the phase space are being
Table 4-64: Matrices of the elastic constants of the first (left) and the third (right) BPA-PC structure, strain fluctuation formula, averaging time: 250 ps (200 - 450 ps), 300 K

<table>
<thead>
<tr>
<th></th>
<th>$K^{I} / \langle \eta_{ik} \eta_{lm} \rangle^{-1} [\text{GPa}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\langle V \rangle \langle \eta_{ik} \eta_{lm} \rangle^{-1} [\text{GPa}]$</td>
</tr>
<tr>
<td>$6.96$</td>
<td>3.93 $4.63$ 0.17 $-0.05$ 0.13</td>
</tr>
<tr>
<td>3.93</td>
<td>6.90 $4.67$ 0.27 $-0.16$ 0.36</td>
</tr>
<tr>
<td>$4.63$</td>
<td>4.67 $6.19$ 0.14 $-0.02$ 0.06</td>
</tr>
<tr>
<td>0.17</td>
<td>0.27 0.14 1.17 0.15 $-0.07$</td>
</tr>
<tr>
<td>$-0.05$</td>
<td>$-0.16$ $-0.02$ 0.15 0.90 0.06</td>
</tr>
<tr>
<td>0.13</td>
<td>0.36 0.06 $-0.07$ 0.06 1.09</td>
</tr>
</tbody>
</table>

Figure 4.55: Convergence of the Lamé constants of BPA-PC at 300 K, dotted lines mark the range of the experimental results. Within a time accessible by MD and present computers, $\lambda$ converges in the range of the experimental results, whereas $\mu$ still seems to further reduce. This is in accord with observations made with other polymeric systems: the normal components of the elastic constants always converge significantly faster than the shear components.

The results of three MD simulations at 100 K, where the strain fluctuations were averaged over the last 50 ps of the 100 ps runs are in good agreement with experimental data from BAYER as can be seen in Figure 4.56.

The search for a method which would improve the convergence behaviour lead to the following computer experiment: As already mentioned, the information about the actual pressure was used to compute the bulk modulus $K$ by transforming Eq. (1-82) to

$$\Delta \rho = -K \cdot \frac{\Delta V}{V}.$$  

((1-82))
The bulk modulus could now be obtained from a linear regression of a $\Delta p$ vs. $\Delta V/\langle V \rangle$ plot.

Figure 4.57 shows such a plot with MD data of the first structure. The linear regression of the point cloud yielded an intercept of $1523 \pm 5$ bar, which was subtracted from the above plot, because its origin is the correction pressure of...
1600 bar (reduced somewhat by the finite stepsize of the MD integration). The slope \((-K)\) is \(-4.954 \pm 0.095\) GPa, being just at the lower margin of the experimental range\(^{93a}\) of 5.0 - 6.1 GPa.

The resulting elastic matrices from the second half of a 200 ps ToN-MD simulation of the BAYER structure mentioned at the end of chapter 4.8.3.3 are displayed in Table 4-66. There are no fundamental differences between these matrices and those of Table 4-65.

### 4.8.5 Discussion and Conclusions

The comparison with experimental density, radius of gyration, cohesive energy density, and Lamé constants was made at the appropriate place in the presentation of the results. The three structures that were 'condensed from the gas phase' reached a stable density after about 100 ps. The agreement between the simulated and the experimental density was almost perfect, in contrast to the end-to-end distances and the radii of gyration. Due to the affine compression, the microstructures were several times too compact compared to the corresponding RIS values. The elastic constants obtained from strain (and stress-strain) fluctuations, however, were not significantly influenced by this, as a comparison with a more carefully produced structure from BAYER revealed. It was even possible to grasp the influence of temperature on the elastic constants by performing ToN-MD simulations at 100 and 300 K. The results again agreed well with experimental data.

It can be concluded that the global 'shape' of a molecule in an amorphous body is of no influence to the elastic constants. The method of generating and equilibrating amorphous microstructures needn't be capable of relaxing the molecule on large scales. It is more important that the 'local' polymer structure is well equilibrated to obtain reasonable elastic constants.
Static minimum energy evaluations of the elastic constants, performed by Hutnik et al.\textsuperscript{Hutni93a}, yielded values that were in general too high ($\lambda = 5.35 \pm 1.15$, $\mu = 2.06 \pm 0.65$). Although the generalized coordinates of Hutnik's model reduce the dimensionality of the phase space considerably, the same explanation of the observed deviations as in the present work is evident. It is therefore not possible to obtain physically meaningful elastic constants from static minimum energy calculations, since the local curvature of the energy hypersurface is not directly related to the curvature of the thermally accessible phase space volume.
5 Conclusions

5.1 Summary

It could be shown that the elastic constants of polymeric systems could be determined with the Parrinello-Rahman strain and the novel stress-strain fluctuation formula. These fluctuation methods have been applied for the first time to the field of polymer science. Crystalline monocrystals of polyethylene, polypropylene, cellulose-1β, and polyamide-6 and amorphous microstructures of polyamide-6, polyamide-12, and polycarbonate have been simulated using the Parrinello-Rahman Nose-Hoover molecular dynamics. In all cases, the simulated elastic constants were in good agreement with experimental values.

The statistical nature of the fluctuation formula implies a dependence of the results on the length of a simulation run. Due to the establishment of the second fluctuation formula, it became possible to quantify the degree of convergence of a simulation. This convergence criterion allows to make estimates of the precision of the elastic constants.

The accuracy of the elastic constants is determined by a number of factors: Maybe the most important one was not subject of this work: Although the generation of forcefields made considerable progress in the recent years, the representation of a quantum mechanical by classical interactions still remains - besides the generation of amorphous microstructures - the most disputable point in the methodology. The other factors like the system size, the sampling method, and the duration of the simulation can be controlled sufficiently well. It has been shown for nearest-neighbour Lennard-Jones solids that the system size and the sampling method hardly influence the final elastic constants. Of course, they influence the convergence behaviour, which in turn determines the necessary simulation (and CPU) time.

Attempts have been made to improve the convergence by switching to other ensembles, but no significant improvements could be achieved. It might be concluded, that the sampling efficiency of polymeric systems does not significantly change going from one ensemble to the other. While, e.g., the elastic constants obtained from stress-strain fluctuations of the Lennard-Jones solid converged significantly faster at low temperatures, no such effect could be observed for polymeric systems.

It could also be shown, that the elastic constants of amorphous polymers do not depend on the global conformation of the chain. It is therefore not necessary to completely equilibrate a microstructure by long simulation runs or to gen-
erate very good starting structures, as long as the local conformation is in agreement with experimental values.

But it turned out that the fluctuation distributions, which are proportional to the elastic constants, strongly depend on the canonicity of the sampling algorithm. Non-canonical integrators significantly change the results, as does a wrong treatment of the long-range Coulombic interactions by charged atom groups or unsuitable summation methods.

Elastic constants are equilibrium properties and it is not meaningful to compute them for systems that undergo a relaxation process. The simulation system must therefore be at least in a quasi-equilibrium, without noticeable changes or drifts in the relevant cell parameters and stress.

Besides these caveats, the fluctuation methods provide robust simulation algorithms, which can reproduce the influence of temperature and the effects of small molecules on the elastic constants of amorphous and crystalline polymers. There are already simulations of polymers with short fiber reinforcements reported in the literature.\textsuperscript{95a} The canonical constant-stress, constant-temperature molecular dynamics sampling method mainly used for this work, also allows - with caution - to derive dynamical information like relaxation spectra and diffusion constants.

\subsection*{5.2 Outlook}

At present, the simulation runs necessary to obtain good statistics for the fluctuations are rather long ($O(10^5 - 10^6)$ steps for 20 - 30 Å cells) and require days or weeks of CPU time on an average workstation. But the performance of computers doubles every 18 months\textsuperscript{96a}, so this problem will be less important in the future. As it has now become possible to compute the elastic constants of purely amorphous and purely crystalline polymers with reasonable accuracy, it is the next logical step, to attack semicrystalline polymers. Although a variety of models\textsuperscript{64a,91a} exists, that link the microscopic with the macroscopic properties of a compound material, a new mesoscopic model was developed, which allows to simulate the effect of the shape and the distribution of the inclusions (crystallites) on the mechanical properties.\textsuperscript{97a,97b} This approach tessellates a cell containing the amorphous matrix, the crystalline reinforcing particles and the interface between them into small discrete elements. With the knowledge of the complete matrix of the elastic constants of the matrix and the reinforcing particles, it will be possible to compute the elastic behaviour of a polymeric system as a whole.
Appendices

Appendix A: Coordinate Transformations

A-1: Direction Cosines

Consider two right-handed, orthogonal coordinate systems with the same origin, but different relative orientation (Fig. A.1).

In order to determine the matrix that transforms one system into the other, the direction cosines between the axes of the reference and the transformed coordinate system are calculated. In Fig. A.1, the direction cosine between a unit vector $e_i'$ of the transformed system and a unit vector $e_j$ of the system of reference is

$$a_{ij} = \cos (e_i', e_j) = e_i' \cdot e_j.$$  \hspace{1cm} (A-1)

The vector $e_i'$ can be expressed in terms of $e_1, e_2, e_3$ by the relation

$$e_i' = (e_i' \cdot e_1) e_1 + (e_i' \cdot e_2) e_2 + (e_i' \cdot e_3) e_3$$

or

$$e_i' = a_{ij} e_j,$$  \hspace{1cm} (A-2)

leading to the transformation matrix $A$, which, operating on the components of a vector $r$ in the reference coordinate system, yields the components of the vector $r'$ in the transformed system:
The transformation matrix from the primed system to the unprimed system is given by the inverse of the transformation matrix

\[
\mathbf{r} = \mathbf{A}^{-1}\mathbf{r}' = \mathbf{A}^{-1}\mathbf{Ar}.
\]  

(A-4)

The nine components of the transformation matrix \(\mathbf{A}\) are not independent, since a coordinate system with arbitrary orientation, but fixed origin, has just three degrees of freedom. The connections between the direction cosines arise from the fact, that the basis vectors in both coordinate systems are orthogonal to each other and have unit magnitude. These six conditions can be expressed formally as

\[
a_{ij}a_{ik} = \delta_{jk} \quad j, k = 1, 2, 3,
\]  

(A-5)

where \(\delta_{jk}\) represents the Kronecker symbol and the summation convention over repeated indices is used.

A-2: Transformation of the Matrix of the Elastic Constants

Given the transformation matrix \(\mathbf{A}\), with elements \(a_{ij}\) (Eq. (A-3)), that connects a unprimed reference and a primed, transformed coordinate system. The fourth-rank tensor \(C_{ijkl}\) transforms according to

\[
C_{ijkl}' = a_{im}a_{jn}a_{ko}a_{lp}C_{mnop},
\]  

(1-50)

while the 6x6-matrix \(C_{mn}\) of the elastic constants transforms like

\[
C_{op} = C_{mn}q_{om}q_{pn},
\]  

(A-6)

with

\[
q_{ij} = \begin{bmatrix}
a_{11}^2 & a_{12}^2 & a_{13}^2 & 2a_{12}a_{13} & 2a_{13}a_{11} & 2a_{12}a_{11} \\
a_{21}^2 & a_{11}^2 & a_{23}^2 & 2a_{23}a_{22} & 2a_{23}a_{21} & 2a_{22}a_{21} \\
a_{31}^2 & a_{32}^2 & a_{11}^2 & 2a_{33}a_{32} & 2a_{33}a_{31} & 2a_{32}a_{31} \\
a_{31}a_{21} & a_{32}a_{22} & a_{33}a_{23} & a_{33}a_{22} + a_{32}a_{23} & a_{33}a_{21} + a_{31}a_{23} & a_{33}a_{21} + a_{31}a_{22} + a_{32}a_{21} \\
a_{31}a_{11} & a_{32}a_{12} & a_{33}a_{13} & a_{33}a_{12} + a_{32}a_{13} & a_{33}a_{11} + a_{31}a_{13} & a_{33}a_{11} + a_{31}a_{12} + a_{32}a_{11} \\
a_{21}a_{11} & a_{12}a_{22} & a_{13}a_{23} & a_{13}a_{22} + a_{12}a_{23} & a_{13}a_{21} + a_{11}a_{23} & a_{13}a_{21} + a_{11}a_{22} + a_{12}a_{21}
\end{bmatrix}
\]  

(A-7)
To transform the compliance matrix, again Eq. (A-6) is used, but with a slightly different \( q \)-matrix, where the elements at the intersections of column 1, 2, and 3 with row 4, 5, and 6 are multiplied with a factor of 2, whereas the elements at the intersection of column 4, 5 and 6 with row 1, 2, and 3 are divided by a factor of 2.

**A-3: The Eigenvalues and Eigenvectors of a 4th rank tensor**

The basic formalism of the eigenvalues and eigenvectors of a 4th rank tensor \( A \) is given by the equation

\[
A_{ijkl}x_{kl} = \lambda x_{ij} = \lambda \delta_{ik}\delta_{jl}x_{kl} \quad (A-8)
\]

The introduction of the Kronecker-deltas is necessary to perform the suffix substitution. The following set of equations needs to be solved:

\[
(A_{ijkl}-\lambda \delta_{ik}\delta_{jl}) x_{kl} = 0 \quad (A-9)
\]

i.e. eigenmatrices \( x_{kl} \) are deformations (\( \varepsilon_{kl} \)) where the resulting stress (\( \sigma_{ij} \)) is proportional to the applied strain, if \( A_{ijkl} \) is the elasticity tensor \( C_{ijkl} \). The proportionality factor \( \lambda \) is the eigenvalue belonging to this system.

The above equations are also valid, if the Voigt notation is used, with one major difference: Assuming, that the eigenstresses are the same (\( \sigma_{ij} = \sigma_i \)), the eigenstrains will become

\[
\lambda_{3x3x3x3}\varepsilon_{kl} = \lambda_{6x6}\varepsilon_k \quad (A-10)
\]

The \( \varepsilon_{kl} \) transform to \( e_k \) according to Eq. (1-55) (\( \varepsilon_{kl} = e_k \) if \( k = l \), and \( \varepsilon_{kl} = \frac{1}{2} e_k \) if \( k \neq l \)), which results in

\[
\lambda_{3x3x3x3}\varepsilon_k = \lambda_{6x6}e_k \quad \lambda_{3x3x3x3} = 2\lambda_{6x6} \quad (A-11)
\]

i.e. the eigenvalues obtained from the full 3x3x3x3 tensor of the elastic constants differ by a factor of 2 from those obtained from the Voigt representation of the matrix of the elastic constants, if the indices \( k \) and \( l \) are different. This is the case for the Voigt numbers 4, 5 and 6.

**A-4: General Transformation Matrix**

If the reference or the transformed coordinate system are not orthogonal or if the unit vectors in the two systems are not of the same length, the transformation matrix from the reference to the transformed coordinate system can be constructed by expressing the unit vectors of the transformed system in terms of the
reference system. In \( n \) dimensions, there are \( n \) such basis vectors \( (a_1, a_2, \ldots, a_n) \), which form the columns of a transformation matrix \( A \),

\[
A = \begin{bmatrix} a_1 & a_2 & \ldots & a_n \end{bmatrix}.
\]

This transformation matrix is identical with the one defined by Eq. (A-3) if both coordinate systems are orthogonal and have basis vectors of the same length. Otherwise, it is important to distinguish between co- and contravariant components of the transformation matrix. Renton87, Budiansky74

**A-5: Metric Tensor**

The scalar products of the basis vectors \( (a_1, a_2, a_3) \) of a 3-dimensional coordinate system form the metric tensor \( g \) by Sands82

\[
g_{ik} = a_i \cdot a_k
\]

or, in matrix notation

\[
g = h^\top h,
\]

where \( h \) is tensor containing the base vectors as its columns,

\[
h = \begin{bmatrix} a_1 & a_2 & a_3 \end{bmatrix}.
\]

In Eqs (A-12) and (A-15), different symbols were used for the matrix containing the basis vectors of a coordinate system in its columns. The transformation matrix \( A \) connects two arbitrary coordinate systems and is not linked with any physical quantity. It therefore forms a matrix. The tensor \( h \) is used in this work to describe the shape of a crystallographic unit cell or a simulation cell and transforms itself according to Eq. (1-12) and thus forms a tensor.

**A-6: Jacobian Matrix**

Given the function

\[
y = y(x),
\]

a matrix

\[
J_{ij} = \frac{\partial y_i}{\partial x_j}
\]

can be defined Bronstein91, which is called the Jacobian matrix of the function \( y \). For the above (Appendix A-1) transformation
the Jacobian $\mathbf{J}$ connects the basis vectors of the two coordinate systems by

$$e_i' = J_{ij}e_j \quad \text{and} \quad e_i = J_{ij}^{-1}e_j'. \quad (A-19)$$

For a canonical transformation, the determinant of the Jacobian, $\det(\mathbf{J}) = \frac{V}{V_0} = \pm 1$, (A-20)

indicating that the volume of the unit cell (in phase space) remains constant upon the transformation.

**A-7: Euler Angles**

A coordinate system $\{x,y,z\}$ is rotated in a first step by an angle $\phi$ around its z-Axis (Fig. A.2a) forming the new coordinates $\{\xi,\eta,z\}$. Then these new coordinates are rotated around the $\xi$-axis by an angle $\theta$ (Fig. A.2b). The resulting coordinate system $\{\xi',\eta',\zeta\}$ is again rotated around its new $\zeta$-axis by the angle $\psi$ to its final state $\{x',y',z\}$ (Fig. A.2c). All rotations are performed counterclockwise!

The transformation matrices of the three rotations are given by
Appendix B: Finite Elasticity and Cell Shape Tensor

The finite strain between a reference cell shape tensor \( \mathbf{H} \) and an actual shape tensor \( \mathbf{h} \) can be derived as follows:

Consider a reference cell \( \mathbf{H} \) containing a connecting vector \( \mathbf{R} \) and a

\[
\mathbf{Z}(\phi) = \begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix},
\]

(A-21)

\[
\mathbf{X}(\theta) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos\theta & \sin\theta \\ 0 & -\sin\theta & \cos\theta \end{bmatrix},
\]

(A-22)

and

\[
\mathbf{Z}(\psi) = \begin{bmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{bmatrix}.
\]

(A-23)

These three operations are applied in sequence and the product matrix \( \mathbf{A} \) then follows as

\[
\mathbf{A} = \begin{bmatrix} \cos\psi\cos\phi - \cos\theta\sin\psi\sin\phi & \cos\psi\sin\phi - \cos\theta\cos\phi\sin\psi & \sin\psi\sin\theta \\ -\sin\psi\cos\phi - \cos\theta\sin\phi & \sin\psi\sin\phi - \cos\theta\cos\phi\sin\psi & \cos\psi\sin\theta \\ \sin\theta\sin\phi & -\sin\theta\cos\phi & \cos\theta \end{bmatrix},
\]

(A-24)

The inverse transformation from \( \{x',y',z'\} \) to \( \{x,y,z\} \) is given immediately by the transposed matrix \( \mathbf{A}^T \)

\[
\mathbf{A}^{-1} = \mathbf{A}^T = \begin{bmatrix} \cos\psi\cos\phi - \cos\theta\sin\psi\sin\phi & -\sin\psi\cos\phi - \cos\theta\sin\phi & \sin\psi\sin\theta \\ \cos\psi\sin\phi & \sin\psi\sin\phi - \cos\theta\cos\phi\sin\psi & \cos\psi\sin\theta \\ \sin\theta\sin\phi & \cos\psi\sin\theta & \cos\theta \end{bmatrix},
\]

(A-25)

For generalized coordinate MD algorithms however, the use of Euler angles can lead to singularities in the dynamics. To avoid these problems, so-called quaternions \(^7\text{Evans}77\text{a},^7\text{Evans}77\text{b}\) or modified Euler angles can be used.

Appendix B: Finite Elasticity and Cell Shape Tensor

B-1: Finite Strain From Cell Shape Tensor

The finite strain between a reference cell shape tensor \( \mathbf{H} \) and an actual shape tensor \( \mathbf{h} \) can be derived as follows:

Consider a reference cell \( \mathbf{H} \) containing a connecting vector \( \mathbf{R} \) and a
deformed cell $h$ containing the transformed connecting vector $r$ (Fig. 1.4). The relation between $R=[X_1,X_2,X_3]^T$ and $r=[x_1,x_2,x_3]^T$ can be written as

$$s_i = H_{ij}^{-1}X_j \quad \text{or} \quad s_i = h_{ij}x_j \quad (B-1)$$

$$x_i = h_{ij}s_j = h_{ij}H_{jk}^{-1}X_k$$

So the translation vector $u$ is given by

$$u_i = r_i - R_i = x_i - X_i = h_{ij}H_{jk}^{-1}X_k - X_i. \quad (B-2)$$

To obtain the finite strain according to Eq. (1-29), the following derivation must be made,

$$\frac{\partial u_j}{\partial X_j} = h_{ik}H_{kl}^{-1}\frac{\partial X_l}{\partial X_j} - h_{ik}(h)^{-1}_{kj}\delta_{ij} - \delta_{ij} \quad (B-3)$$

$$= h_{ik}H_{kj}^{-1} - \delta_{ij},$$

using for the second equation the properties of an orthogonal cartesian coordinate frame and for the third the fact, that multiplication with a Kronecker delta exchanges the indices of a matrix. The product of the gradients of the translation vector is

$$\frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} = (h_{ik}H_{li}^{-1} - \delta_{ki})(h_{km}H_{mj}^{-1} - \delta_{kj})$$

$$= h_{ik}H_{li}^{-1}h_{km}H_{mj}^{-1} - h_{ik}H_{li}^{-1}\delta_{ki} - h_{km}H_{mj}^{-1}\delta_{kj} + \delta_{ki}\delta_{kj} \quad (B-4)$$

Combining Eqs (1-29), (B-3), and (B-4), it is found that

$$\eta_{ij} = \frac{1}{2} \left[ \frac{\partial u_i}{\partial X_j} + \frac{\partial u_j}{\partial X_i} + \frac{\partial u_k}{\partial X_i} \frac{\partial u_k}{\partial X_j} \right]$$

$$= \frac{1}{2} \left[ h_{ik}H_{lj}^{-1} - \delta_{ij} + h_{jl}H_{li}^{-1} - \delta_{ji} + h_{km}H_{mj}^{-1}h_{kn}H_{nj}^{-1} - h_{in}H_{nj}^{-1} - h_{jm}H_{mi}^{-1} + \delta_{ij} \right] \quad (B-5)$$

$$= \frac{1}{2} \left[ h_{km}H_{mi}^{-1}h_{kn}H_{nj}^{-1} - \delta_{ij} \right],$$

which, after transposing (=interchanging the indices), using the fact that the inverse of a transpose equals the transpose of the inverse, and rearranging some matrices, results in Eq. (1-36),
Appendix B: Finite Elasticity and Cell Shape Tensor

According to Eq. (A-14), $h_{ik}^{T}h_{km}$ forms the metric tensor component $g_{lm}$ of the deformed cell, allowing to write Eq. (1-36) as

$$\eta_{ij} = \frac{1}{2} \left[ H_{ij}^{T-1} g_{lm} H_{mj}^{T-1} - \delta_{ij} \right]. \quad (B-6)$$

B-2: Finite Stress (Thermodynamic Tension) from Cell Shape Tensor

Equation (1-40),

$$t_{st} = J\sigma_{ij} \frac{\partial X_s}{\partial x_i} \frac{\partial X_t}{\partial x_j} \quad \text{or} \quad \sigma_{ij} = J^{-1} \frac{\partial X_s}{\partial x_i} \frac{\partial X_t}{\partial x_j} t_{st}, \quad (1-40)$$

expresses the relation between the actual stress $\sigma$ on the deformed cell and the thermodynamic tension $t$ referring to the undeformed cell. Using Eq. (B-1), one easily finds that

$$\frac{\partial X_s}{\partial x_i} = \frac{\partial H_{so}^{-1} x_p}{\partial x_i} = H_{so}^{-1} \delta_{ip} \quad \text{and} \quad \frac{\partial X_t}{\partial x_j} = \frac{\partial H_{tq}^{-1} x_r}{\partial x_j} = H_{tq}^{-1} \delta_{jr} \quad (B-7)$$

leading to

$$J\sigma_{ij} \frac{\partial X_s}{\partial x_i} \frac{\partial X_t}{\partial x_j} = J\sigma_{ij} H_{so}^{-1} \delta_{ip} H_{tq}^{-1} \delta_{jr}$$

$$= J\sigma_{pr} H_{so}^{-1} H_{tq}^{-1}$$

$$= J H_{so}^{-1} \sigma_{pr} h_{iq}^{-1} H_{qt}$$

which, in matrix notation, is equivalent to Eq. (1-41). The actual stresses as a function of the thermodynamic tensions can be found in an analogous manner.

B-3: Symmetry of the Thermodynamic Stress Tensor

The thermodynamic tension tensor $t$ is linked to the instantaneous stress tensor $\sigma$ by

$$t = J H \sigma h^{-1}, \quad (1-41)$$

where $\sigma$ is a symmetric tensor, $H$ and $h$ are general tensors and $J$ is a scalar. The transpose of Eq. (1-41) can be written as
\[
t^T = \left( JHh^{-1}\sigma h^{-1}H^T \right)^T = JH^T h^{-1}T \sigma^T h^{-1}T H^T,
\]
(B-9)
since
\[
(AB)^T = B^T A^T \quad \Leftrightarrow \quad (ABC)^T = C^T B^T A^T.
\]
(B-10)
Using the fact, that \( \sigma^T = \sigma \) and that the inverse of the transpose of a matrix equals the transpose of the inverse, Eq. (B-9) can be transformed to the familiar
\[
t^T = JHh^{-1}\sigma h^{-1}H^T - t
\]
(B-11)
proving that the tensor of the thermodynamic tensions is indeed symmetric.

**Appendix C: Random Number Generators**

A good overview over a great variety of random number generators can be found in 'Numerical Recipies'. \cite{Pressetal92} A discussion of the linear congruential and the Lagged Fibonacci random number generator is also given in Ref. \cite{Widmann96a}

**C-1: Multiplicative Congruential Algorithm**

The multiplicative congruential random number generation used in this work is based on the 'minimal standard' proposed by Park and Miller \cite{ParkMiller88a}, which generates a sequence of integer random numbers by
\[
\eta_{n+1} = a\eta_n \mod m
\]
(C-1)
with \( a = 75 = 16807 \) and \( m = 2^{31}-1 = 2147483647 \).

To prevent overflows on a 32 bit computer, Schrage's method is used and Eq. (C-1) is written as
\[
\begin{align*}
\eta_{n+1} &= a(\eta_n \mod q) - r(\eta_n/q) & \text{if } \geq 0 \\
\eta_{n+1} &= a(\eta_n \mod q) - r(\eta_n/q) + m & \text{if } < 0
\end{align*}
\]
(C-2)
with
\[
q = m/a = 127773 \\
r = m \mod a = 2836
\]
(C-3)
Since this minimal standard (ran0 in 'Numerical Recipies' \cite{Pressetal92}) does not pass all statistical tests extremely well and successive numbers differ by at most a factor of 16807 - which leads to problems if extremely small numbers are generated - a modification (ran1 in 'Numerical Recipies') was actually used.
Besides some safeguards that prevent initialization with $\eta_1 = 0$ and the return of endpoint values, a Bays-Durham shuffling was used to further randomize the output. This algorithm produces about $10^8$ ($= m/20$) random numbers that pass all statistical test. The listing below is a TCL version, that was used by DISCOVER to produce random numbers for a Hybrid Monte Carlo simulation:

```tcl
set randomSeed 222222
set ldum -567
set ia 16807
set im 2147483647
set am [expr 1.0 / $im ]
set iq 127773
set ir 2836
set ntab 32
set ndiv [expr 1 + {($im -1) / $ntab}]
set eps 1.2e-7
set rnmx [expr 1.0 - $eps ]
set iy 0
for [set i [expr $ntab + 7]] [$i >- 0) (incr i -1) ];
  set iv($i) 0
}
proc random [...] {global la im am lq ir ntab ndiv eps rnmx ldum
  global iy iv
  if (($idum <- 0) || (!$iy) ) {
    if {(-$idum) < 1} then {$idum = 1) else {$idum = -$idum}
    for (set j [expr $ntab + 7]} [{$j >= 0) (incr j -1) ];
      set k [expr $idum/$iq]
      $idum - $ia * ($idum - $k * $iq) - $ir * $k
      if {$idum < 0] [ $idum = $idum + $im]
      if {$j < $ntab} [set iv($j) $idum]
    }
    set iy $iv(0)
  }
  set k [expr $idum/$iq]
  $idum - $ia * ($idum - $k * $iq) - $ir * $k
  if {$idum < 0] [ $idum = $idum + $im]
  set j [expr $iy / $ndiv ]
  set iy $iv($j)
  set iv($j) $idum
  if {($am * $iy) > $rnmx} then [ return $rnmx] \ 
    else [ return [ expr $am * $iy ]]
}

C-2: Lagged Fibonacci Algorithm

The second algorithm that was used in this work is a highly portable and vectorizable code that uses lagged Fibonacci series.\textsuperscript{Petersen93a} The basic math of the code is quite simple,

\[ t = \eta_{n-r} + \eta_{n-s} \]

\[ \eta_n = t - \text{float}(\text{int}(t)) \]  \hspace{1cm} (C-4)
but permits - with \( r = 273 \) and \( s = 607 \) - to calculate reasonably good random numbers with extremely long periods \((2^{48} \cdot (2^{607} - 1))\).

The code from Petersen\textsuperscript{Petersen93a} is fully vectorizable, fast and portable to all machines used in this work (SGI Indigo and Crimson, IBM RS6000/560 and DEC Alpha) and was therefore used in all Monte Carlo simulations. It is, however, not as well characterized as the multiplicative congruential algorithm, but seems to be reasonably random (Marsaglia plots in 2D and 3D reveal no patterns). Normally, Monte Carlo simulations are not erroneous due to a 'bad' random number generator, but because of systematic errors due to finite relaxation times in finite lattices.\textsuperscript{Stauffer96a}

Appendix D: Phase Space Volume Preservation of Integrators

D-1: Introduction

The integration can be viewed as a transformation in phase-space that transforms old coordinates \( x \) and velocities \( v \)

\[
(x, v) \rightarrow (x', v') \tag{D-1}
\]

to new coordinates \( x' \) and velocities \( v' \). According to Eq. (A-17), the Jacobian of this transformation is

\[
\begin{bmatrix}
\frac{\partial x'}{\partial x} & \frac{\partial x'}{\partial v} \\
\frac{\partial x}{\partial x} & \frac{\partial x}{\partial v} \\
\frac{\partial v'}{\partial x} & \frac{\partial v'}{\partial v}
\end{bmatrix}. \tag{D-2}
\]

For the integration algorithm to be canonical, it must be volume-preserving in the phase space, i.e. its Jacobian-determinate must be 1 (Eq. (A-20)).

D-2: The Velocity Verlet Algorithm

The Velocity-Verlet algorithm is defined by\textsuperscript{Swpe82a}

\[
x' = x + \Delta t v + \frac{1}{2} \Delta t^2 \frac{f(x)}{m}
\]

\[
v = v + \frac{1}{2} \frac{\Delta t}{m} [f(x) + f(x')] = v + \frac{1}{2} \frac{\Delta t}{m} \left[ f(x) + f\left( x + \Delta t v + \frac{1}{2} \Delta t^2 \frac{f(x)}{m} \right) \right]. \tag{D-3}
\]

The differentiations of Eq. (D-2), performed on the next few lines,
\[
\frac{dx'}{dx} = 1 + \frac{1}{2} \frac{\Delta t^2}{m} \frac{df}{dx}
\]

\[
\frac{dx'}{dv} = \Delta t
\]

\[
\frac{dv'}{dx} = \frac{1}{2} \frac{\Delta t^2}{m} \left[ \frac{df}{dx} \bigg|_x + \frac{df}{dx} \bigg|_{x'} \left( 1 + \frac{1}{2} \frac{\Delta t^2}{m} \frac{df}{dx} \right) \right],
\]

\[
\frac{dv'}{dv} = 1 + \frac{1}{2} \frac{\Delta t^2}{m} \frac{df}{dx} \bigg|_x \cdot \Delta t
\]

result in the following determinate of the Jacobian:

\[
\begin{vmatrix}
\frac{dx}{dx'} & \frac{dx}{dv'} \\
\frac{dv}{dx'} & \frac{dv}{dv'} \\
\end{vmatrix} = 1 + \frac{1}{2} \frac{\Delta t^2}{m} \frac{df}{dx} \bigg|_x + \frac{1}{2} \frac{\Delta t^2}{m} \frac{df}{dx} \bigg|_{x'} \cdot \Delta t
\]

\[
-\frac{1}{2} \frac{\Delta t^2}{m} \frac{df}{dx} \bigg|_x - \frac{1}{2} \frac{\Delta t^2}{m} \frac{df}{dx} \bigg|_{x'} - \frac{1}{4} \frac{\Delta t^4}{m} \frac{df}{dx} \bigg|_x \frac{df}{dx} \bigg|_{x'}
\]

It can thus be shown analytically that the velocity Verlet integrator is in principle capable of delivering canonical trajectories.

**D-3: The ABM4 and Runge-Kutta Integrators**

ABM4 (Adams-Bashforth-Moulton forth order) is a predictor-corrector method\textsuperscript{AllenTildesley89}, which requires two energy evaluations per timestep. The method itself is not self-starting - the first three steps are generated by the Runge-Kutta method\textsuperscript{MSIDiscov} First, the predictor step is carried out as

\[
r_p(t + \Delta t) = r(t) + \frac{\Delta t}{24} \left( 55v(t) - 59v(t - \Delta t) + 37v(t - 2\Delta t) - 9v(t - 3\Delta t) \right)
\]

\[
v_p(t + \Delta t) = v(t) + \frac{\Delta t}{24} \left( 55a(t) - 59a(t - \Delta t) + 37a(t - 2\Delta t) - 9a(t - 3\Delta t) \right)
\]

Using \(r_p\) and \(v_p\), \(v(t + \Delta t)\) and \(a(t + \Delta t)\) are calculated, which involves a force evaluation. With these values, the corrector is carried out as

\[
r_c(t + \Delta t) = r(t) + \frac{\Delta t}{24} \left( 9v(t + \Delta t) + 19v(t) - 5v(t - \Delta t) + v(t - 2\Delta t) \right)
\]

\[
v_c(t + \Delta t) = v(t) + \frac{\Delta t}{24} \left( 9a(t + \Delta t) + 19a(t) - 5a(t - \Delta t) + a(t - 2\Delta t) \right)
\]

The corrected \(r_c\) and \(v_c\) are used to compute \(v(t + \Delta t)\) and \(a(t + \Delta t)\), requiring another energy evaluation.

It does not seem to be possible to proof the area-preservation for the ABM4 algorithm analytically, for there is a whole history of variables that determine the
actual step. It is therefore necessary to establish a simple model system and to perform the integration of the trajectories and the check for the conservation of the phase space volume numerically.

**D-4: The Model System**

Serge Santos coded a predictor-corrector method with a Runge-Kutta start-up sequence and made the comparison of its behaviour to the velocity-Verlet and the Leapfrog algorithm. The program computes seven trajectories with each method for a number of particles: one trajectory with the initial set of coordinates and velocities and six trajectories with small deviations in one of the space and velocity components. The volume of the phase space at the beginning and at the end is compared. If the volume remains constant, this can be viewed as a demonstration of the area-preservation (not a proof, of course).

A new spherical potential was used with the following form:

\[
E = \frac{\varepsilon}{\sigma} \left( \frac{n}{n-1} \right)^{n-1} \cdot \left( \frac{r}{n\sigma} \right)^{n-1} \cdot (r - n\sigma),
\]  

where \( \sigma \) and \( \varepsilon \) are interaction parameters and \( n \) is a number proportional to the steepness of the potential.

![Figure D.1: Plots of the model potential for \( n = 2,3,...,8 \). At \( r = 0 \), the energy is zero and reaches a minimum of \(-\varepsilon\) at \( r = (n-1)\sigma \). The energy is zero again at \( r = n\sigma \) and raises then proportional to \( r^n \).](image)

Particles were inserted randomly at places where the potential energy was
negative. The velocity of the particles was also chosen randomly from the Boltzmann distribution of a given temperature. A small box in phase space around the atoms was transformed and the volume of this box was measured at the beginning and at the end. To be precise, the ratio of the final and initial volumes is obtained by an extrapolation of the box volume to infinitely small values in several steps.

If an algorithm is area-preserving, the ratio of the initial and the final volume

\[
\frac{V_{\text{final}}}{V_{\text{initial}}} \rightarrow 1.0
\]

is exactly 1.0.

**D-5: The Results**

As Table D-1 shows, only the Velocity Verlet algorithm is canonical (which can be proved analytically, too). The other two algorithms show bigger or smaller deviations from canonicity.

The Runge-Kutta and the ABM4 algorithm show the same results after one step, because the ABM4 integrator is started by a Runge-Kutta sequence. On the average, the Leapfrog algorithm behaves similar to velocity Verlet. This is not surprising, since the two methods - differing in the details of implementation - are algebraically equivalent.\(^{Frenkel96a}\)

This failure to sample the phase space canonically can have a drastic influence on the results, as the following data exhibits:

At BAYER, \(T\alpha N\) simulations of 100 ps (in steps of 0.5 fs) without equilibration were performed on several BPA-PC cubes of 20 Å. The equilibration was skipped because the generation of the cubes involved multiple stages of minimi-
Table D-1: The conservation of the phase-space volume by different integration schemes.
Parameters: 1 MD step, $T = 300\, K$, $\sigma = 3.94\, \text{Å}$, $n = 5$, $|\Delta x| = 0.5\, \text{Å}$, $|\Delta v| = 0.5\, \text{Å/fs}$, decrement factor = 0.8, # of decrements = 3

<table>
<thead>
<tr>
<th>Particle #</th>
<th>Vel.verlet</th>
<th>ABM4 = Runge-Kutta</th>
<th>Leapfrog</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.00000 ± 0.0</td>
<td>0.29871 ± 0.00019</td>
<td>0.82373 ± 0.06229</td>
</tr>
<tr>
<td>2</td>
<td>1.00000 ± 0.0</td>
<td>1.00180 ± 0.00001</td>
<td>1.00382 ± 0.00006</td>
</tr>
<tr>
<td>3</td>
<td>1.00000 ± 0.0</td>
<td>0.75618 ± 0.00322</td>
<td>0.99186 ± 0.08841</td>
</tr>
<tr>
<td>4</td>
<td>1.00000 ± 0.0</td>
<td>0.27641 ± 0.00001</td>
<td>1.01526 ± 0.00116</td>
</tr>
<tr>
<td>5</td>
<td>1.00000 ± 0.0</td>
<td>0.68185 ± 0.00001</td>
<td>0.99405 ± 0.00181</td>
</tr>
<tr>
<td>6</td>
<td>1.00000 ± 0.0</td>
<td>0.28967 ± 0.04553</td>
<td>0.98855 ± 0.04987</td>
</tr>
<tr>
<td>7</td>
<td>1.00000 ± 0.0</td>
<td>0.71601 ± 0.00006</td>
<td>1.04379 ± 0.00821</td>
</tr>
<tr>
<td>8</td>
<td>1.00000 ± 0.0</td>
<td>0.92880 ± 0.00007</td>
<td>1.02598 ± 0.00119</td>
</tr>
<tr>
<td>9</td>
<td>1.00000 ± 0.0</td>
<td>0.89946 ± 0.00011</td>
<td>0.95504 ± 0.00241</td>
</tr>
<tr>
<td>10</td>
<td>1.00000 ± 0.0</td>
<td>0.40716 ± 0.00001</td>
<td>1.05048 ± 0.00668</td>
</tr>
</tbody>
</table>

zation and MD simulations. While the other parameters were held constant, two different integrators, the ABM4 and the velocity variant of the Verlet algorithm were used. The elastic constants were calculated from the Parrinello-Rahman strain fluctuation approach. The next table shows, that they proved to be very sensitive to the choice of the integrator:

Table D-2: The elastic constants of BPA-PC (strain fluctuations)

<table>
<thead>
<tr>
<th>Method</th>
<th>$\lambda$ [GPa]</th>
<th>$\mu$ [GPa]</th>
<th>$\rho$ [g/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABM4</td>
<td>8 - 10</td>
<td>3 - 3.5</td>
<td>1.205</td>
</tr>
<tr>
<td>Velocity-Verlet</td>
<td>4.2 - 4.8</td>
<td>0.8 - 1.2</td>
<td>1.185</td>
</tr>
<tr>
<td>Experiment</td>
<td>4.2 - 5.7</td>
<td>0.8 - 1.1</td>
<td>1.20</td>
</tr>
</tbody>
</table>

As can be clearly seen, correct values for the elastic constants can only be obtained if the phase space is sampled correctly.
Appendix E: Reduced Units

If a system consists of identical particles which interact only with a simple Lennard-Jones potential, its behaviour is completely specified by a few parameters like the particle mass $m_a$, the distance of zero interaction energy $\sigma$, and the depth of the potential $\epsilon$. It is convenient to define the fundamental quantities of mass, distance and energy in terms of these parameters in order to obtain results that are independent of the particular choice of $m_a$, $\sigma$, and $\epsilon$. The physical quantities convert as follows:

\[
\begin{align*}
m^* &= \frac{m}{m_a} & \text{a)} \\
r^* &= \frac{r}{\sigma} & \text{b)} \\
E^* &= \frac{E}{\epsilon} & \text{c)} \\
T^* &= \frac{kT}{\epsilon} & \text{d)} \\
\rho^* &= \rho \sigma^3 & \text{e)} \\
p^* &= \frac{\rho \sigma^3}{\epsilon} & \text{f)} \\
t^* &= \left(\frac{\epsilon}{m \sigma^2}\right)^{1/2} t & \text{g)} \\
f^* &= \frac{f}{\sigma} & \text{h)} \\
C_{ij}^* &= C_{ij} V / N k T & \text{i)}
\end{align*}
\]

and so on.

Using reduced units, the functional form of the Lennard-Jones $m-n$ potential (Eq. (2-8)) and the expression of the forces simplify to

\[
U^* = 4 \left[ \frac{1}{r^*^m} - \frac{1}{r^*^n} \right] \quad \text{(E-2)}
\]

and

\[
f_{\alpha\beta k}^* = 24 \left( \frac{x_k^{n+2}}{r_{\alpha\beta}^n} - 2 \frac{x_k^{m+2}}{r_{\alpha\beta}^m} \right) \quad \text{(E-3)}
\]

which greatly increases the computational efficiency.\cite{AllenTildesley89}

For MD simulations of Lennard-Jones systems, it is necessary to obtain the distribution of the initial velocities and the equations of motion in reduced units. Expressing the velocities in reduced units,

\[
\begin{align*}
\mathbf{v}^* &= \left( \frac{m}{\epsilon} \right)^{1/2} \mathbf{v} & \Rightarrow \mathbf{v} &= \left( \frac{\epsilon}{m} \right)^{1/2} \mathbf{v}^* , \quad \text{(E-4)}
\end{align*}
\]
allows to write the distribution of initial velocities as

\[ p^* (v^*) dv^* = \left( \frac{1}{2\pi T^*} \right)^{\frac{1}{2}} \exp \left( -\frac{v_i^*}{2T^*} \right) \sqrt{\varepsilon} dv^* = \left( \frac{1}{2\pi T^*} \right)^{\frac{1}{2}} \exp \left( -\frac{v_i^*}{2T^*} \right) dv^* \]  

(E-5)

which is identical to a gaussian distribution with a mean value of 0 and a second moment of \( \sqrt{T^*} \). The velocity-Verlet integrator (Eq. (2.77)) is written in reduced units as

\[ r^* (f^* + 8f^*) = r^* (f^*) + \frac{1}{2} \delta t^* a^* (f^*) \]  

(E-6)

\[ v^* (f^* + 8f^*) = v^* (f^*) + \frac{1}{2} \delta t^* [a^* (f^*) + a^* (f^* + 8f^*)] \]

with the acceleration

\[ a^* = \left( \frac{\sigma m}{\varepsilon} \right) a \quad \Leftrightarrow \quad a = \frac{v}{t} = \left( \frac{\varepsilon}{\sigma m} \right) a^*. \]  

(E-7)

Appendix F: Elastic constants of ‘ordered’ it-PP

A \( \tau N \)-MD simulation of 1000 ps (2.10^6 steps) has been performed with a completely ordered it-PP structure. The averages of the strain and the stress-strain fluctuations of the last 500 ps have been used to calculate the matrix of the elastic constants:

Table F-1: Elastic constants averaged over the last 500 ps of a 1000 ps \( \tau N \)-MD simulation at 300 K. Non-zero components are bold faced.

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<tr>
<th>( \frac{kT}{\langle V \rangle} \langle \eta_{ij} \eta_{lm} \rangle^{-1} )</th>
<th>( \langle \eta_{ij} \sigma_{ij} \rangle \langle \eta_{nj} \eta_{lm} \rangle^{-1} )</th>
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The difference to the matrix of the disordered structure (Table 4-30) is not significant, although the components, which should be zero due to the crystal symmetry, are in general smaller.
Appendix G: Cluster Dynamics and Elastic Constants of PA-6

G-1: Cluster Dynamics of Water in Amorphous PA-6

This appendix lists in tabular form the water cluster sizes of three amorphous PA-6 microstructures with 35 water molecules at 150, 300, and 450 K.

Table G-1: 150 K, Structure 1

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### Table G-9: 450 K, Structure 3

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</tr>
</tbody>
</table>
G-2: Elastic Constants of 'Dry' and 'Wet' PA-6

In the next eight tables, the elastic constants of PA-6 are listed for the dry and wet microstructures at 0, 150, 300, and 450 K. The elastic constants were obtained from the stress-strain fluctuations of the last 500 ps of the 1000 ps TtN-MD runs.

Table G-10: Static minimum energy elastic constants of 'dry' and 'wet' PA-6

<table>
<thead>
<tr>
<th>Dry, 0 K, Structure 1</th>
<th>Wet, 0 K, Structure 1</th>
<th>Wet, 0 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.5 6.1 5.9 -0.4 0.0 0.0</td>
<td>13.6 6.8 6.3 -0.6 0.5 0.9</td>
<td>13.9 6.6 6.7 0.3 0.2 0.3</td>
</tr>
<tr>
<td>6.1 14.3 6.6 -0.2 -0.2 0.4</td>
<td>6.6 13.7 6.1 -1.4 -0.4 -1.0</td>
<td>6.6 13.5 6.3 0.5 0.2 0.0</td>
</tr>
<tr>
<td>5.9 6.6 10.7 0.1 -0.2 0.0</td>
<td>6.5 6.1 14.9 -0.6 -0.4 -0.1</td>
<td>6.7 6.3 13.5 0.3 -0.2 -0.3</td>
</tr>
<tr>
<td>-0.4 -0.2 0.1 3.4 -0.3 -0.2</td>
<td>-0.6 -1.4 -0.6 3.3 0.6 0.2</td>
<td>0.3 0.5 0.3 2.8 -0.1 -0.1</td>
</tr>
<tr>
<td>0.0 -0.2 -0.2 -0.3 2.8 0.0</td>
<td>0.5 -0.4 -0.4 0.6 3.5 -0.3</td>
<td>0.2 0.2 -0.2 -0.1 3.3 -0.1</td>
</tr>
<tr>
<td>0.0 0.4 0.0 -0.2 0.0 3.1</td>
<td>0.9 -1.0 -0.1 0.2 -0.3 3.4</td>
<td>0.3 0.0 -0.3 -0.1 -0.1 3.5</td>
</tr>
</tbody>
</table>

Table G-11: Elastic constants of 'dry' PA-6 at 150 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Dry, 150 K, Structure 1</th>
<th>Dry, 150 K, Structure 2</th>
<th>Dry, 150 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.4 5.2 4.2 -0.3 0.6 -0.2</td>
<td>8.5 6.1 6.1 0.4 -0.3 0.1</td>
<td>11.9 6.3 5.2 -0.1 0.3 -0.7</td>
</tr>
<tr>
<td>6.0 12.9 6.8 0.3 0.2 0.4</td>
<td>7.2 11.5 6.4 -0.1 0.0 0.1</td>
<td>6.5 9.4 5.0 -0.1 -0.6 0.0</td>
</tr>
<tr>
<td>4.9 6.8 8.7 -0.3 0.4 0.0</td>
<td>5.5 4.7 9.1 0.0 0.6 0.0</td>
<td>4.5 4.3 8.3 -0.3 -0.3 -0.2</td>
</tr>
<tr>
<td>-0.4 0.3 -0.3 2.4 -0.3 0.0</td>
<td>0.5 -0.1 0.0 2.1 -0.3 -0.2</td>
<td>-0.1 -0.1 0.3 1.6 0.1 -0.3</td>
</tr>
<tr>
<td>0.6 0.2 0.3 -0.3 1.6 0.0</td>
<td>-0.3 0.0 0.6 -0.2 2.9 -0.1</td>
<td>0.3 -0.5 -0.4 0.2 1.7 0.0</td>
</tr>
<tr>
<td>-0.3 0.4 0.0 0.0 0.0 1.8</td>
<td>0.1 0.1 0.0 -0.2 -0.1 2.4</td>
<td>-0.6 0.0 -0.2 -0.3 0.0 1.7</td>
</tr>
</tbody>
</table>

Table G-12: Elastic constants of 'wet' PA-6 at 150 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Wet, 150 K, Structure 1</th>
<th>Wet, 150 K, Structure 2</th>
<th>Wet, 150 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6 4.6 5.0 0.0 -0.7 0.6</td>
<td>12.2 6.5 7.1 -0.1 0.2 0.4</td>
<td>11.6 6.4 6.1 -0.0 -0.3 0.2</td>
</tr>
<tr>
<td>7.1 12.5 8.2 -0.2 -0.0 0.3</td>
<td>6.4 10.7 5.8 0.4 -0.3 0.6</td>
<td>7.1 13.1 7.9 0.3 -0.3 0.0</td>
</tr>
<tr>
<td>5.6 6.0 10.6 0.3 -0.1 1.0</td>
<td>7.2 6.1 10.1 -0.5 0.3 -0.3</td>
<td>5.0 5.9 9.6 0.2 -0.0 -0.4</td>
</tr>
<tr>
<td>0.0 -0.2 0.4 2.2 0.0 0.3</td>
<td>-0.1 0.4 0.5 2.2 -0.2 0.5</td>
<td>-0.0 0.3 0.2 1.9 -0.1 -0.3</td>
</tr>
<tr>
<td>-0.7 -0.0 -0.1 0.0 2.0 0.3</td>
<td>0.2 -0.3 0.3 -0.2 2.0 -0.5</td>
<td>-0.2 -0.2 0.0 -0.1 2.2 -0.2</td>
</tr>
<tr>
<td>0.8 0.2 0.1 0.3 0.3 1.5</td>
<td>0.5 0.6 -0.3 0.5 -0.5 1.8</td>
<td>0.2 0.0 -0.5 -0.4 -0.3 2.4</td>
</tr>
</tbody>
</table>

λ = 5.71 ± 0.42, μ = 2.10 ± 0.26
λ = 5.81 ± 0.26, μ = 2.06 ± 0.16
λ = 5.27 ± 0.29, μ = 2.05 ± 0.18
Table G-13: Elastic constants of 'dry' PA-6 at 300 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Dry, 300 K, Structure 1</th>
<th>Dry, 300 K, Structure 2</th>
<th>Dry, 300 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.9 4.1 4.2 0.1 0.3 0.5</td>
<td>5.3 5.1 4.7 0.0 0.1 0.1</td>
<td>7.7 4.9 4.1 0.2 0.3 0.4</td>
</tr>
<tr>
<td>4.6 6.7 4.4 0.2 0.2 0.2</td>
<td>5.8 8.8 4.9 0.1 0.3 0.2</td>
<td>4.4 6.7 4.3 0.3 0.1 0.0</td>
</tr>
<tr>
<td>4.7 4.4 6.4 0.2 0.0 0.1</td>
<td>4.2 3.8 5.7 0.1 0.5 0.3</td>
<td>3.4 3.9 5.7 0.2 0.2 0.4</td>
</tr>
<tr>
<td>-0.2 -0.2 -0.2 1.1 0.0 0.1</td>
<td>0.0 0.1 0.1 1.2 -0.2 -0.2</td>
<td>0.2 0.3 0.2 0.8 0.1 0.5</td>
</tr>
<tr>
<td>0.3 -0.2 0.0 0.0 0.1 2.3</td>
<td>0.1 0.2 0.5 0.2 1.1 0.0</td>
<td>0.2 -0.1 -0.2 0.1 1.0 -0.1</td>
</tr>
<tr>
<td>-0.6 -0.2 -0.1 0.1 0.8</td>
<td>0.1 0.2 0.4 0.2 0.0 1.6</td>
<td>-0.4 0.0 0.4 0.5 0.1 1.4</td>
</tr>
</tbody>
</table>

$\lambda = 4.35 \pm 0.11, \mu = 0.99 \pm 0.07$

Table G-14: Elastic constants of 'wet' PA-6 at 300 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Wet, 300 K, Structure 1</th>
<th>Wet, 300 K, Structure 2</th>
<th>Wet, 300 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.7 4.2 4.2 0.1 -0.2 0.2</td>
<td>5.9 3.5 5.0 -0.2 0.1 0.2</td>
<td>7.2 5.0 5.3 0.1 -0.3 0.6</td>
</tr>
<tr>
<td>5.2 7.4 5.2 0.3 -0.1 0.2</td>
<td>4.1 5.4 4.0 -0.1 -0.2 0.2</td>
<td>4.8 7.3 5.0 -0.1 -0.0 0.5</td>
</tr>
<tr>
<td>4.3 4.3 6.0 -0.1 -0.2 0.3</td>
<td>5.2 4.2 5.9 -0.1 0.2 -0.1</td>
<td>4.6 4.5 6.4 -0.1 -0.1 -0.1</td>
</tr>
<tr>
<td>0.1 0.3 -0.1 0.9 0.0 0.1</td>
<td>-0.2 -0.1 -0.1 0.8 -0.2 0.1</td>
<td>0.1 -0.1 -0.1 0.7 0.1 0.0</td>
</tr>
<tr>
<td>-0.2 -0.1 -0.1 0.0 0.5 0.2</td>
<td>-0.1 -0.2 -0.2 0.9 -0.2</td>
<td>-0.3 -0.0 -0.1 0.1 0.7 0.2</td>
</tr>
<tr>
<td>0.1 0.1 0.4 0.1 0.2 0.3</td>
<td>0.2 -0.2 -0.1 0.1 -0.2 0.5</td>
<td>0.6 0.5 -0.1 0.0 0.2 0.6</td>
</tr>
</tbody>
</table>

$\lambda = 4.53 \pm 0.11, \mu = 0.78 \pm 0.07$

Table G-15: Elastic constants of 'wet' PA-6 at 450 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Dry, 450 K, Structure 1</th>
<th>Dry, 450 K, Structure 2</th>
<th>Dry, 450 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0 1.5 1.6 0.2 -0.2 0.0</td>
<td>2.3 1.9 1.7 -0.2 -0.1 0.2</td>
<td>3.2 2.4 2.6 0.1 -0.1 -0.2</td>
</tr>
<tr>
<td>2.6 3.5 3.0 0.1 -0.2 0.0</td>
<td>3.5 4.0 3.3 -0.1 -0.1 0.0</td>
<td>2.9 3.6 3.0 0.2 0.1 0.1</td>
</tr>
<tr>
<td>1.9 2.1 2.3 -0.1 0.0 0.1</td>
<td>1.6 1.7 2.1 -0.1 -0.1 0.1</td>
<td>2.4 2.3 2.8 0.1 0.1 0.1</td>
</tr>
<tr>
<td>0.3 0.1 0.2 0.3 0.0 0.1</td>
<td>-0.2 -0.1 -0.1 0.2 0.0</td>
<td>0.1 0.1 0.1 0.3 0.0 -0.1</td>
</tr>
<tr>
<td>-0.2 -0.1 -0.0 0.0 0.2 0.0</td>
<td>-0.1 -0.0 -0.1 0.3 0.0</td>
<td>-0.1 -0.1 -0.1 0.0 0.2 -0.1</td>
</tr>
<tr>
<td>0.0 0.0 0.1 -0.1 0.1 0.2</td>
<td>0.2 0.0 0.1 0.0 0.0 0.3</td>
<td>-0.2 0.1 -0.1 -0.1 0.4</td>
</tr>
</tbody>
</table>

$\lambda = 2.14 \pm 0.07, \mu = 0.23 \pm 0.04$

Table G-16: Elastic constants of 'wet' PA-6 at 450 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Wet, 450 K, Structure 1</th>
<th>Wet, 450 K, Structure 2</th>
<th>Wet, 450 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5 1.2 1.1 -0.0 -0.1 0.0</td>
<td>1.7 1.4 1.3 0.0 0.1 0.3</td>
<td>1.7 1.4 1.7 -0.1 -0.1 0.1</td>
</tr>
<tr>
<td>1.0 1.2 1.0 -0.1 -0.1 -0.0</td>
<td>1.3 1.3 1.3 0.0 0.1 0.2</td>
<td>0.7 0.8 0.8 0.0 0.0 -0.1</td>
</tr>
<tr>
<td>0.6 0.8 0.6 -0.0 -0.0 -0.0</td>
<td>0.7 0.6 0.7 -0.0 0.1 0.1</td>
<td>0.6 0.5 0.7 0.0 -0.0 -0.1</td>
</tr>
<tr>
<td>-0.0 -0.1 -0.0 0.0 0.0 0.0</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
<td>-0.0 0.0 0.0 -0.0 0.1 0.0</td>
</tr>
<tr>
<td>-0.1 -0.1 -0.0 0.0 0.1 0.0</td>
<td>0.1 0.0 0.1 0.0 0.1 0.0</td>
<td>0.1 0.0 0.0 0.0 0.1 -0.1</td>
</tr>
<tr>
<td>0.0 -0.0 -0.1 -0.0 0.0 0.2</td>
<td>0.3 0.2 0.2 0.0 0.0 0.2</td>
<td>-0.1 -0.1 -0.1 0.0 -0.1 0.1</td>
</tr>
</tbody>
</table>

$\lambda = 0.85 \pm 0.02, \mu = 0.10 \pm 0.01$

$\lambda = 1.06 \pm 0.05, \mu = 0.07 \pm 0.03$

$\lambda = 0.92 \pm 0.04, \mu = 0.07 \pm 0.02$
Appendix H: Elastic Constants of PA-12

In the next eight tables, the elastic constants of PA-6 are listed for the dry and wet microstructures at 0, 150, 300, and 450 K. Except the static minimum energy approach, all matrices were calculated from the fluctuations of the stresses and strains in the last 500 ps of the 1000 ps TttN-MD simulation.

Table H-1: Elastic constants of 'dry' PA-12 at 150 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Dry, 150 K, Structure 1</th>
<th>Dry, 150 K, Structure 2</th>
<th>Dry, 150 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.7 4.3 3.9 0.1 -0.5 -0.2</td>
<td>4.7 5.4 6.5 -1.4 -0.8 -0.2</td>
<td>7.5 4.6 4.6 0.0 0.2 0.3</td>
</tr>
<tr>
<td>4.3 6.6 3.2 0.3 -0.2 -0.5</td>
<td>5.2 7.7 5.2 0.6 -1.0 -1.9</td>
<td>4.5 7.6 4.3 0.1 0.4 -0.1</td>
</tr>
<tr>
<td>4.0 3.4 6.5 0.4 -0.4 -0.2</td>
<td>6.9 4.0 4.5 0.7 1.1 1.1</td>
<td>4.5 4.2 8.2 0.1 0.2 -0.1</td>
</tr>
<tr>
<td>0.1 0.4 0.3 1.4 -0.1 -0.1</td>
<td>-1.1 0.5 0.0 0.5 0.2 0.6</td>
<td>0.0 0.2 0.1 1.4 -0.2 -0.3</td>
</tr>
<tr>
<td>-0.5 -0.2 -0.2 -0.1 1.5 0.1</td>
<td>-0.9 -0.6 1.0 0.3 1.3 -0.5</td>
<td>-0.4 0.3 0.8 -0.1 1.7 -0.1</td>
</tr>
<tr>
<td>-0.3 0.5 -0.2 0.0 0.1 1.0</td>
<td>0.7 -1.5 0.7 -1.3 -0.7 0.1</td>
<td>0.0 0.1 -0.3 0.0 -0.1 1.9</td>
</tr>
</tbody>
</table>

\[ \lambda = 3.89 \pm 0.20, \mu = 1.49 \pm 0.13 \]

Table H-2: Elastic constants of 'wet' PA-12 at 150 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Wet, 150 K, Structure 1</th>
<th>Wet, 150 K, Structure 2</th>
<th>Wet, 150 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.4 3.9 4.5 -0.2 0.1 0.4</td>
<td>6.6 4.0 4.1 0.2 -0.3 -0.6</td>
<td>7.3 4.2 4.1 -0.1 0.4 0.2</td>
</tr>
<tr>
<td>3.9 7.2 4.4 0.0 -0.4 -0.8</td>
<td>3.9 5.8 4.0 -0.8 -0.3 0.2</td>
<td>4.2 6.4 3.4 0.0 -0.2 0.1</td>
</tr>
<tr>
<td>4.5 4.4 7.0 -0.7 -0.3 -0.1</td>
<td>4.3 3.9 7.8 -0.5 0.4 0.1</td>
<td>4.0 3.4 6.0 -0.1 -0.4 0.1</td>
</tr>
<tr>
<td>0.0 -0.3 -0.1 1.3 0.0 0.0</td>
<td>0.3 -0.4 0.2 1.4 0.0 0.1</td>
<td>0.0 -0.1 0.0 1.1 0.0 -0.3</td>
</tr>
<tr>
<td>-0.1 -0.4 -0.1 0.1 1.3 -0.4</td>
<td>0.0 -0.3 -0.2 -0.3 1.2 -0.1</td>
<td>-0.3 -0.3 -0.1 -0.1 1.4 -0.3</td>
</tr>
<tr>
<td>0.1 -0.7 -0.2 0.0 -0.1 1.0</td>
<td>0.0 -0.2 0.1 0.0 -0.1 0.9</td>
<td>0.2 0.1 0.0 -0.2 -0.2 0.7</td>
</tr>
</tbody>
</table>

\[ \lambda = 4.38 \pm 0.18, \mu = 1.38 \pm 0.12 \]

Table H-3: Elastic constants of 'dry' PA-12 at 300 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Dry, 300 K, Structure 1</th>
<th>Dry, 300 K, Structure 2</th>
<th>Dry, 300 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.6 2.6 2.6 -0.2 0.1 -0.3</td>
<td>3.3 2.6 2.8 0.2 0.3 0.3</td>
<td>4.4 2.9 3.1 0.0 0.3 -0.1</td>
</tr>
<tr>
<td>2.7 3.1 2.3 0.0 -0.3 -0.3</td>
<td>2.5 3.4 2.8 -0.2 0.0 0.1</td>
<td>2.9 4.3 2.5 0.1 0.2 -0.1</td>
</tr>
<tr>
<td>2.6 2.2 3.3 -0.2 -0.1 -0.1</td>
<td>2.7 2.9 3.7 0.3 0.0 0.2</td>
<td>3.0 2.5 4.4 0.0 0.2 -0.2</td>
</tr>
<tr>
<td>-0.2 0.0 -0.2 0.4 0.0 0.0</td>
<td>0.1 -0.1 0.2 0.4 0.0 0.1</td>
<td>0.0 0.0 0.1 0.7 0.2 0.1</td>
</tr>
<tr>
<td>0.1 0.3 -0.1 0.0 0.5 0.1</td>
<td>0.2 0.1 0.2 0.0 0.7 0.1</td>
<td>0.2 0.1 0.3 0.2 0.6 -0.2</td>
</tr>
<tr>
<td>-0.3 -0.2 -0.1 0.0 0.1 0.5</td>
<td>0.3 0.2 0.2 0.0 0.0 0.3</td>
<td>-0.1 -0.1 -0.3 0.2 -0.2 0.4</td>
</tr>
</tbody>
</table>

\[ \lambda = 2.48 \pm 0.09, \mu = 0.44 \pm 0.05 \]
#### Table H-4: Elastic constants of 'wet' PA-12 at 300 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Wet, 300 K, Structure 1</th>
<th>Wet, 300 K, Structure 2</th>
<th>Wet, 300 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 2.9 3.0 -0.1 0.2 0.0</td>
<td>3.8 2.8 3.1 0.1 -0.2 0.0</td>
<td>4.0 2.7 2.9 -0.1 0.1 0.0</td>
</tr>
<tr>
<td>3.0 3.5 2.6 0.1 -0.1 -0.2</td>
<td>2.8 3.4 2.6 0.1 -0.2 0.6</td>
<td>2.5 3.6 2.4 -0.1 0.0 0.0</td>
</tr>
<tr>
<td>3.2 2.7 4.3 -0.5 -0.1 -0.2</td>
<td>3.0 2.7 3.8 0.2 0.1 -0.1</td>
<td>2.8 2.4 3.1 -0.1 0.0 -0.2</td>
</tr>
<tr>
<td>-0.1 -0.1 -0.2 0.5 0.1 0.0</td>
<td>0.1 0.2 0.1 0.7 0.2 0.1</td>
<td>-0.1 -0.1 0.0 0.4 0.1 0.0</td>
</tr>
<tr>
<td>0.1 -0.1 0.1 0.1 0.5 -0.1</td>
<td>0.0 -0.2 -0.1 0.0 0.5 0.2</td>
<td>0.0 0.0 0.2 0.1 0.3 -0.1</td>
</tr>
<tr>
<td>0.0 -0.2 -0.3 0.1 0.0 0.6</td>
<td>0.2 0.3 -0.1 -0.1 0.1 0.6</td>
<td>0.0 0.0 -0.2 0.1 -0.1 0.4</td>
</tr>
</tbody>
</table>

\[ \lambda = 2.87 \pm 0.11, \mu = 0.56 \pm 0.07 \]

#### Table H-5: Elastic constants of 'wet' PA-12 at 450 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Dry, 450 K, Structure 1</th>
<th>Dry, 450 K, Structure 2</th>
<th>Dry, 450 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 1.1 1.1 0.0 0.0 0.0</td>
<td>1.6 1.4 1.4 0.0 0.1 0.0</td>
<td>0.8 0.6 0.5 0.0 0.1 0.1</td>
</tr>
<tr>
<td>1.1 1.2 1.1 0.0 0.1 0.1</td>
<td>1.2 1.3 1.2 0.0 0.0 0.0</td>
<td>0.6 0.7 0.5 0.0 0.0 0.0</td>
</tr>
<tr>
<td>1.2 1.2 1.3 0.0 0.1 0.0</td>
<td>1.1 1.1 1.2 0.0 0.0 0.1</td>
<td>0.5 0.5 0.5 0.0 0.0 0.1</td>
</tr>
<tr>
<td>0.0 -0.1 0.0 0.1 0.0 0.0</td>
<td>0.0 0.0 0.0 -0.1 0.0 0.0</td>
<td>0.0 0.0 0.0 0.0 0.1 0.0</td>
</tr>
<tr>
<td>0.1 0.1 0.0 0.0 0.1 0.0</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
<td>0.0 0.0 0.0 0.0 0.0 0.1</td>
</tr>
<tr>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
<td>-0.1 0.1 0.1 0.0 0.0 0.0</td>
<td>0.0 0.0 0.0 0.0 0.0 0.1</td>
</tr>
</tbody>
</table>

\[ \lambda = 1.10 \pm 0.02, \mu = 0.09 \pm 0.01 \]

#### Table H-6: Elastic constants of 'wet' PA-12 at 450 K, stress-strain fluctuation approach

<table>
<thead>
<tr>
<th>Wet, 450 K, Structure 1</th>
<th>Wet, 450 K, Structure 2</th>
<th>Wet, 450 K, Structure 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6 0.4 0.3 0.0 0.0 0.0</td>
<td>1.1 1.1 1.0 0.0 -0.2 -0.1</td>
<td>0.9 0.7 0.8 0.1 0.1 0.0</td>
</tr>
<tr>
<td>0.5 0.8 0.4 0.1 0.0 -0.1</td>
<td>1.0 1.5 1.2 0.0 -0.1 0.0</td>
<td>0.7 0.8 0.8 0.0 0.1 -0.1</td>
</tr>
<tr>
<td>0.3 0.3 0.5 0.0 0.0 -0.1</td>
<td>0.9 1.2 1.3 0.1 0.1 -0.1</td>
<td>0.8 0.8 1.1 0.0 0.0 0.1</td>
</tr>
<tr>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
<td>0.0 0.1 0.0 0.1 0.0 0.0</td>
<td>0.0 0.0 0.0 0.0 0.0 0.0</td>
</tr>
<tr>
<td>0.0 0.0 0.0 0.0 0.1 0.0</td>
<td>-0.1 -0.1 -0.1 0.1 0.1 0.0</td>
<td>0.1 0.1 0.1 0.0 0.0 0.0</td>
</tr>
<tr>
<td>[-0.1 0.0 -0.1 0.0 0.0 0.1]</td>
<td>[0.0 -0.1 -0.1 -0.1 0.1 0.0]</td>
<td>[0.0 0.0 -0.1 0.0 0.0 0.1]</td>
</tr>
</tbody>
</table>

\[ \lambda = 0.38 \pm 0.04, \mu = 0.11 \pm 0.03 \]

\[ \lambda = 1.10 \pm 0.05, \mu = 0.10 \pm 0.03 \]

\[ \lambda = 0.79 \pm 0.04, \mu = 0.07 \pm 0.03 \]
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Education

1973 - 1978        Primary school in Olten
1978 - 1986        Gymnasium B in Olten and Lucerne
1986 - 1992        Undergraduate studies in materials science at the
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                    Diploma thesis *Modelling of the Sorption of Water in
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                    guidance of Dr. A. Gusev
1993 - 1997        Postgraduate studies in the research group of Prof.
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Professional and Teaching Experience

1987 - 1991        Assistance at the Institute of Forming Technology
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1989 - 1997        Software development for Vibrotest AG in Buchrain
1993 - 1997        Assistance at the Institute of Polymers
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                    exercises)