Master Thesis

Constitutive law for single crystal silicon (SCSi) based on molecular dynamic potentials

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Diploma Thesis

Constitutive Law for Single Crystal Silicon (SCSi) based on Molecular Dynamic Potentials

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February, 2006

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Abstract

Using the Modified Embedded Atom Method (MEAM) a new material model was made accessible to FEM computations. This new model takes into account the molecular dynamics of diamond cubic crystals. It owns a degree of freedom that is not yet used in other potentials that are utilized: the internal displacement of the two sub-lattices in the crystal. This enables the model to reproduce the microscopic relaxation in such crystals as well as the Raman-frequencies in phonon dispersion diagrams that can be measured experimentally. For the case of single crystal silicon (SCSi) all three stiffness moduli were reproduced. Comparisons with experiments for the determination of the ultimative strength of SCSi showed that it behaves softer than real single crystal silicon.

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"Silicon is a test case for the development of empirical potentials for covalent materials. Its great technological importance, the vast amount of relevant experimental and theoretical studies available, and its intrinsic interest as the representative covalent material make it an ideal candidate for exploring to what extent the empirical potential approach can be exploited."

M.Z. Bazant, E. Kaxiras and J.F. Justo [1]
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Nomenclature

Within this thesis, scalars are typesetted in standard letters, vectors are printed bold, second order tensors are set bold and sanserif. Higher order tensors are set in blackboard bold letters. Bold upper case letters indicate quantities in the reference configuration, whereas bold lower case letters are quantities in the actual configuration.

Argument lists of functions are defined by [...] (e.g. \( f[x] \) is a function \( f \) with argument \( x \)), the list is order sensitive, i.e. \( g[\alpha, \beta] \neq g[\beta, \alpha] \).

Indices \( i, j, k \) and \( l \) designate either to which atom a quantity belongs or components of tensor quantities.

A good introduction into the algebra of vectors and tensors can be found in the first chapter of G.A. Holzapfel’s book ”Nonlinear solid mechanics” [2]. Therein are explained most common operators as contractions \([\cdot]\), double contractions \([\cdot;] \) and tensor products \([\otimes]\) which are used in this thesis.

The transposition \([ \ ]^T\) transposes the two outermost slots on the right of a tensor.

Scalars

- \( \alpha_i \) Decay factor for the universal energy function
- \( \beta_i \) Exponential decay factors for the atomic densities
- \( \lambda_j \) Stretch of vector \( \mathbf{m}_j \)
- \( \phi_{ij} \) Cosine of the angle between vectors \( \mathbf{m}_i \) and \( \mathbf{m}_j \)
- \( \Psi \) Pair potential
- \( \rho \) Strain energy density
- \( \rho \) Mass density
- Electron density
- \( \zeta \) Kleinman parameter
- \( a \) Lattice constant of a unit cell
- \( A_i \) Scaling factor for the embedding energy
- \( C^0_i \) Tensor coefficient
- \( E_0 \) Sublimation energy
- \( E_{< >} \) Elastic module
- \( E_{tot} \) Total deformation energy
- \( f_R \) Raman frequency
- \( J \) Volume ratio, \( J = \det [\mathbf{F}] \)
CONTENTS

\[ N \quad \text{Number of nearest neighbors} \]
\[ R_0 \quad \text{Initial bond length} \]
\[ r_{ij} \quad \text{Distance between atoms } i \text{ and } j \]
\[ s_i \quad \text{Geometry depending weighting factor} \]
\[ S_i^0 \quad \text{Tensor coefficient} \]
\[ S_{ij} \quad \text{Compliance} \]
\[ t_i \quad \text{Weighting factor for the atomic densities} \]
\[ Z_i \quad \text{Number of nearest neighbors} \]

**Vectors**

\[ e_i \quad \text{Orthonormal basis vector of the Euclidean space, } e_i \cdot e_j = \delta_{ij} \]
\[ G \quad \text{Internal force vector} \]
\[ M_j \quad \text{Structural vector} \]
\[ R_i \quad \text{Position vector of atom } i \]
\[ Z \quad \text{Vector of inner displacement} \]

**Higher order tensors**

\[ A \quad \text{First internal strain tensor} \]
\[ B \quad \text{Second internal strain tensor} \]
\[ C \quad \text{Elasticity} \]
\[ C^0 \quad \text{Partial elasticity} \]
\[ D \quad \text{Force-strain coupling tensor} \]
\[ \sigma \quad \text{Cauchy stress} \]
\[ C \quad \text{Right Cauchy-Green tensor} \]
\[ c' \quad \text{Jaumann stress rate} \]
\[ E \quad \text{Internal elasticity} \]
\[ F \quad \text{Deformation gradient} \]
\[ I \quad \text{Unity tensor} \]
\[ S \quad \text{Second Piola-Kirchhoff stress} \]
\[ S^0 \quad \text{Partial second Piola-Kirchhoff stress} \]
Functions and Operators

\( \chi \) Push forward Piola transformation

\( F \) Embedding function

Abbreviations

1NN-MEAM First Nearest Neighbor Modified Embedded Atom Method

2NN-MEAM Second Nearest Neighbor Modified Embedded Atom Method

DFT Density Functional Theory

EAM Embedded Atom Method

FEM Finite Element Method

ICP Ion Coupled Plasma

KOH Kalium-Hydroxide

LDA Local Density Approximation

MEAM Modified Embedded Atom Method

PUC Primitive Unit Cell

RIE Reactive Ion Etching

SCSi Single Crystal Silicon

StW Stillinger-Weber

UBER Universal Binding Energy Relation
1 Introduction

Single Crystal Silicon (SCSi) is used in a wide range of microelectronical and micromechanical applications. Its importance as a basic material comes from the well known process engineering (e.g. lithography) which allows to produce very exact structures in micron and sub-micron scales. Unfortunately, the surface topology is still governed by process based variations in nanometer scales e.g. sharp notches using anisotropic etching in KOH (kalium-hydroxide) or diffuse surface roughness by dry etching processes as ICP/RIE (Ion Coupled Plasma / Reactive Ion Etching). The presence of notches and roughness leads to difficulties in dimensioning such structures what often ends up with catastrophic failure. One major reason for this is the coupling between the governing surface varieties and the brittleness of single crystal silicon. Covalent bonded materials do not have any plastic regime, they stay elastic till the moment of failure. Dents, notches or cracks which act as stress amplifiers are the starting point for cracks leading to mirror-like flanks.

1.1 Continuum approach

The continuum approach is the major tool when designing structures where the dimensions of the deformed part are far from atomic length-scale. Under knowledge of geometry, outer forces and with locally defined partial differential equations the displacement and stress fields in the structure can be found. In case of SCSi, the absence of plastic deformation suggests the usage of an elastic potential, i.e. the stored elastic energy per undeformed unit-volume. With the local stresses one hopes to be able to find location and moment of the critical material state which induces the observed crack propagation. It is obvious that the complexity of the model leads to different statements.

Linear elastic calculations: for well posed problems a unique solution exists. A benefit is the simplicity of the constitutive law with a limited number of experimental verifiable elastic moduli as well as low costs in computation. But its validity is restricted to infinitesimal small elastic deformations and material rotations. At sharp notches and cracks nonphysical stress singularities are observed.

Nonlinear hyperelastic calculations: in contrast to linear elastic calculations also valid for high deformations and rotations as can occur e.g. at the bottom of notches. If a nonlinear elastic potential is smooth and derived from atomistic models with finite dissociation energy, static stable solutions only exist for limited outer loads. Dynamic crack propagation can be observed when overcritical loads are applied. At singular geometries like sharp notches or cracks the critical material state occurs at infinitesimal small outer loads and presents the problem of vanishing notch resistance.
1 INTRODUCTION

Statical solutions of Finite Element Method (FEM) computations show a mesh dependant behavior.

The fact that linear elastostatics itself is not able to give any indications about tensile strength led to three completions to the continuum-mechanical field equations:

**Concept of ideal strength:** a failure criterion is formulated in dependence of the deformation or stress tensor (e.g. von Mises, Tresca, ...). This criterion defines a domain surrounding the zero-point in the deformation or stress space for which the material is stable. Once a material point of a structure reaches the boundary of this domain, a crack should appear in this point. In the case of notches or cracks this concept cannot be used without restrictions since stress singularities occurring also at infinitesimal outer loads induce the instantaneous failure.

**Concept of energy balance:** the fact that new surfaces need energy for their formation led Griffith to the formulation of his criterion of the energy release rate. A crack grows only then if the decrease of stored total elastic energy per crack-length increment is higher than the surface energy needed for the formation of the new crack flanks. This criterion is necessary but not sufficient. Furthermore, if no initial crack exists, no prediction can be done.

**Concept of the critical stress intensity factor:** to explain the strong decrease of strength in the presence of notches the singular stress-fields near the bottom of notches or near the crack tip are characterized by so-called stress intensity factors. Their values at the outer loads that lead to failure are regarded as material specific constants. Without well defined notches or cracks no predictions can be done.

1.2 Actual theoretical and experimental problems

Apparently a sort of duality exists in the above models: if a theory explains failure phenomena, it explains either the failure of smooth geometries or the failure at singular geometries like notches or cracks, but never both the same time. The reason is the fact that condensed matter is not a continuum but a compound of (discrete) atoms.

Nowadays it is a general accepted fact that the atomic length-scale cannot be neglected in attempting an adequate description of brittle fracture. With the inclusion of the atomic scale the problem becomes multi scaled: the size of a typical structure is in the order of 1mm, one atom is in the range of some angstrom. A factor of $10^7$ separates this scales, this means for a FEM calculation an intensive local mesh-refinement which considerably rises computational costs.

Once the nanoscopically small critical zones are resolved additional questions
come up. At critical loads very high strains of about 20-30% exist in the near field of a stress amplifier. Because of lack of rotational invariance a linear elastic description is not any more admissible. The invariant but nonlinear theory requires the definition of an appropriate elastic potential, which in contrast to the linear elastic theory is not a simple quadratic form in the strain. A nonlinear theory includes constitutive nonlinearities, about which typically not much is known. The construction of such a potential is not standardizable and has to be done within the context of the actual physical problem.

Finally, there is a problem for which no continuum theory, even one with the correct strain energy potential, can provide good results. This is the case of highly inhomogeneous deformations as occur e.g. at the tips of surface cracks or atomically sharp notches. Classical continuum theories use locally defined density-fields, one of them is the strain energy potential. This localization is only valid if the state of strain is approximately homogeneous within the range of influence of the atomic bonding-partner (Cauchy-Born-rule) and so a relation between deformation gradient and energy density can be established. Obviously, this is not true for critically loaded notches or cracks where the bond-length changes from atom-pair to atom-pair. In this case the embedding-energy becomes a real function of all neighbors positions. The reduction of these degrees of freedom to a local deformation gradient is a too gross simplification, what ends up in a pathological behavior of the derived theories. The extreme consequences are either stress singularities or the absence of fracture toughness.

1.3 Anharmonic expansions of the elastic potential

Despite the above mentioned problems of continuum mechanics, one can compute a lot with it. How much this is depends to a great part on the knowledge about the elastic potential. A continuum mechanical field solution can be regarded as plausible as long as the definitions of the local deformation gradient and stress tensor are plausible.

If exactness should be guaranteed till fracture then the elastic potential must be correctly defined even at extreme strains. Once this is done the question arises whether some information about material strength, is contained in the elastic potential. In the past some material laws were developed for silicon with exactly this questions as background. An extension of the linear elastic theory was an invariant under rotation, multidimensional Taylor expansion of the elastic potential expressed in Green-Lagrange-strains $E_{ij} = \frac{1}{2} (F_{ki}F_{kj} - \delta_{ij})$:

$$
\Psi = \frac{1}{2} C_{ijkl}^{(2)} E_{ij} E_{kl} + \frac{1}{6} C_{ijklmn}^{(3)} E_{ij} E_{kl} E_{mn} + \frac{1}{24} C_{ijklmnrs}^{(4)} E_{ij} E_{kl} E_{mn} E_{rs} + \ldots
$$

The material tensors $C_{ijkl}^{(2)}, C_{ijklmn}^{(3)}, C_{ijklmnrs}^{(4)} \ldots$ contain the coefficients of the Taylor expansion and are known as Brugger-constants since their definition in 1963 through K. Brugger. With one- or two-fold derivation of $\Psi$ with respect to $E_{ij}$ the second Piola-Kirchhoff stress tensor $S_{ij} = \frac{\partial \Psi}{\partial E_{ij}}$ and the elasticity tensor
\[ C_{ijkl} = \frac{\partial^2 \Psi}{\partial E_{ij} \partial E_{kl}} \] are obtained. In contrast to the linear theory the stiffness moduli of such theories are genuine functions of the state of deformation and so the positivity of the stiffness tensor might change with deformation. A. Ruoff was the first in 1977-81 who tried to derive thereof local failure criterions. The idea was that the decrease of stiffness as it can be observed in virtual 1D tensile tests with a horizontal tangent on the stress curve defines the ultimate strength. Unfortunately there is no solid background behind this postulated criterion. Since the Brugger-constants were measured in a reliable way only up to third order yet no reasonable convergence analysis could be done. A second deficiency of this failure criterion is its definition itself. A 1D analysis with stress-strain-curve is typically not enough to find the first material instabilities with certitude.

A mathematically founded concept was presented in 1903 by Hadamard and is used nowadays under the name strong ellipticity or strong rang-1 convexity. The idea was that a homogeneous medium is "strongly" elastic if any harmonic flat wave with wave-vector \( \mathbf{k} \) and polarization \( \mathbf{u} \) propagates with a real, non-vanishing velocity. In the nonlinear theory this means:

\[ A_{ijkl} u_i k_j u_k k_l > 0 \ , \quad A_{ijkl} = \delta_{ik} S_{jl} + F_{im} F_{kn} C_{mijnl} \]  

(1.2)

It was shown that the above test might be violated although no change in stiffness is observable in the stress-strain-curves. One reason are e.g. instable shear-modes normal to the tensile direction. The Taylor expansion is not very handy since the number of independent elastic constants explodes for higher order material tensors, even for the cubic orthotropic silicon: 3, 6, 11, . . . . The computational effort needed to class the 11 constants plus null to the 6561 components of \( C_{ijklmnrs}^{(4)} \) is not negligible. Another problem is the question how much Taylor expansion terms are needed to reproduce experimental results. Last but not least the experimental determination of Brugger constants of orders higher than 3 poses a lot of problems.

The presented example shows the possibilities as well as the problems defining an elastic potential within the framework of nonlinear continuum mechanics:

- Hyperelastic potentials allow the definition of constitutive laws which can be implemented in commercial FEM software packages and therefor can be used to compute the stress-strain-answer for any structure.
- The potential has to be rotationally invariant, which is ensured by the use of Green-Lagrange strains or any other objective strain measure.
- The definition of a potential is best carried out within a simple theoretical framework.
- Symmetries of the material must be respected.
- Model parameters must be determinable by means of experiments.
A theoretical failure calculation allows the derivation of local stability criteria.

The aim of the present work is the theoretical and computational exploitation of the material law as well as the strength of single crystal silicon. A new constitutive law within the framework of nonlinear hyperelasticity will be established using the strain energy density derived from the Modified Embedded Atom Method (MEAM) potential. Stress and elasticity tensors will be obtained by analytical derivations with respect to kinematic quantities. The implementation of the material law in a FEM software allows the comparison of theoretically and experimentally obtained stress-strain curves and thereof the verification or falsification of the model.
2 Methods

The aim of this work was the implementation of a new material model into a commercial FEM software (ABAQUS\textsuperscript{1}). Instead of using one of the popular empirical potentials that exist for SCSi, as for example the Stillinger-Weber, a semi-empirical potential based on quantum mechanical considerations called MEAM (Modified Embedded Atom Method) was chosen. In order to simplify the computations the first nearest neighbor MEAM formalism presented below (see section 2.2.2 on page 22) was considered. This formalism gives the total deformation energy in function of distances between neighboring atoms and angles between two different bonds. The total deformation energy can be converted into a strain-energy density by a straightforward calculation

\[ \Psi = \frac{2}{V_{PUC}} E_{tot} \]  

where \( V_{PUC} \) is the volume of the Primitive Unit Cell (PUC). The factor of two comes from the fact that one PUC contains two atoms which own the same deformation energy for the same deformation gradient as will be shown in section 3.1.1 on page 26.

Things get somehow more difficult since the crystal lattice of SCSi contains two sub-lattices that can shift relative to each other. This fact is accompanied by the appearance of optical phonon spectra that are used to experimentally determine strains in crystals. Next section 2.1 highlights some important points.

2.1 Solid state physics of SCSi

At room temperature and ambient pressure silicon atoms take a diamond cubic form with cubic-orthotropic symmetry. Four sp\(^3\) orbitals build covalent bonds with four nearest neighbors leading to regular tetraeders. The bond length of this structure is \( R_0 = 235.2 \text{pm} \) and the angles \( \theta_0 = \arccos(-\frac{1}{3}) \approx 109.5^\circ \).

Figure 2.1 on the following page shows a cubic unit cell of SCSi which has a side length of 543.1pm. There are only four different bond orientations in the cell: \( <111> \), \( <\bar{1}11> \), \( <1\bar{1}1> \) and \( <\bar{1}1\bar{1}> \). In an orthogonal Cartesian coordinate system with base vectors \( e_i (e_i \cdot e_j = \delta_{ij}) \) four structural vectors \( M_i \) can be defined which give the bond orientations:

\[
M_1 = \frac{1}{\sqrt{3}} (1,1,1)^T, \quad M_2 = \frac{1}{\sqrt{3}} (-1,-1,1)^T \\
M_3 = \frac{1}{\sqrt{3}} (1,-1,-1)^T, \quad M_4 = \frac{1}{\sqrt{3}} (-1,1,-1)^T
\]  

(2.2)

Two neighboring atoms do not own the same bond orientations, their bonds are point inverted, see figure 2.2 on the next page. It seems that the SCSi lattice are in fact two sub-lattices that are stacked into each other, i.e. the primitive unit cell (PUC) contains two atoms. This has interesting physical implications, first that SCSi is softer than expected since the two lattices can shift relative to each

\textsuperscript{1}ABAQUS, Inc., ABAQUS, version 6.4-1, 2003
Figure 2.1: Cubic unit cell of SCSi. The side length of the cell is 543.1pm (black). Note the four different bond types $<111>$, $<\bar{1}11>$, $<1\bar{1}1>$ and $<11\bar{1}>$.

Figure 2.2: Two neighboring atoms have point inverted bonds, in fact the SCSi lattice consists of two nested sub-lattices.
other. The second implication is the appearance of optical phonon branches in the phonon spectrum.

**Inner elasticity** As the crystal is deformed the two sublattices move relative to each other. Taking into account this sublattice shift, the strain-energy density becomes a function of the right Cauchy-Green tensor $C$ and the so-called sublattice shift vector $Z$, so that $\Psi = \Psi [C, Z]$. But in the static case $Z$ is also a function of $C$, the sublattice shift will be established in such a way that the potential energy is minimized and so $\Psi = \Psi [C, Z, C]$.

The second Piola-Kirchhoff stress tensor defined as $S_{ij} = 2 \frac{\partial \Phi}{\partial C_{ij}}$ thus is:

$$
S_{ij} = 2 \frac{d \Psi}{d C_{ij}}
$$

$$
= 2 \left( \frac{\partial \Psi}{\partial C_{ij}} + \frac{\partial \Psi}{\partial Z_m} \frac{d Z_m}{d C_{ij}} \right)
$$

$$
= 2 \frac{\partial \Psi}{\partial C_{ij}} + \frac{\partial \Psi}{\partial Z_m} 2 \left( \frac{d Z_m}{d C_{ij}} \right)
$$

$$
= S^0_{ij} + G_m A_{mij} \quad (2.3)
$$

where in the last step three quantities have been defined:

$$
S^0_{ij} = 2 \frac{\partial \Psi}{\partial C_{ij}} \quad \text{Partial second Piola-Kirchhoff tensor} \quad (2.4a)
$$

$$
G_m = \frac{\partial \Psi}{\partial Z_m} \quad \text{Internal force vector} \quad (2.4b)
$$

$$
A_{mij} = 2 \left( \frac{d Z_m}{d C_{ij}} \right) \quad \text{First internal strain tensor} \quad (2.4c)
$$

A physical interpretation of the internal force vector is that $G$ is the referential force density that one sublattice feels as attraction or repulsion from the other one.

The total differentiation of the second Piola-Kirchhoff stress tensor leads to the
2 METHODS

referential elasticity tensor $C$:

$$C_{ijkl} = 4 \frac{d^2\Psi}{dC_{ij} dC_{kl}}$$

Partial elasticity tensor (2.6a)

$$D_{mkl} = 2 \frac{d^2\Psi}{dZ_m dC_{kl}}$$

Force-strain coupling tensor (2.6b)

$$E_{mn} = \frac{d^2\Psi}{dZ_m dZ_n}$$

Internal elasticity tensor (2.6c)

$$B_{mijkl} = 4 \frac{d^2Z_m}{dC_{ij} dC_{kl}}$$

Second internal strain tensor (2.6d)

If it is assumed that the sublattice shift $Z$ minimizes the potential energy for all deformation gradients some constraints appear: The internal force must be zero.

$$G = 0$$

(2.7)

The internal elasticity $E$ has to be positive stable definite in order to provide a minimum.

$$E > 0$$

(2.8)

The changes of the internal force vector for small variations of $C$ are to be zero.

$$\frac{2 dG_m}{dC_{ij}} = 2 \frac{d^2\Psi}{dZ_m dC_{ij}} + \frac{d^2\Psi}{dZ_m dZ_n} \left( 2 \frac{dZ_n}{dC_{ij}} \right)$$

$$= D_{mij} + E_{mn} A_{mij} = 0$$

(2.9)
Last three equations can be used to simplify equations (2.3) and (2.5):

\[
S_{ij} = S_{ij}^0 \tag{2.10a}
\]
\[
C_{ijkl} = C_{ijkl}^0 - E_{mn}^{-1}D_{mij}D_{nkl} \tag{2.10b}
\]

These two equations are only valid if equations (2.7) to (2.9) hold. Applying a push-forward Piola-transformation it can be shown that the same relations hold for the spatial configuration. Here this will be shown for equation (2.10b) only:

\[
c_{ijkl} = \chi(C_{ijkl}) = \frac{1}{J}F_{im}F_{jn}F_{ko}F_{lp}C_{mnop}
\]
\[
= \frac{1}{J}F_{im}F_{jn}F_{ko}F_{lp}\left(C_{mnop}^0 - E_{rs}^{-1}D_{rmn}D_{sop}\right)
\]
\[
= c_{ijkl}^0 - \frac{1}{J}F_{im}F_{jn}F_{ko}F_{lp}E_{rs}^{-1}D_{rmn}D_{sop}
\]

\[
e_{xy} = \chi(E_{xy})
\]
\[
e_{xy} = \frac{1}{J}F_{xr}^{-T}F_{ys}^{-T}E_{rs}
\]
\[
e_{xy}^{-1} = JF_{xr}^{-T}F_{ys}^{-T}
\]
\[
\rightarrow E_{rs}^{-1} = \frac{1}{J}F_{xr}^{-T}F_{ys}^{-T}e_{xy}^{-1}
\]

\[
c_{ijkl} = \frac{1}{J}F_{im}F_{jn}F_{ko}F_{lp}F_{xr}^{-T}F_{ys}^{-T}e_{xy}^{-1}D_{rmn}D_{sop}
\]
\[
\]

where \( F_{ij} \) are the components of the deformation gradient \( F \).

The push-forward versions of the most important tensors can be obtained with the following relations

\[
\sigma_{ij} = \frac{1}{J}F_{ik}F_{lj}S_{kl} \quad \text{(Cauchy-stress tensor)} \tag{2.12a}
\]
\[
c_{ijkl}^0 = \frac{1}{J}F_{im}F_{jn}F_{ko}F_{lp}C_{mnop}^0 \tag{2.12b}
\]
\[
d_{ijk} = \frac{1}{J}F_{il}F_{jm}F_{kn}^{-T}D_{lmn} \tag{2.12c}
\]
\[
e_{ij} = \frac{1}{J}F_{il}^{-T}F_{jm}^{-T}E_{lm} \tag{2.12d}
\]
\[
g_i = \frac{1}{J}F_{ik}^{-T}G_k \tag{2.12e}
\]

Using already the push-forward versions \( \chi [ \ ] \) of the derivatives of the deformation measures (formulas b) in appendix A.5 on page 52) in formulas A.4 to A.8 on pages 48–50 its only necessary to multiply these with the factor \( \frac{1}{J} \) to obtain the spatial quantities.

A routine that computes the stresses and stiffness of such a material must possess a subroutine that minimizes the internal force tensor \( G \) (or in spatial coordinates
first and calculates afterwards the stress and stiffness tensors $S$ and $C$ (or $\sigma$ and $c$), respectively. A good survey on the inner elasticity can be found in two papers of C.S.G. Cousins [3, 4], however only in a linear context.

**Phonon spectrum** Except at zero temperature atoms in a crystal do vibrate about their equilibrium (zero temperature) positions. Using the symmetries of a crystal these vibrations can be analyzed in terms of collective modes, called phonons. Solving the potential energy problem of a crystal for its eigenfrequencies one finds that these can generally split into two groups: the acoustic and the optic mode, labeled A and O, respectively. The acoustic mode is present in every crystal. Two neighboring masses (atoms or groups of atoms) move together in the same direction as is the case in an acoustic wave whose wavelength is longer than the typical atomic distance. In the optical mode two neighboring masses move in opposition, this at higher frequencies than the acoustic mode. In the case of atoms with different electric charges this corresponds to an oscillating electric dipole moment, which can be excited by electromagnetic waves. A necessary and sufficient condition for the existence of optical modes is a primitive unit cell with more than one atom. This is the case with SCSi where the PUC contains two atoms, both are silicon atoms, but they own different bond orientations.

For each of the modes three frequencies exist, one for longitudinal waves (L) and two for transversal waves (T). The frequencies for the L and T modes can be degenerate, i.e. they can coincide.

These phonon frequencies can be measured experimentally and since they depend on the equilibrium positions of the atoms they are used for the determination of strain in the crystal. This is done by Raman-spectroscopy where the so-called Raman-frequencies $f_R$ are measured. The Raman-frequencies belong to the optical mode at the $\Gamma$-point (LTO($\Gamma$)), i.e. at the center of the Brillouin zone. The experientially determined value of the Raman-frequency for SCSi is (for a unstrained crystal) about 15.53 THz (Table A.1 on page 57). The Raman-frequencies can be calculated using the internal elasticity tensor $e$, they depend on the eigenvalues of it:

$$f_R = \frac{1}{\pi R_0} \sqrt{\frac{J \text{eig}[e]}{\rho}}$$

(2.13)

where $R_0$ is the initial bond-length, $J$ the volume ratio and $\rho$ the referential mass density (table A.1 on page 57).

In the case of the referential configuration the internal elasticity tensor has a triply degenerate eigenvalue. For strained configurations the eigenvalues split up into two or three eigenvalues that are double or not degenerate, respectively. A potential formulation should be able to reproduce this physical properties.
2 METHODS

2.2 Potentials

Potential formulations of strain energy densities are the corner stones of hyperelasticity. The assumption of a single-valued energy function allows the computation of all mechanical properties, especially stresses and stiffness. Potentials can be obtained either empirically or semiempirically. Empirical potentials are obtained by fitting quite arbitrary functions to experimental data whereas semiempirical potentials are based on a deeper insight into the mechanics of elasticity and often make use of physically justified functional terms obtained from underlying theories.

Recently several potentials were developed, especially for silicon for its industrial importance as well as its availability as a quasi perfect crystal. Besides others the Stillinger-Weber potential was developed [5]. It is presented in the next section 2.2.1 as a typical and widely used empirical potential form. Section 2.2.2 on the following page presents the Embedded Atom Method (EAM) and its modification, the Modified Embedded Atom Method (MEAM).

2.2.1 Empirical potentials: Stillinger-Weber

In order to describe interactions in solid and liquid forms of silicon F.H. Stillinger and T.A. Weber developed the Stillinger-Weber (StW) potential [5]. The StW potential $\Psi_{StW}$ considers two- and three-body contributions $\nu_2$ and $\nu_3$, respectively:

$$\Psi_{StW} = \sum_i \nu_2 [i] + \sum_{i,j} \nu_3 [i,j]$$  \hspace{1cm} (2.14)

$$\nu_2 [r_{ij}] = \varepsilon f_2 [r_{ij}/\sigma]$$

$$\nu_3 [r_i, r_j, r_k] = \varepsilon f_3 [r_i/\sigma, r_j/\sigma, r_k/\sigma]$$

$r_i$ being the position vector of atom $i$ and $r_{ij}$ the distance between atoms $i$ and $j$.

The two energy and length units $\varepsilon$ and $\sigma$ are defined the way that $f_2$ has depth $-1$ and $f_2 [2^{1/6}]$ vanishes. $f_3$ possesses full translational and rotational symmetry.

For the pair potential a form was chosen that cuts off at a radius $r = a$ without discontinuities in any derivative with respect to $r$:

$$f_2 [r] = \begin{cases} A(Br^{-p} - r^{-q}) \exp \left[ (r - a)^{-1} \right], & r < a \\ 0, & r \geq a \end{cases}$$  \hspace{1cm} (2.15)
with $A$, $B$, $p$ and $a$ being positive. The three-body term is split up into 3 terms:

$$f_3[r_i, r_j, r_k] = h[r_{ij}, r_{ik}, \theta_{ijk}] + h[r_{ji}, r_{jk}, \theta_{ijk}] + h[r_{ki}, r_{kj}, \theta_{ikj}]$$  \hspace{1cm} (2.16)

$$h[r_{ij}, r_{ik}, \theta_{ijk}] = \begin{cases} 
\lambda \exp \left( \gamma (r_{ij} - a)^{-1} + \gamma (r_{ik} - a)^{-1} \right) \times \\
\left( \cos [\theta_{ijk}] + \frac{1}{3} \right)^2, \\
0, \\
r < a \\
r \geq a 
\end{cases}$$  \hspace{1cm} (2.17)

In the reference structure with $\cos [\theta_{ijk}] = -\frac{1}{3}$ the three-body term vanishes identically and so favors the tetrahedral configuration.

In fact the Stillinger-Weber potential is the simplest potential formulation. Nevertheless classical mechanical properties could be reproduced with it but also phase transitions as well as fracture behavior. This is the reason for its popularity in molecular dynamics simulations. Empirical potentials like the StW work well in the regime where they were fitted, nevertheless leaving this regime it is uncertain whether they are applicable or not.

### 2.2.2 Semiempirical potentials: Embedded atom methods

An exact energetic description of a system of atoms (e.g. a crystal) is given by quantum mechanics. The system is described in terms of the many-body time independent Schrödinger equation

$$\mathcal{H} \Psi \left[ \{r_I, r_i\} \right] = E \Psi \left[ \{r_I, r_i\} \right]$$  \hspace{1cm} (2.18)

where $\mathcal{H}$ is the hamiltonian operator, $\Psi \left[ \{r_I, r_i\} \right]$ the many-body wavefunction that describes the state and $E$ the energy eigenvalue of the system. $r_I$ and $r_i$ describe the positions of the ions and the electrons, respectively.

A simplification can be obtained by applying the Born-Oppenheimer approximation: The ions typically having masses three to five orders of magnitude higher than the electrons can be treated like classical particles moving much slower than the light electrons. Thus the ion positions might be treated as parameters and so $\Psi$ is thought of as being dependent only on the electronic degrees of freedom.

Although the Born-Oppenheimer approximation substantially simplifies the problem, solving the Schrödinger equation for $\Psi \left[ \{r_i\} \right]$ remains a difficult task, especially when considering the nature of electrons. The exchange property claims that if two electrons of same spin interchange positions, $\Psi$ must change its sign. The correlation property tells that each electron is influenced by the motion of all other electrons.

Neglecting the interactions between electrons $\Psi$ takes the following form

$$\Psi^H \left[ \{r_i\} \right] = \prod_i \psi_i \left[ r_i \right]$$  \hspace{1cm} (2.19)
with \( i \) running over all electrons. The wavefunctions \( \psi_i \) are normalized single-particle states. This is known as the Hartree approximation (see superscript \( H \)).

By incorporating the exchange property into the Hartree approximation one arrives at the Hartree-Fock approximation. This can be done by properly antisymmetrizing the Hartree wavefunctions, using the Slater determinant

\[
\Psi_{HF} = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1[r_1] & \psi_1[r_2] & \ldots & \psi_1[r_N] \\
\psi_2[r_1] & \psi_2[r_2] & \ldots & \psi_2[r_N] \\
\vdots & \vdots & \ddots & \vdots \\
\psi_N[r_1] & \psi_N[r_2] & \ldots & \psi_N[r_N] 
\end{vmatrix}
\] (2.20)

where \( N \) is the total number of electrons. This determinant possess the desired property, interchanging the positions of two electrons is equal to the interchange of the corresponding columns in the determinant what changes sign of \( \Psi_{HF} \).

Despite of all the above mentioned approximations it remains a difficult task to find \( \Psi \) and the results will not be in perfect accordance with experiment.

In 1964/65 Hohenberg, Kohn and Sham presented two papers with the basic ideas of a theory called Density Functional Theory (DFT) [6, 7]. In contrast to the many-body Schrödinger equation which uses the many-body wavefunction \( \Psi([r_I, r_i]) \) this theory uses only the total density of electrons \( n[r] \). As can be shown \( n[r] \) is uniquely defined by an external potential \( V[r] \). But the external potential determines the wavefunction, so that the wavefunction is a unique function of the total density of electrons.

**Embedded-atom method** Within the last years M.I. Baskes and other authors presented in a series of papers [8, 9, 10, 11, 12] a new energy formulation based on ab initio calculations, i.e. DFT and LDA. M.S. Daw and M.I. Baskes developed the Embedded-Atom Method (EAM) to calculate ground-state properties of metal systems [8]. A starting point was an earlier theory, the quasiatom theory originally used treating impurities in metals. It is assumed that an impurity experiences a locally uniform, or only slightly nonuniform, environment. Every quasiatom owns an energy

\[
E_{\text{quas}} = E_Z[\rho_h[r]]
\] (2.21)

where \( \rho_h[r] \) is the electron density of the host without impurity at \( r \) and \( E_Z \) is the quasiatom energy with atomic number \( Z \). The total energy is then the sum of the quasiatom energy with a lattice energy from pair potentials:

\[
E_{\text{tot}} = E_{\text{quas}} + E_{\text{lat}}
\] (2.22)

Within the EAM all atoms are treated as being embedded in a host built up by all other atoms. The total energy is the sum of the individual contributions of each atom where each atom is assumed to experience a locally uniform electron
gas. The energy of an atom in a uniform electron gas relative to the energy of the same atom separated from the gas is defined as the embedding energy \( F_i \):

\[
E_{\text{tot},i} = F_i[\rho_{h,i}]
\]

\( \rho_{h,i} \) being the density of the host at the position \( \mathbf{r}_i \) but without atom \( i \).

But the above equation is not convincing. The assumption of extreme locality, and of a uniform positive background leads to unrealistic properties of the solid. The assumption of extreme locality can be avoided by a redefinition of \( \rho_{h,i} \) being now a density averaged over a finite region. A second problem comes from the neglect of the core-core repulsion. In a new formulation of \( E_{\text{tot}} \) the short-range pairwise repulsion between the cores takes the form

\[
E_{\text{tot},i} = F_i[\rho_{h,i}] + \frac{1}{2}\sum_{j \neq i} \phi_{ij}[r_{ij}]
\]

where \( \phi_{ij}[r_{ij}] \) is the short-range pair potential which takes as argument the distance between atoms \( i \) and \( j \).

In a paper of 1987 M.I. Baskes applies the EAM to covalent materials, especially to silicon [9]. For a simple first-neighbor model of a homogeneous monatomic solid the total energy \( E_{\text{tot}} \) is

\[
E_{\text{tot}}[r] = F[n_1 \rho^a[r]] + 0.5 n_1 \phi[r]
\]

where \( n_1 \) is the number of first neighbors in the reference structure, \( \rho^a \) the spherically averaged atomic electron density at a distance \( r \) from the nucleus, \( F \) is the embedding function and \( \phi \) is the pair interaction.

In case of an uniform expansion or contraction the Universal Binding Energy Relation (UBER) \( E_r \) describes well the energy \( E_{\text{tot}} \) [13]:

\[
E_r[a^*] = -E_0 (1 + a^*) e^{-a^*}
\]

\[
a^* = \beta (r - R_1)
\]

\[
\beta = (9B\Omega_0/R_1^2 E_0)^{1/2}
\]

with \( E_0 \) being the sublimation energy, \( R_1 \) the equilibrium first neighbor distance, \( B \) the bulk modulus and \( \Omega_0 \) the equilibrium atomic volume.

Using the pair interaction \( \phi \) found by equaling equations (2.25) and (2.26) and by taking the embedding function to be given by

\[
F[\rho] = E_0[\rho/\bar{\rho}] \ln[\rho/\bar{\rho}]
\]

the total energy of \( n \) first-nearest neighbors is

\[
E_n = \frac{n}{n_1} E_r[a^*] + E_0 \frac{n\rho^a}{\bar{\rho}} \ln \left[ \frac{n}{n_1} \right]
\]

Here \( \bar{\rho} \) is the density an atom sees at equilibrium in the initial reference structure. The choice of the embedding function \( F \) is justified by additional calculations [9].
The energy formulation (2.28) agrees with structural energies and bond lengths. However, two problems arise, both related to the shear elastic constants. Using equation (2.28) for SCSi one ends up with $C_{11} = C_{12}$ what does not reflect the true nature of silicon, see table A.1 on page 57. An inclusion of additional neighbors in the model leads to better results. The second problem is a resulting positive Cauchy discrepancy $C_{12} - C_{44}$ whereas the experimental one is negative (see table A.1 on page 57). Additional neighbors do not solve the problem at all, the problems origin is the non-directionality of the model. Using spherically averages of the electron density the directionality of the bonding in silicon is lost. The inclusion of the discussed effects leads to the

Modified embedded-atom method  

The Modified Embedded-Atom Method (MEAM) adds more distant neighbors and angle-dependent densities to the EAM formalism. The total energy is given by

$$E_{tot} = \sum_i F_i [\rho_i] + \frac{1}{2} \sum_{i,j \neq j, j \neq i} \rho_i [r_{ij}] (2.29)$$

$$\rho_i = \sum_{j \neq i} \rho^n [r_{ij}] - a \sum_{j,k, j \neq i, k \neq i} (1 - 3 \cos^3 [\theta_{jik}]) \rho^n [r_{ij}] \rho^n [r_{ik}] (2.30)$$

$F_i [\rho_i]$ is given by equation (2.27) and $a$ is a constant to be determined by fitting the shear moduli and $\theta_{jik}$ is the included angle between atoms $j,i$ and $k$. The two terms of the density are linearly superposed. The first term is an atomic density whilst the second is a angular correction term. The form of the angular term is chosen in a way that minimizes the total energy under a tetrahedral distortion of the electron density and that vanishes in an ideal cubic structure (where $\theta_{jik} = \arccos (-1/3)$).

The energy per atom for a monatomic homogeneous solid under uniform expansion or contraction is given by

$$E [r_1] = E_r [a^*] = F [\rho_i [r_1]] + 0.5 n_1 \Phi [r_1] (2.31)$$

$$\Phi [r_1] = \sum_s \phi [a_s r_1] \frac{n_s}{n_1} (2.32)$$

where $r_1$ is the first-neighbor distance, $n_s$ is the number of $s$th neighbors and $a_s$ is the ratio of the $s$th-neighbor distance to the first-neighbor distance. $\Phi$ is defined by equation (2.31), to obtain $\phi$ from (2.32) requires a cutoff radius $r_c$ so that beyond $r_c$ all functions are zero (see A.9.2 on page 64 for a derivation):

$$\phi [r_1] = \Phi [r_1] - \sum_{s \neq 1} \frac{n_s}{n_1} \Phi [a_s r_1] + \left( \frac{n_s}{n_1} \right)^2 \Phi [a_s^2 r_1]$$

$$r_1 > \frac{r_c}{a_s a_3} (2.33)$$
In a paper of 1989 [10] M.I. Baskes et al. present a host electron density $\rho_{h,i}$ that includes an angle-dependant term which vanishes for ideal cubic structures.

$$\rho_{h,i} = \sum_{j \neq i} \rho^0_j (r_{ij}) + \sum_{j,k} (a^1_j a^1_k \cos [\theta_{jik}] - a^2_j a^2_k (1 - 3 \cos^2 [\theta_{jik}])) \times \rho^0_j (r_{ij}) \rho^0_k (r_{ik}) (2.34)$$

where $\rho^0_j$ is the atomic density depending on the type of atom $j$, $\theta_{jik}$ is the angle between atoms $j,i$ and $k$ and the $a^n_i$ are atom dependent constants. Note that the above equation (2.34) is identical to equation (2.30) if $(a^2_i)^2 = a$ and $a^1_i = 0$.

The only things that are unknown yet are the atomic density and the parameters of the MEAM. The latter ones are obtained by fitting the elastic shear constants whereas the former one is chosen by the authors of the paper to be

$$\rho^0_i (r) = \rho^0_i \left( \frac{r}{r_1} \right)^{m_i} e^{-\alpha_i (r-r_1)} (2.35)$$

where $m_i$ is obtained from the atomic density for an isolated atom and $\alpha_i$ is a free parameter.

**First nearest neighbor MEAM** M.I. Baskes presented 1992 a paper [11] wherein a MEAM formulation is applied to a large number of elements including silicon. Unlike in the previous paper [10] the formulation is restricted to first nearest neighbors only (1NN-MEAM). As in the original MEAM formulation the total energy $E_{tot}$ of a system is given by (compare with formulation (2.29)):

$$E_{tot} = \sum_i E_i = \sum_i \left( F_i [\bar{\rho}_i] + \frac{1}{2} \sum_{j \neq i} \phi_{ij} [r_{ij}] \right) (2.36)$$

where $\bar{\rho}_i$ is the background electron density at site $i$ and $\phi_{ij}$ is the pair interaction between the central atom and the neighboring ones separated by $r_{ij}$. $E_i$ is the direct energy contribution of atom $i$ which can be written as

$$E_i = F_i [\bar{\rho}_i / Z_i] + \frac{1}{2} \sum_{j \neq i} \phi_{ij} [r_{ij}] (2.37)$$

Here the background density $\bar{\rho}_i$ is renormalized by the number of nearest neighbors $Z_i$.

Analogue to equation (2.31) an energy per atom of the reference structure $E^0_i [r]$ in function of nearest-neighbor distance can be defined as

$$E^0_i [r] = F_i [\bar{\rho}^0_i / Z_i] + \frac{Z_i}{2} \phi_{ii} [r] (2.38)$$
where $\bar{\rho}_i^0$ is the background electron density $\bar{\rho}_i$ for the reference configuration. The last equation allows the calculation of the pair interaction term $\phi[r]$:

$$\phi_{ii}[r] = \frac{2}{Z_i} \left( E_i^0[r] - F_i \left[ \frac{\bar{\rho}_i^0}{Z_i} \right] \right)$$

Combining equations (2.37) and (2.39) the energy contribution $E_i$ is obtained:

$$E_i = \frac{1}{Z_i} \sum_{j \neq i} E_i^0[r_{ij}] + \left( F_i \left[ \bar{\rho}_i / Z_i \right] - \frac{1}{Z_i} \sum_{j \neq i} F_i \left[ \bar{\rho}_i^0[r_{ij}] / Z_i \right] \right)$$

It is interesting to identify the physical meaning of the two terms appearing in (2.40). The former is the average of the energy per atom in the reference structure. The second term is the difference between the embedding energy at the background electron density seen by atom $i$ and the average embedding energy of this atom in the reference structure at the nearest neighbor distances. The energy $E_i^0[r]$ is the same as in the EAM (2.26) on page 20:

$$E_i^0[r] = -E_0 (1 + a^*) e^{-a^*}$$

$$a^* = \beta \left( \frac{r}{R_0^i} - 1 \right)$$

$$\beta = (9B\Omega_0/E_0)^{1/2}$$

with $R_0^i$ being the equilibrium nearest-neighbor distance. The embedding function is depending only on the electron density

$$F_i[\rho] = A_i E_i^0 \rho \ln [\rho]$$

where $A_i$ is a free parameter.

Remains to identify the background electron densities $\bar{\rho}_i$ and $\bar{\rho}_i^0$. A linear combination of the squares of partial background densities $\rho_i^{(l)}$ gives $\bar{\rho}_i$:

$$(\bar{\rho}_i)^2 = \sum_{l=0}^{3} t_i^{(l)} \left( \rho_i^{(l)} \right)^2$$

where the $t_i^{(l)}$ are model parameters to be determined. A partial background density $\rho_j^{(l)}$ represents the atomic electron density of a type-$j$ atom at a distance
\( r_{ij} \) from site \( i \):
\[
\rho_i^{(0)} = \sum_{j \neq i} \rho_j^{a(0)} [r_{ij}] \quad (2.44a)
\]
\[
\rho_i^{(1)} = \sum_{\alpha} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} \rho_j^{a(1)} [r_{ij}] \right)^2 \quad (2.44b)
\]
\[
\rho_i^{(2)} = \sum_{\alpha, \beta} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} x_{ij}^{(\beta)} \rho_j^{a(2)} [r_{ij}] \right)^2 - \frac{1}{3} \left( \sum_{j \neq i} \rho_j^{a(2)} [r_{ij}] \right)^2 \quad (2.44c)
\]
\[
\rho_i^{(3)} = \sum_{\alpha, \beta, \gamma} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} x_{ij}^{(\beta)} x_{ij}^{(\gamma)} \rho_j^{a(3)} [r_{ij}] \right)^2 \quad (2.44d)
\]

With \( x_{ij}^{(\alpha)} = r_{ij}^{(\alpha)} / r_{ij} \) where \( r_{ij}^{(\alpha)} \) is the \( \alpha \) component of the distance vector \( r_{ij} \) and \( \rho_j^{a(l)} [r_{ij}] \) are the atomic electron densities given by
\[
\rho_j^{a(l)} [r_{ij}] = \exp \left( -\beta_i^{(l)} \left( r_{ij} / R_i^{0} \right) \right) \quad (2.45)
\]

The \( \beta_i^{(l)} \) are parameters to be determined.

The background densities for the reference structure \( \bar{\rho}_i^0 \) are weighted sums over the atomic electron densities \( \rho_i^{a(l)} [r_{ij}] \):
\[
\left( \bar{\rho}_i^0 [r_{ij}] \right)^2 = \sum_{l=0}^{3} t_i^{(l)} s_i^{(l),0} \left( \rho_i^{a(l)} [r_{ij}] \right)^2 \quad (2.46)
\]

with \( s_i^{(l),0} \) being free parameters dependant only on the geometry of the considered structure.

Table 2.1 on the next page gives the parameters proposed by M.I. Baskes for the MEAM potential in the case of SCSi. Parameters for other materials can be found in [11].

Second nearest neighbor MEAM In a paper published 2000 Yeong-Joo Lee and M.I. Baskes expand the first nearest neighbor MEAM to a second nearest neighbor MEAM (2NN-MEAM) formulation [12]. The background of this expansion was the realization that a formalism including only first nearest neighbor atoms does not sufficiently represent bcc metals.
Table 2.1: Parameters for the MEAM proposed by M.I. Baskes [11] for diamond cubic silicon. $E^0_i$ is the sublimation energy, $R^0_i$ the nearest-neighbor distance, $\alpha_i$ the decay factor for the universal energy function, $A_i$ the scaling factor for the embedding energy. The $\beta^{(l)}_i$ are the exponential decay factors for the atomic densities, the $t^{(l)}_i$ the weighting factors for the atomic densities and the $s^{(l)}_i$ geometry depending factors.

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<th>$E^0_i$ [eV]</th>
<th>$R^0_i$ [Å]</th>
<th>$\alpha_i$ [-]</th>
<th>$A_i$ [-]</th>
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<td>$\beta^{(3)}_i$ [-]</td>
</tr>
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<td>5.50</td>
<td>5.50</td>
</tr>
<tr>
<td>$t^{(0)}_i$ [-]</td>
<td>$t^{(1)}_i$ [-]</td>
<td>$t^{(2)}_i$ [-]</td>
<td>$t^{(3)}_i$ [-]</td>
</tr>
<tr>
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</tr>
<tr>
<td>$s^{(0)}_i$ [-]</td>
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<td>$s^{(2)}_i$ [-]</td>
<td>$s^{(3)}_i$ [-]</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>$\frac{32}{3}$</td>
</tr>
</tbody>
</table>
3 Results

3.1 Implementation

Before using the MEAM potential as material model for an implementation in the FEM software ABAQUS some modifications were made on it. The first modification was the introduction of deformation measures, i.e. stretches $\lambda_j$ and cosines of bond angles $\phi_{jk}$, described in section 3.1.1. Other modifications concern the formalism itself, especially notation was simplified, see section 3.1.2 on page 28.

3.1.1 Deformation measures

Two position vectors describing referential positions of atoms in sublattice one and two are defined:

\begin{align*}
R_1 & \quad \text{Referential position vector in an atom of sublattice 1} \\
R_2 & \quad \text{Referential position vector in an atom of sublattice 2}
\end{align*}

The point of origin is chosen at the center of a bond. With this choice holds: if $R$ is an element of sublattice 1 then $-R$ is an element of sublattice 2. An inversion of sign for a position vector $R$ interchanges the sub-lattices.

The knowledge that two neighboring atoms belong to different sub-lattices allows the definitions of the undeformed and deformed structural vectors from atom $a$ to atom $b$ (where the two atoms are first neighbors):

\begin{align}
M_{ab} &= \frac{1}{R_0} (R_b - R_a) \tag{3.1a} \\
m_{ab} &= \frac{1}{R_0} (r_b - r_a) = F (M_{ab} + Z) \tag{3.1b}
\end{align}

It is clear from the definition of $M_{ab}$ that the structural vectors are normalized for the reference configuration.

Within the Cauchy-Born approximation a deformation gradient $F$ might be used as the local generator of a homogeneous deformation.

\[
F = \frac{\partial x}{\partial X} \tag{3.2}
\]

Respecting the inner degrees of freedom, the kinematically minimal definition of such a deformation is given as

\begin{align*}
 r_1 &= F \left( R_1 - \frac{R_0}{2} Z \right) \quad \text{for an atom of sublattice 1} \\
 r_2 &= F \left( R_2 + \frac{R_0}{2} Z \right) \quad \text{for an atom of sublattice 2}
\end{align*}

where $Z$ is the sublattice shift vector introduced in section 2.1 and $R_0$ is the initial bond length which is used as a scaling factor.
If only vectors outgoing from atom \( a \) are regarded, the indices \( a \) can be omitted and \( M_{ab} \) can be written as \( M_k \). With this definitions, the measure of stretch of one bond \( \lambda \) introduced.

\[
\lambda_j = \frac{M_j}{R_0} = \left| \left| m_j \right| \right| = \sqrt{m_j \cdot m_j} \]

\[
= \sqrt{C : (M_j + Z) \otimes (M_j + Z)}
\]

(3.3)

where \( C \) is the Right-Cauchy-Green tensor: \( C = F^T F \).

Another measure of deformation is the cosine of the angle between two bonds. Regarding first neighbors only, the situation is simple: the central atom belongs to one sublattice and the two other atoms belong to the other sublattice.

\[
\phi_{jk} = \cos \theta_{ijk} = \frac{m_j \cdot m_k}{\left| m_j \right| \left| m_k \right|} \]

\[
= \frac{1}{2\lambda_j \lambda_k} C : ((M_j + Z) \otimes (M_k + Z) + (M_k + Z) \otimes (M_j + Z))
\]

(3.4)

Here, special care was taken of the fact that \( \phi_{jk} \) is symmetric, this is done by explicitly symmetrizing the tensor. An analytical expression lacking formal symmetry would lead to severe problems if \( \phi_{jk} \) is later differentiated with respect to \( C \).

It can be shown, that the deformation measures are identical for atoms of different sub-lattices, if the same deformation gradient is applied. This fact reduces the computational effort needed to compute the potential energy density by a factor of two; taking the deformation gradient constant over the PUC and its environment, it is sufficient to compute the energy of one atom and take it twice.

**Invariance of \( \lambda_j \):** with the definition of the point of origin at the center of a bond, a change of the sub-lattices changes the sign of the structural vectors \( M_j \) as well as the sign of the inner displacement \( Z \). This has no influence on \( \lambda_j \) since \( \lambda_j^2 \) is a quadratic form in \( (M_j + Z) \).

**Invariance of \( \phi_{jk} \):** a change of the sub-lattices changes the signs of the structural vectors \( M_j \) and \( M_k \) as well as the sign of the inner displacement vector \( Z \). As a result, the sign of \( \phi_{jk} \) remains the same.

Additionally to \( \lambda_j \) and \( \phi_{jk} \) their first and second derivatives with respect to \( C \) and \( Z \) and their combination are needed. These results are presented appendix A.5 on page 52ff.
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3.1.2 MEAM formalism

In order to simplify the original MEAM formalism presented by M.I. Baskes [11] some changes are introduced:

1. Original variables and function names were replaced by simpler expressions.
2. Considering only one central atom $i$ the index $i$ was omitted.
3. The total deformation energy $E_{tot}$ is replaced by the strain energy density $\Psi$.
4. Argument lists of functions take only indices of the involved atoms as input.
5. Relations (2.44b-d) on page 24 were replaced by relations (A.24a-c) on page 63 showing directly the $\cos \theta = \phi$ dependance of this terms.
6. The ratios $r_{ij}R_0$ were replaced by the equivalent stretch $\lambda$.

The formalism used in this work is presented in appendix A.1 on page 45.

Remark to point 2.: as shown in the previous section 3.1.1 on page 26 the deformation measures $\lambda_j$ and $\phi_{jk}$ are the same for atoms of different sub-lattices if the same deformation gradient is applied. As a result of this only one atom of the PUC has to be considered for the energy calculation. This allows to omit the indices $i$ in the deformation measures, i.e. $\lambda_j$ stands for $\lambda_{ij}$ and $\phi_{jk}$ for $\phi_{jik}$.

Remark to point 3.: in this new formalism only the factor $\gamma = 2E_0/V_{PUC}$ is afflicted with units, all other terms are dimensionless. The dimension of $\gamma$ is energy per volume, i.e. $[\gamma] = \frac{J}{m^3}$ or $[\gamma] = \frac{eV}{\AA^3}$, allowing the choice between SI-units and atomar units. $\gamma$ invokes the volume of the PUC $V_{PUC}$ which can be calculated as a mixed product of the three vectors from one corner of the unit cell to the nearest three face centered atoms (see figure 3.1 on the next page):

$$V_{PUC} = \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) = \frac{a^3}{4} \quad (3.5)$$

$$\mathbf{a}_1 = [1, 1, 0]^T \frac{a}{2}$$
$$\mathbf{a}_2 = [0, 1, 1]^T \frac{a}{2}$$
$$\mathbf{a}_3 = [1, 0, 1]^T \frac{a}{2}$$

Once the potential is established the important referential tensor quantities $S_0^0$, $G$, $C^0$, $D$ and $E$ (equations (2.4a-b) and (2.6a-c) on pages 13–14, respectively) can be calculated, see appendix A.3 on page 48. At this step it is important to remark that the tensor coefficients do not change for the different tensor quantities only their basis tensors do.

The tensor coefficients $S_i^0$ and $C_i^0$ found by deriving the second Piola-Kirchhoff
stress tensor $S^0$ and the partial elasticity tensor $C^0$, respectively, are presented in the appendix A.4 on page 51. The derivatives of the basis functions of the MEAM potential which assemble the tensor coefficients are given in section A.2 in the appendix on page 46.

The basis tensor which form the tensor quantities are linear combinations of the first and second derivatives of the deformation measures $\lambda_j$ and $\phi_{jk}$ with respect to the right Cauchy-Green tensor $C$ and the sublattice shift vector $Z$. These quantities are given in appendix A.5 on page 52.

### 3.1.3 The algorithm

A routine that takes as input the right Cauchy-Green tensor $C$ and computes the stresses and stiffness must have a relaxation part where a sublattice shift $Z$ is that minimizes the potential energy. This minimization can be done by a Newton-algorithm. The general rule for a Newton search is

$$x^{k+1} = x^k - (\nabla \otimes \nabla f(x^k))^{-1} \cdot \nabla f(x^k)$$

where $f(x^k)$ is the function to be minimized depending of the the variables $x$ and $k$ is the counter. In our case $x = Z$ and $f = \Psi$, the derivations are done with respect to $Z$ so that $\nabla \Psi$ is $G$ and $\nabla \otimes \nabla \Psi$ gets $E$. So, the Newton-algorithm in this special case is

$$Z^{k+1} = Z^k - E^{-1}[Z^k]G[Z^k] = Z^k + \Delta Z^k$$

(3.7a)

or, in index notation

$$Z_i^{k+1} = Z_i^k - E_{ij}^{-1}[Z^k]G_j[Z^k] = Z_i^k + \Delta Z_i^k$$

(3.7b)

To avoid that the Newton-algorithm starts every time with the same initial vector, the sublattice shift vector of the former increment $Z_{old}$ is passed to the
actual increment which uses it as initial guess.

Since FE-formalisms are typically formulated in the updated Lagrangian form, not the referential stresses and stiffness are required but the spatial (actual) ones, i.e. the Cauchy-stress $\sigma$ and the spatial stiffness tensor $c$. This are the push-forward versions of the referential tensors $S$ and $C$, i.e. the right Piola-Kirchhoff stress tensor and the referential stiffness tensor, respectively. Using referential quantities for the relaxation part implies the additional computation of the spatial quantities afterwards, time and effort are doubled. Better would be to compute everything in spatial quantities, even the relaxation. This has one disadvantage: under rigid-body motion the Newton-algorithm must find a new internal shift vector $z$ even if the relative positions of the atoms do not change. Partially this can be avoided by preconditioning the vector:

$$
\hat{z}_{\text{new}} = F_{\text{new}} Z_{\text{old}} = F_{\text{new}} F_{\text{old}}^{-1} Z_{\text{old}} = F_{\text{new}} F_{\text{old}}^{-1} z_{\text{old}}
$$

$$
\hat{z}_{\text{new}} = \Delta F z_{\text{old}}
$$

(3.8)

where $\hat{z}_{\text{new}}$ is the preconditioned vector and $\Delta F = F_{\text{new}} F_{\text{old}}^{-1}$ is the incremental deformation gradient. This procedure has the disadvantage that not only rigid-body motions are used for the preconditioning but also stretches. This could be avoided by using not $\Delta F$ but $\Delta R$ of a polar decomposition $\Delta F = \Delta R \Delta U$. $\Delta R$ is an orthogonal tensor which represents the rotations only but not the stretches:

$$
\Delta F = \Delta R \Delta U
$$

(3.9a)

$$
\Delta U^2 = \Delta F^T \Delta F = \sum_{i=1}^{3} \lambda_i n_i \otimes n_i
$$

(3.9b)

$$
\Delta U = \sum_{i=1}^{3} \sqrt{\lambda_i} n_i \otimes n_i
$$

(3.9c)

$$
\Delta R = \Delta F \Delta U^{-1}
$$

where $\lambda_i$ are the eigenvalues and $n_i$ the eigenvectors of the tensor $\Delta U^2$. But as the computation of the eigenvalues and -vectors needs much effort the former preconditioning procedure is used.

ABAQUS requires from the routine also the tangent operator of the Jaumann stress rate, $c^J$, which is defined as follows:

$$
c^J_{ijkl} = \frac{1}{2} (\delta_{ik}\sigma_{jl} + \delta_{il}\sigma_{jk} + \delta_{jl}\sigma_{ik} + \delta_{jk}\sigma_{il}) + c_{ijkl}
$$

(3.10)

Figure 3.2 on the following page gives a scheme of the algorithm that was implemented as user defined material in ABAQUS.

### 3.1.4 The subroutine UMAT

The implementation of user defined material models into ABAQUS can be done with the definition of a subroutine called UMAT in a fortran file with extension
Figure 3.2: Scheme of the algorithm that was programmed and used as a user-defined material model in FEM computations with ABAQUS. The subroutine gets as input the new and the old deformation gradient $F_{\text{new}}$ and $F_{\text{old}}$, respectively and the old sublattice shift vector $z_{\text{old}}$. It uses a Newton algorithm for the relaxation part. If the Newton algorithm needs more than 20 iterations it is probable that the time increment that ABAQUS tries to do is too large; a cutback is enforced. After relaxing the material it continues with calculating the stress tensor $\sigma$, the elasticity tensor $c$, the Jaumann stress rate $c^J$ and the Raman-frequencies $f_R$. The subroutine returns $\sigma, c^J, z_{\text{new}}, f_R$. 
The skeleton of such subroutines is shown in appendix A.7 on page 58. Each subroutine begins with the declaration of the variables that are passed in by ABAQUS. It must be followed by the inclusion of the file ABA_PARAM.INC that contains information about the system on which the simulation is running. Specifically in the UMAT routine is the line CHARACTER*8 MATERL which is needed to pass in the name of the material. After that line the dimensions of the matrices are defined, this definitions can be augmented by the definition of intrinsic variables that are used inside the routine. The variables PROPS can be used to pass parameters defined in the graphical interface of ABAQUS to the routine. This option was finally not used, since the passed variables are singles with a mantissa of only 6 places what is too little for a correct computation of the stresses.

Once all variables are defined the main code which does all the needed computations comes. At the end the variables STRESS, DDSDDE and STATEV must be defined. The variable STRESS returns the Cauchy stress to ABAQUS, DDSDDE the tangent operator of the Jaumann stress rate and STATEV the solution dependent state variables. These solution dependent state variables can be used to pass information from one increment to the next, here especially used to pass the Raman-frequencies \( f_R \) (STATEV(1-3)) and the internal sublattice shift vector \( z \) (STATEV(4-6)).

The subroutine SDVINI is used to set the solution dependent state variables STATEV to an initial value, here zero (returns zero for any solution dependent state variable that has no defined initial condition).

Appendix A.7.1 on page 59 shows the dialogs of ABAQUS CAE in which the user defined material model is enabled and the material parameters are defined.

### 3.2 Verifications

Once the subroutine is implemented and debugged additional tests have to be done to ensure the material law works properly. One of this tests is the objectivity test where independence under rigid body rotation is tested. Another test is the verification of the elastic and stiffness moduli of the user defined material.

#### 3.2.1 Objectivity test

For this test a tetragonal geometry was created that was meshed with only one tetragonal element (element type C3D4). The three small legs of this tetrahedron have a length of unity and form right angles that were fixed with connectors. One of this three legs was combined with an axial connector that can be actuated (figure 3.3 on the next page). The axial connector was then actuated with an oscillating displacement of \( \pm 0.01 \) what corresponds to a relative displacement of 1%.

The objectivity test was done by comparing the stress response in the connector of a simulation with the tetrahedron fixed in space with the one of a simulation with a tetrahedron rotating around a point. It could be shown that
Figure 3.3: The model that was used for objectivity tests. A connector ‘translator’ was applied to the leg normal to the base that was fixed by connectors named ‘weld’. The connector ‘translator’ assures the normality and can be actuated in its axial direction. The connectors ‘weld’ fix the relative position of two connected points.

both responses are identical what means that the constitutive law is objective (figure 3.4 on the following page).

3.2.2 Elastic and stiffness moduli

The implementation of the MEAM formalism into the subroutine UMAT of ABAQUS can be tested by verifying the stiffness moduli. M.I. Baskes uses the shear elastic constants $\gamma$ and $\gamma'$ as well as the bulk modulus $B$ for fitting the material parameters [10, 11]. These constants can be converted into the stiffness moduli $C_{11}$, $C_{12}$ and $C_{44}$ by a simple calculation (see e.g. [14]):

\[
\begin{align*}
C_{11} &= \frac{4}{3} \gamma' + B \quad \text{(3.11a)} \\
C_{12} &= -\frac{2}{3} \gamma' + B \quad \text{(3.11b)} \\
C_{44} &= \gamma \quad \text{(3.11c)}
\end{align*}
\]

From these stiffness moduli the elastic moduli are obtained which are used for further verification, too. $E_{<100>}$, $E_{<110>}$ and $E_{<111>}$ are the elastic moduli in the crystal directions $<100>$, $<110>$ and $<111>$, respectively. The best way
is to calculate in an intermediate step the compliances:

\[ S_{11} = \frac{C_{11} + C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})} \]  \hspace{1cm} (3.12a)

\[ S_{12} = -\frac{C_{12}}{(C_{11} - C_{12})(C_{11} + 2C_{12})} \]  \hspace{1cm} (3.12b)

\[ S_{44} = \frac{1}{C_{44}} \]  \hspace{1cm} (3.12c)

From these compliances the elastic moduli are accessed in a straightforward way:

\[ E_{<100>^\ast} = \frac{1}{S_{11}} \]  \hspace{1cm} (3.13a)

\[ E_{<110>^\ast} = \frac{4}{2S_{11} + 2S_{12} + S_{44}} \]  \hspace{1cm} (3.13b)

\[ E_{<111>^\ast} = \frac{3}{S_{11} + 2S_{12} + S_{44}} \]  \hspace{1cm} (3.13c)

The material constants and the stiffness and elastic moduli obtained in that theoretical way are resumed in table 3.1 on the next page.

Numerically the stiffness and elastic moduli were determined by simulation of a cube under tension (except for the stiffness moduli \( C_{44} \) where the cube was sheared). The geometries as well as the boundary conditions that were realized...
Table 3.1: Material constants, stiffness and elastic moduli the MEAM parameters are based on. \( \gamma \), \( \gamma' \) and \( B \) are the constants M.I. Baskes uses directly for the fitting of the potential parameters \([10, 11]\). Moduli marked with diamonds ♦ are the ones obtained with the FE-simulation and the ones with asterisks * are experimentally measured values out of \([15]\).

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>( 0.48 \text{ eV/Å}^3 )</th>
<th>( 76.90 \text{ GPa} )</th>
<th>( C_{11} )</th>
<th>( 1.023 \text{ eV/Å}^3 )</th>
<th>( 163.956 \text{ GPa} )</th>
<th>( *164.0 ) GPa</th>
<th>( *165.773 ) GPa</th>
<th>( E_{\langle 100 \rangle} )</th>
<th>( 0.795 \text{ eV/Å}^3 )</th>
<th>( 127.418 \text{ GPa} )</th>
<th>( *127.0 ) GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma' )</td>
<td>( 0.31 \text{ eV/Å}^3 )</td>
<td>( 49.67 \text{ GPa} )</td>
<td>( C_{12} )</td>
<td>( 0.403 \text{ eV/Å}^3 )</td>
<td>( 64.621 \text{ GPa} )</td>
<td>( *64.0 ) GPa</td>
<td>( *63.924 ) GPa</td>
<td>( E_{\langle 110 \rangle} )</td>
<td>( 1.029 \text{ eV/Å}^3 )</td>
<td>( 164.868 \text{ GPa} )</td>
<td>( *164.0 ) GPa</td>
</tr>
<tr>
<td>( B )</td>
<td>( 0.61 \text{ eV/Å}^3 )</td>
<td>( 97.73 \text{ GPa} )</td>
<td>( C_{44} )</td>
<td>( 0.48 \text{ eV/Å}^3 )</td>
<td>( 76.90 \text{ GPa} )</td>
<td>( *78.0 ) GPa</td>
<td>( *79.619 ) GPa</td>
<td>( E_{\langle 111 \rangle} )</td>
<td>( 1.141 \text{ eV/Å}^3 )</td>
<td>( 182.773 \text{ GPa} )</td>
<td>( *176.0 ) GPa</td>
</tr>
</tbody>
</table>

in ABAQUS are presented in appendix A.8 on pages 60–61. The stress-strain curves for different material orientations obtained with the cube under tension are shown in figure 3.5 on the following page. The moduli were obtained by a numerical differentiation of the stress-strain curves. As can be seen in table 3.1 their values agree very well with the ones that were used by M.I. Baskes for the fit of the material parameters.

### 3.2.3 Improvements

During the verifications it was remarked that ABAQUS could not find any converging solution for a body on which act neither forces nor displacements. The reason for this was found in numerical uncertainties in the order of \( 10^{-5} \) that are apparent in the UMAT routine. Variables are declared as doubles in the UMAT routine which have a mantissa of 15. During most of the routine the error is in the order of \( 10^{-15} \) but multiplying the resulting tensor quantities with \( \gamma \) which has (in SI-units) an order of \( 10^{10} \) the error rises to \( 10^{-5} \). Especially influenced is the stress tensor \( \sigma \) which should be 0 in the reference configuration but due to the numerical error it is not. This forces ABAQUS which uses the stress tensor \( \sigma \) as quality criteria to find an other equilibrium state, which cannot be found.

So, the numerical fluctuations must be filtered out of the stress tensor \( \sigma \). A filter which does so must be objective in order to keep the whole routine objective. The idea was now to construct a filter function which uses the norm of \( \sigma \) as parameter. The norm gives an idea of the ”magnitude” of a tensor. Once
Figure 3.5: Stress-strain curves obtained for a cube under tension in $<100>$, $<110>$ and $<111>$ directions. As can been observed, the material has its maximal strength in $<111>$-direction. The elastic modulus decreases with increasing strain.
3 RESULTS

this "magnitude" gets smaller than a certain threshold value $\sigma_{TOL}$, $\sigma$ should converge smoothly to zero. A filter function doing so is given by

$$f = \tanh^2 \left( \left( \frac{||\sigma||}{\sigma_{TOL}} \right)^2 \right)$$ (3.14)

see figure 3.6 on the following page, the filtered $\sigma_f$ gets simply

$$\sigma_f = f \cdot \sigma$$ or in index notation $(\sigma_f)_i = f \cdot \sigma_i$ (3.15)

With a tolerance $\sigma_{TOL}$ that is one-hundredth of $\gamma$ good results were obtained; ABAQUS converged for unstressed and unstrained configurations.

3.3 Parameter optimization

Once the stress and stiffness tensors were established, it was found that neither the partial elasticity $C_{044}$ nor the Raman frequency $f_R$ fit values found in literature for the unstrained structure. $C_{044}$ is expected to be about 111GPa, a value that comes from DFT computations [1], with the MEAM potential and the parameters given in table 2.1 on page 25 about 250GPa are obtained. The Raman frequency $f_R$ is with 26.68THz also too high, measures were about 15.53THz [16]. It seems that the parameter set given by M.I. Baskes [11] corrects the too high partial elasticity $C_{044}$ with an unrealistic Raman frequency to get the correct value for $C_{44}$:

$$C_{44} = C_{044}^0 - E^{-1} [f_R] D^2 = C_{044}^0 - \frac{1}{\sqrt{3}} \zeta D$$ (3.16)

where $E$ and $D$ are the nonzero components of $E$ and $D$ in the reference configuration.

To correct this inconvenience a refitting of the parameters $s_i$, $t_i$, $\beta_i$ and $A$ was strived. Since parameters $s_i$ depend only on geometry and $A$ is determined from phase diagrams [11] this parameters are not accessible to a refitting, only parameters $t_i$, $\beta_i$ are. $t_1$ is set equal 1 without loss of generality [11]. The parameters $\beta_i$ which determine the exponential decay of the electron densities with increasing stretches are restricted to be positive. The new parameter set should reproduce correctly following properties where the numerical values are given in table A.1 on page 57:

1. The three stiffness $C_{11} = C_{11}^0$, $C_{12} = C_{12}^0$ and $C_{44}$

2. The partial stiffness $C_{44}^0$

3. The Kleinman parameter $\zeta = \sqrt{3} \frac{D}{E}$

The Kleinman parameter $\zeta$ is a measure for the relative sublattice shift under $C_{44}$ shear.

The analytical formulas for $C_{11}$, $C_{12}$, $C_{44}^0$, $C_{44}$ and $\zeta$ in the reference structure
Figure 3.6: Filter $f$ that is used to filter out the numerical error in the stress tensor $\sigma$. This filter functions cuts smoothly the norm of $\sigma$ once it becomes smaller than $\sigma_{TOL}$.

can be determined from formulas (A.5) to (A.8) on pages 48-50 in a straightforward manner. An additional restriction $R$ comes from the fact that the second Piola-Kirchhoff stress tensor must vanish in the reference structure. This is generally not true for the components on the diagonal which do not vanish for all parameter sets.

$$f[t_i, \beta_i] = w_1 \left( C_{11}^{\text{lit.}} - C_{11}[t_i, \beta_i] \right)^2 + w_2 \left( C_{12}^{\text{lit.}} - C_{12}[t_i, \beta_i] \right)^2$$
$$+ w_3 \left( C_{44}^{\text{lit.}} - C_{44}[t_i, \beta_i] \right)^2 + w_4 \left( C_{44}^{\text{lit.}} - C_{44}[t_i, \beta_i] \right)^2$$
$$+ w_5 \left( \zeta^{\text{lit.}} - \zeta[t_i, \beta_i] \right)^2 + w_6 R[t_i, \beta_i]^2$$  \hspace{1cm} (3.17)

is a formulation of the problem that allows to find the minimum of the function $f[t_i, \beta_i]$. The superscript \text{lit} indicates the values found in literature and the factors $w_i$ are weighting factors which allow to adjust the weight of each term, necessary especially since the terms have different orders of magnitude.

With Mathematica, formulation (3.17) and the restriction $\beta_i > 0$ the following parameter set was found:

$$t_0 = 1.0 \quad \beta_0 = 11.8427$$
$$t_1 = 2.55994 \quad \beta_1 = 23.4047$$
$$t_2 = 5.94752 \quad \beta_2 = 8.16022$$
$$t_3 = -0.250182 \quad \beta_3 = 213.014$$

The resulting material properties are

$C_{11} = 1.03375 \quad (1.0347) \text{ eV/Å}$
$C_{12} = 0.397107 \quad (0.3990) \text{ eV/Å}$
$C_{44}^a = 0.7 \quad (0.7) \text{ eV/Å}$
$C_{44} = 0.4969 \quad (0.4969) \text{ eV/Å}$
$\zeta = 0.74 \quad (0.74)$
$\kappa_R = 11.86 \quad \text{THz}$
where the values that were strived are given in brackets. Obviously all of the directly optimized parameters are very good approximated, only the Raman frequency \( f_R \) that results is more than 20\% less than the experimentally measured one (15.53THz).

Optimizations where the Raman frequency was also included in \( f_\{\{t, \beta\}\} \) showed that either the property set \( \{C_{11}, C_{12}, C''_{44}, C_{44}, \zeta\} \) can be approximated or the Raman frequency \( f_R \), but not both the same time.

Testing the new set of parameters it was found that with this set the second Piola-Kirchhoff stress tensor gets complex, at least for certain deformation gradients that are not equal identity. There must be more restrictions for the parameter set if not the reference structure is regarded. As it turned out to be a very complex matter to guarantee that the stress tensor stays real for all admissible deformation gradients the refitting was postponed. All computations were therefore done with the originally proposed parameters.

### 3.4 Simulation of the experiment

One of the most interesting aspects of this work was the comparison of the experiments described in [17] and a simulation of them using the new material model. For this reason the new user defined material model was incorporated into an already existing simulation that was done by O. Keller. A description of the setup as well as details about symmetries and contact conditions can be found in chapter 4 of [18].

Simulated was the best whisker that was found within the experiments up to date, this whisker exercised a force of 70.2mN to the clamps before it broke where the inter-clamp distance was 1.565mm. The geometry of this whisker is given in figure 3.7. Only one fourth of the whisker is simulated, this helps to avoid computational effort. Nevertheless one simulation till the clamps have a distance of 0.9mm of each other takes about 5 hours.

From the output of the simulation the inter-clamp distance and the contact force were extracted. The plots force vs. inter-clamp distance was compared with experimental values, see figure 3.8 on page 41. These results were also compared with a linear elastic calculation where stiffness constants were used.

![Figure 3.7](image.png)

Figure 3.7: Geometry of the whisker that was simulated. Its dimensions depth and length were halved due to the symmetry conditions that are applied. Additionally the crystallographic planes are indicated.
first from literature [15] and second the ones indicated by M.I. Baskes (see tabular 3.1 on page 35). Experimentally determined forces were found to be between forces that were obtained in simulations using the MEAM potential and linear-elastic simulations.
Figure 3.8: Comparison between the force acting against the clamps that was measured in experiments and the force that was found in simulations. It can be seen that the measured force is between the simulation where the MEAM-potential was used and linear elastic simulations (with non-linear geometry).
4 Conclusion

A new material model was made accessible to FEM computations. The "MEAM-material" was derived from a potential form that takes into account the molecular dynamics of diamond cubic crystals. It incorporates a degree of freedom that is not used in other potentials utilized so far: the internal displacement of the two sublattices in the crystal. The fact that two neighboring atoms do not own bonds that are oriented in the same directions means that there exist two sub-lattices. This sub-lattices shift relative to each other while the crystal is subjected to a deformation, minimizing the elastically stored deformation energy.

Two consequences arise of the implementation of this sub-lattice shift in the potential, the first is that all three stiffness moduli of SCSi can be reproduced, there are enough parameters to span them independently. The second consequence is the accessibility of Raman-frequencies. Potential forms that do not take into account the sub-lattice shift can only reproduce the acoustic branches of the phonon dispersion relation, one longitudinal and two transversal acoustic waves. The MEAM model gives also the three optical branches of the phonon dispersion diagram. These branches are in the reference structure triply degenerate but with increasing strain they become non-degenerate. Therefore they can be used as a measure of inner elasticity which is done by Raman-spectroscopy.

During the analytical derivation of the stress and stiffness tensors it was found that the Raman-frequencies are with about $26\,\text{THz}$ too high compared with experimentally measured values ($15.53\,\text{THz}$, [16]). The reason for this is, that with the actual values of the parameters the partial stiffness $C_{44}^0$ is too high, what is compensated with a too high Raman-frequency. The idea was to find an other parameter set that does not have this problem. For this reason the parameters were refitted to experimentally known data where the restriction is that the stress tensor $\sigma$ must be zero in the reference configuration. But it turned out that there must be other restrictions guaranteeing that stresses stay real. As the problem turned out to be more time-consuming than initially thought it was postponed.

The numerical implementation was done in a FORTRAN sub-routine which can be used in ABAQUS as user-defined material model. A central question was whether the relaxation part should be done with referential quantities or with spacial ones. Referential quantities have the advantage that they are not afflicted by superimposed rigid body rotations which helps to find the sub-lattice shift vector $Z$. On the other hand it would have been necessary to compute both, the referential quantities as well as the spatial ones. So, the usage of only the spatial quantities was chosen but with a preconditioning of the starting vector for the relaxation routine. The old sub-lattice shift vector is passed on to the new time increment and preconditioned with the old and the new deformation gradient. This helps the relaxation part, which is in fact a Newton-algorithm, to converge. With this procedure it normally finds a valid solution within one iteration.

First it was planned to feed the material parameters by use of the \texttt{STATEV}-array
to the UMAT routine, but it turned out that ABAQUS passes the values only with single-precision, which is not enough. Especially the stress tensor $\sigma$ caused problems. The diagonal components of it were non-zero in the reference structure, what led to severe problems.

One major problem that arose during the implementation was the numerical precision, although working with doubles, the numerical error let ABAQUS not find any solution for the case of a non-stressed and non-strained solid. The solution of that problem was finally found in the incorporation of a filter function which filters the stress tensor $\sigma$ for small norms. $\sigma$ is the most problematic quantity since ABAQUS uses it for evaluating the force residuals and so decides whether a configuration has reached static equilibrium.

The first step once the numerical implementation was finished was the verification of the objectivity of the routine and whether the stiffness and the elastic moduli were correctly reproduced. The former test was done by comparing the force responses of a tetrahedron to a strain of one percent for the case of a fixed geometry with the case of a rotating geometry. As expected the routine was in fact objective. The latter test was done by deforming a cube with appropriate deformation modes and numerical derivations of the stress-strain responses. The stiffness as well as the elastic moduli turned out to be reproduced correctly.

The last but most interesting step was the comparison of the experimentally determined values with the simulation. For this reason the simulation that was already set up by O. Keller was used with the user defined "MEAM-material" model and the geometry of the best whisker that was found in experiments up to date. It seemed that the force that acts on the clamps for the same inter-clamp distance is lower in the simulation (-11.6%, just before the whisker broke in the experiment) than in the experiment. In contrast, linear elastic computations show as expected a much stiffer behavior (+7.4%) than in reality. One reason for the discrepancy between simulation with "MEAM-material" and the experiments could be that the stiffness moduli that are represented with the potential do not correspond to the real ones, perhaps they decrease too much with increasing strain. A simulation with a much wider range of inter-clamp distances could at least show if the forces are in agreement for the lower part.
5 Outlook

Although the new material model was successfully implemented there remain some points that can be done in future.

- A next step would be to understand why the model has not the same stiffness as the whiskers that were used in experiments. Are the model parameters not correct or is it an intrinsic problem of that model that the stiffness does not evolve with increasing strain as in reality?

- The refitting of the model parameters is certainly a worthwhile thing. If it could be shown that the Raman-frequencies can not be reproduced correctly this would mean that the model lacks still some important physical properties.

- More experiments should be simulated to get a feeling whether the discrepancy between experiment and simulation is always that way or whether the error changes from case to case.

- A comparison with other constitutive laws would allow to find the benefits and the disadvantages of the model. Is its behavior with increasing strain better than other models? Exists other models that give better values for the Raman-frequencies?

- Application of the strong ellipticity failure criterion. Does it provide usable information about the failure strength of SCSi?

- Clarify whether the usage of more than only first nearest neighbors would help to ameliorate the models exactness.
A Appendix

A.1 The MEAM strain energy density

\[ \Psi = \frac{1}{N} \sum_j G[j] + \left( F - \frac{1}{N} \sum_j H[j] \right) \]  

(A.1)

\[ G[j] = -\gamma (1 + \alpha (\lambda_j - 1)) e^{-\alpha (\lambda_j - 1)} \]

\[ F = \frac{A \gamma d}{N} \ln \left( \frac{d}{N} \right) \]

\[ H[j] = \frac{A \gamma n[j]}{N} \ln \left( \frac{n[j]}{N} \right) \]

\[ \gamma = \frac{2E_0}{V_{PUC}} \]

\[ d^2 = \sum_{l=0}^{3} (t[l] \rho_l^2) \]

\[ \rho_0 = \sum_j a[j, 0] \]

\[ \rho_1^2 = \sum_{j,k} \Pi[j, k, 1] \]

\[ \rho_2^2 = \sum_{j,k} \Pi[j, k, 2] - \frac{1}{3} \Delta^2 \]

\[ \rho_3^2 = \sum_{j,k} \Pi[j, k, 3] \]

\[ \Delta = \sum_j a[j, 2] \]

\[ \Pi[j, k, l] = a[j, l] a[k, l] \phi_{jk}^l \]

\[ a[j, l] = e^{-\beta(j, l)(\lambda_j - 1)} \]

\[ n[j]^2 = \sum_{l=0}^{3} (t[l] s[l] a[j, l]^2) \]
A.2 Derivation of the MEAM potential

A.2.1 First derivatives

\[
\frac{\partial G_j}{\partial C} = G_1[j] \frac{\partial \lambda_j}{\partial C}
\]

\[
\frac{\partial F}{\partial C} = F_1 \frac{\partial d}{\partial C}
\]

\[
\frac{\partial H_j}{\partial C} = H_1[j] \frac{\partial n[j]}{\partial C}
\]

\[
\frac{\partial d}{\partial C} = d_1 \frac{\partial \rho_0}{\partial C} + d_2 \sum_{l=1}^3 \left( t[l] \left( \sum_{j,k} \frac{\partial \Pi[j,k,l]}{\partial C} \right) \right) + d_3 \frac{\partial \Delta}{\partial C}
\]

\[
\frac{\partial \rho_0}{\partial C} = -\beta[0] \sum_j \left( a[j,0] \frac{\partial \lambda_j}{\partial C} \right)
\]

\[
\frac{\partial \Delta}{\partial C} = -\beta[2] \sum_j \left( a[j,2] \frac{\partial \lambda_j}{\partial C} \right)
\]

\[
\frac{\partial \Pi[j,k,l]}{\partial C} = \Pi_1[j,k,l] \frac{\partial \lambda_j}{\partial C} + \Pi_2[j,k,l] \frac{\partial \phi_{jk}}{\partial C}
\]

\[
\frac{\partial a[j,l]}{\partial C} = -\beta[l] a[j,l] \frac{\partial \lambda_j}{\partial C}
\]

\[
\frac{\partial n[j]}{\partial C} = n_1[j] \frac{\partial \lambda_j}{\partial C}
\]

\[
G_1[j] = \gamma \alpha^2 (\lambda_j - 1) e^{-\alpha(\lambda_j - 1)}
\]

\[
F_1 = \frac{A \gamma}{N} \left( \ln \left[ \frac{d}{N} \right] + 1 \right)
\]

\[
H_1[j] = \frac{A \gamma}{N} \left( \ln \left[ \frac{n[j]}{N} \right] + 1 \right)
\]

\[
d_1 = \frac{1}{d(0)}
\]

\[
d_2 = \frac{1}{2d}
\]

\[
d_3 = -\frac{1}{3d} t[2] \Delta
\]

\[
\Pi_1[j,k,l] = -\beta[l] a[j,l] a[k,l] \phi_{jk}^l
\]

\[
\Pi_2[j,k,l] = l \cdot a[j,l] a[k,l] \phi_{jk}^{l-1}
\]

\[
n_1[j] = -\frac{1}{n[j]} \sum_{l=0}^3 (t[l] s[l] \beta[l] a[j,l] t^2)
\]
A.2.2 Second derivatives

\[
\begin{align*}
\frac{\partial G_1[j]}{\partial C} &= G_2[j] \frac{\partial \lambda_j}{\partial C} \\
\frac{\partial F_1}{\partial C} &= F_2 \frac{\partial d}{\partial C} \\
\frac{\partial H_1[j]}{\partial C} &= H_2[j] \frac{\partial n[j]}{\partial C} \\
\frac{\partial d_1}{\partial C} &= d_4 \frac{\partial \rho_0}{\partial C} + d_5 \sum_{l=1}^{3} \left( t[l] \left( \sum_{j,k} \frac{\partial \Pi[j,k,l]}{\partial C} \right) \right) + d_6 \frac{\partial \Delta}{\partial C} \\
\frac{\partial d_2}{\partial C} &= d_7 \frac{\partial d}{\partial C} \\
\frac{\partial d_3}{\partial C} &= d_8 \frac{\partial \rho_0}{\partial C} + d_9 \sum_{l=1}^{3} \left( t[l] \left( \sum_{j,k} \frac{\partial \Pi[j,k,l]}{\partial C} \right) \right) + d_{10} \frac{\partial \Delta}{\partial C} \\
\frac{\partial \Pi_1[j,k,l]}{\partial C} &= \Pi_3[j,k,l] \left( \frac{\partial \lambda_j}{\partial C} + \frac{\partial \lambda_k}{\partial C} \right) + \Pi_4[j,k,l] \frac{\partial \phi_{j,k}}{\partial C} \\
\frac{\partial \Pi_2[j,k,l]}{\partial C} &= \Pi_4[j,k,l] \left( \frac{\partial \lambda_j}{\partial C} + \frac{\partial \lambda_k}{\partial C} \right) + \Pi_5[j,k,l] \frac{\partial \phi_{j,k}}{\partial C} \\
\frac{\partial n_2[j]}{\partial C} &= n_2[j] \frac{\partial \lambda_j}{\partial C}
\end{align*}
\]

\[
\begin{align*}
G_2[j] &= \gamma \alpha^2 \left( 1 - \alpha (\lambda_j - 1) \right) e^{-\alpha (\lambda_j - 1)} \\
F_2 &= \frac{A \gamma}{dN} \\
H_2[j] &= \frac{A \gamma}{n[j]N} \\
d_4 &= \frac{1}{d^2} t[0] \left( d - \rho_0 d_1 \right) \\
d_5 &= -\frac{1}{d^2} t[0] \rho_0 d_2 \\
d_6 &= -\frac{1}{d^2} t[0] \rho_0 d_3 \\
d_7 &= -\frac{1}{2d^2} \\
d_8 &= \frac{1}{3d^2} t[2] \Delta d_1 \\
d_9 &= \frac{1}{3d^2} t[2] \Delta d_2 \\
d_{10} &= \frac{1}{3d^2} t[2] \left( \Delta d_3 - d \right) \\
\Pi_3[j,k,l] &= \beta \left( t^2 \omega[j,l] a[k,l] \phi_{j,k} \right) \\
\Pi_4[j,k,l] &= -t \cdot \beta \left( t \omega[j,l] a[k,l] \phi_{j,k}^{-1} \right) \\
\Pi_5[j,k,l] &= t \cdot \left( t - 1 \right) a[j,l] a[k,l] \phi_{j,k}^{-2} \\
n_2[j] &= \frac{1}{n[j]} \left( \sum_{l=0}^{2} \left( t[l] s[l] \beta \left( t^2 \omega[j,l] a[j,l] \phi_{j,k}^{-2} \right) \right) - n_1[j]^2 \right) (A.3)
\end{align*}
\]
A.3 Tensor quantities

A.3.1 Partial Second Piola-Kirchhoff Stress Tensor

\[
S^0 = 2 \left( \sum_j \left( S^0_{0}[j] \frac{\partial \lambda_j}{\partial C} \right) + \sum_{j,k} \left( S^0_{02}[j,k] \left( \frac{\partial \lambda_j}{\partial C} + \frac{\partial \lambda_k}{\partial C} \right) + S^0_{03}[j,k] \frac{\partial \phi_{jk}}{\partial C} \right) \right) \quad (A.4)
\]

A.3.2 Partial Elasticity Tensor

\[
C^0 = 4 \left( \sum_j \left( \frac{\partial \lambda_j}{\partial C} \otimes \frac{\partial \lambda_j}{\partial C} + \frac{\partial^2 \lambda_j}{\partial C \otimes \partial C} \right) \right)
+ \sum_{j,k} \left( C^0_{01}[j,k] \frac{\partial \lambda_j}{\partial C} \otimes \frac{\partial \lambda_k}{\partial C} + C^0_{02}[j,k] \left( \frac{\partial \lambda_j}{\partial C} + \frac{\partial \lambda_k}{\partial C} \right) \otimes \left( \frac{\partial \lambda_j}{\partial C} + \frac{\partial \lambda_k}{\partial C} \right) \right)
+ \sum_{i,j,k} \left( C^0_{03}[i,j,k] \frac{\partial \phi_{ij}}{\partial C} \otimes \frac{\partial \phi_{ij}}{\partial C} + C^0_{04}[i,j,k] \left( \frac{\partial \phi_{ij}}{\partial C} + \frac{\partial \phi_{ij}}{\partial C} \right) \otimes \left( \frac{\partial \phi_{ij}}{\partial C} + \frac{\partial \phi_{ij}}{\partial C} \right) \right) \right) \quad (A.5)
\]
A.3.3 Internal Force Tensor

\[
G = \left( \sum_j \left( S^0_j \frac{\partial \lambda_j}{\partial \mathbf{Z}} \right) + \sum_{j,k} \left( S^0_{j,k} \left( \frac{\partial \lambda_j}{\partial \mathbf{Z}} + \frac{\partial \lambda_k}{\partial \mathbf{Z}} \right) + S^0_{3, j,k} \frac{\partial \phi_{jk}}{\partial \mathbf{Z}} \right) \right) \tag{A.6}
\]

A.3.4 Internal Elasticity Tensor

\[
E = \left( \sum_j \left( S^0_j \frac{\partial \lambda_j}{\partial \mathbf{Z}} \otimes \frac{\partial \lambda_j}{\partial \mathbf{Z}} + S^0_j \frac{\partial^2 \lambda_j}{\partial \mathbf{Z} \otimes \partial \mathbf{Z}} \right) + \sum_{j,k} \left( C^0_{1, j, k} \frac{\partial \lambda_j}{\partial \mathbf{Z}} \otimes \frac{\partial \lambda_k}{\partial \mathbf{Z}} + C^0_{1, j, k} \left( \frac{\partial \lambda_j}{\partial \mathbf{Z}} + \frac{\partial \lambda_k}{\partial \mathbf{Z}} \right) \right) \right)
\]

\[
+ C^0_{6, j, k} \frac{\partial \phi_{jk}}{\partial \mathbf{Z}} \otimes S^0_{3, j, k} \frac{\partial^2 \phi_{jk}}{\partial \mathbf{Z} \otimes \partial \mathbf{Z}} + S^0_{3, j, k} \frac{\partial^2 \phi_{jk}}{\partial \mathbf{Z} \otimes \partial \mathbf{Z}} \right) + \sum_{j,k} \left( C^0_{2, [j, i]} \left( \frac{\partial \lambda_j}{\partial \mathbf{Z}} \otimes \frac{\partial \lambda_i}{\partial \mathbf{Z}} + \frac{\partial \lambda_j}{\partial \mathbf{Z}} \otimes \frac{\partial \lambda_i}{\partial \mathbf{Z}} \right) + C^0_{2, [j, k]} \left( \frac{\partial \lambda_j}{\partial \mathbf{Z}} \otimes \frac{\partial \lambda_k}{\partial \mathbf{Z}} + \frac{\partial \lambda_j}{\partial \mathbf{Z}} \otimes \frac{\partial \lambda_k}{\partial \mathbf{Z}} \right) \right)
\]

\[
+ \sum_{h, i, j, k} \left( C^0_{6, [h, i, j, k]} \left( \frac{\partial \lambda_h}{\partial \mathbf{Z}} \otimes \frac{\partial \lambda_i}{\partial \mathbf{Z}} + \frac{\partial \lambda_h}{\partial \mathbf{Z}} \otimes \frac{\partial \lambda_j}{\partial \mathbf{Z}} \right) + C^0_{11, [h, i, j, k]} \frac{\partial \phi_{hi}}{\partial \mathbf{Z}} \otimes \frac{\partial \phi_{jk}}{\partial \mathbf{Z}} \right) \right) \tag{A.7}
\]
A.3.5 Force-Strain Coupling Tensor

\[
D = 2 \left( \sum_j \left( S_0^0[j] \frac{\partial \lambda_j}{\partial Z} \otimes \frac{\partial \lambda_j}{\partial C} + S_1^0[j] \frac{\partial^2 \lambda_j}{\partial Z \partial C} \right) 
+ \sum_{j,k} \left( C_1^0[j,k] \frac{\partial \lambda_j}{\partial Z} \otimes \frac{\partial \lambda_k}{\partial C} + C_2^0[j,k] \left( \frac{\partial \lambda_j}{\partial Z} + \frac{\partial \lambda_k}{\partial C} \right) \otimes \left( \frac{\partial \lambda_j}{\partial C} + \frac{\partial \lambda_k}{\partial C} \right) \right) 
+ C_3^0[j,k] \left( \frac{\partial^2 \lambda_j}{\partial Z \partial C} + \frac{\partial^2 \lambda_k}{\partial Z \partial C} \right) 
+ C_4^0[j,k] \left( \frac{\partial \phi_{jk}}{\partial Z} \otimes \frac{\partial \phi_{jk}}{\partial C} + S_2^0[j,k] \left( \frac{\partial^2 \phi_{jk}}{\partial Z \partial C} + \frac{\partial^2 \phi_{jk}}{\partial Z \partial C} \right) \right) 
+ \sum_{i,j,k} \left( C_5^0[i,j,k] \left( \frac{\partial \lambda_i}{\partial Z} \otimes \frac{\partial \lambda_j}{\partial C} \right) \right. 
+ \left. \left( C_6^0[i,j,k] \left( \frac{\partial \lambda_i}{\partial Z} + \frac{\partial \lambda_j}{\partial C} \right) \otimes \left( \frac{\partial \lambda_i}{\partial C} + \frac{\partial \lambda_j}{\partial C} \right) \right) \right) 
+ \left( C_7^0[i,j,k] \left( \frac{\partial \phi_{hi}}{\partial Z} \otimes \frac{\partial \phi_{jk}}{\partial C} + C_8^0[i,j,k] \left( \frac{\partial^2 \phi_{hi}}{\partial Z \partial C} \right) \right) \right) \right) \right) \quad (A.8)
\]
A.4 Tensor coefficients

\[
S_1^0[j] = \frac{1}{N} G_1[j] - \frac{1}{N} H_1[j] n_1[j] - F_1 d_1 \beta[0] a[j, 0] - F_1 d_3 \beta[2] a[j, 2] \\
S_2^0[j, k] = \sum_{l=1}^{3} (F_1 d_2 t[l] \Pi_1[j, k, l]) \\
S_3^0[j, k] = \sum_{l=1}^{3} (F_1 d_2 t[l] \Pi_2[j, k, l]) \\
S_4^0[j] = \frac{1}{N} G_2[j] - \frac{1}{N} n_1[j]^2 H_2[j] - \frac{1}{N} H_1[j] n_2[j] + F_1 d_1 \beta[0]^2 a[j, 0] + \frac{1}{N} H_1[j] n_2[j] + F_1 d_1 \beta[0]^2 a[j, 0] + \\
S_5^0[j] = \beta[0] (F_2 d_2 d_3 + F_1 d_4) \beta[0] a[j, 0] + (F_2 d_2 d_3 + F_1 d_4) \beta[2] a[j, 2] \\
S_6^0[j] = -(F_2 d_2 d_3 + F_1 d_4) \beta[0] a[j, 0] + (F_2 d_2 d_3 + F_1 d_4) \beta[2] a[j, 2] \\
S_7^0[j, k] = \sum_{l=1}^{3} (t[l] \Pi_1[j, k, l]) \\
S_8^0[j, k] = \sum_{l=1}^{3} (t[l] \Pi_2[j, k, l]) \\
S_9^0[j] = \beta[2] (F_2 d_2 d_3 + F_1 d_4) \beta[0] a[j, 0] + (F_2 d_2 d_3 + F_1 d_4) \beta[2] a[j, 2] \\
S_{10}^0[j, k] = (F_2 d_2 + F_1 d_7) \sum_{l=1}^{3} (t[l] \Pi_1[j, k, l]) \\
S_{11}^0[j, k] = -(d_1 \beta[0] a[j, 0] + d_3 \beta[2] a[j, 2]) \\
S_{12}^0[j, k] = \sum_{l=1}^{3} (t[l] \Pi_3[j, k, l]) \\
S_{13}^0[j, k] = \sum_{l=1}^{3} (t[l] \Pi_4[j, k, l]) \\
S_{14}^0[j, k] = (F_2 d_2 + F_1 d_7) \sum_{l=1}^{3} (t[l] \Pi_2[j, k, l]) \\
S_{15}^0[j, k] = \sum_{l=1}^{3} (t[l] \Pi_5[j, k, l]) \quad (A.9)
\]

\[
C_1^0[j, k] = S_1^0[j] a[k, 0] + S_2^0[j] a[k, 2] \\
C_2^0[i, j, k] = S_1^0[i] S_2^0[j, k] \\
C_3^0[i, j, k] = S_1^0[i] S_1^0[j, k] \\
C_4^0[i, j, k] = S_1^0[i] S_1^0[j, k] \\
C_5^0[h, i, j, k] = d_2 S_2^0[j, k] S_1^0[h, i] \\
C_6^0[h, i, j, k] = d_2 S_1^0[j, k] S_1^0[h, i] \\
C_7^0[j, k] = F_1 d_2 S_2^0[j, k] \\
C_8^0[k, j] = F_1 d_2 S_2^0[j, k] \\
C_9^0[i, j, k] = S_1^0[i] S_1^0[j, k] \\
C_{10}^0[h, i, j, k] = d_2 S_2^0[j, k] S_1^0[h, i] \\
C_{11}^0[h, i, j, k] = d_2 S_1^0[j, k] S_1^0[h, i] \\
C_{12}^0[j, k] = F_1 d_2 S_2^0[j, k] \\
C_{13}^0[j, k] = F_1 d_2 S_2^0[j, k] \quad (A.10)
\]
A.5 Derivatives of the deformation measures

\[ \frac{\partial \lambda_j}{\partial C} = \frac{1}{2\lambda_j} \left( (M_j + Z) \otimes (M_j + Z) + (M_j + Z) \otimes (M_j + Z) \right) \]

\[ \chi \left[ \frac{\partial \lambda_j}{\partial C} \otimes \frac{\partial \lambda_j}{\partial C} \right] = \frac{1}{2\lambda_j^2} \left( (M_j + Z) \otimes (M_j + Z) + (M_j + Z) \otimes (M_j + Z) \right) - \frac{\phi}{2\lambda_j} \left( (M_j + Z) \otimes (M_j + Z) - (M_j + Z) \otimes (M_j + Z) \right) \]

\[ \frac{\partial \phi_{jk}}{\partial C} = \frac{1}{2\lambda_j} \left( (m_j + z) \otimes (m_j + z) + (m_j + z) \otimes (m_j + z) \right) \]

\[ \chi \left[ \frac{\partial \phi_{jk}}{\partial C} \otimes \frac{\partial \phi_{jk}}{\partial C} \right] = \frac{1}{2\lambda_j^2} \left( (m_j + z) \otimes (m_j + z) + (m_j + z) \otimes (m_j + z) \right) - \frac{\phi}{2\lambda_j} \left( (m_j + z) \otimes (m_j + z) - (m_j + z) \otimes (m_j + z) \right) \]
\[
\frac{\partial^2 \phi_{jk}}{\partial \mathbf{C} \otimes \partial \mathbf{C}} = -\frac{1}{4\mathcal{X}_k^2} \left( (M_j + Z) \otimes (M_j + Z) + (M_k + Z) \otimes (M_k + Z) \right) + \frac{1}{4\mathcal{X}_k^2} \left( (m_j + z) \otimes (m_j + z) + (m_k + z) \otimes (m_k + z) \right) + \frac{3}{4\mathcal{X}_k^2} \left( (m_j + z) \otimes (m_k + z) + (m_k + z) \otimes (m_j + z) \right)
\]

\[
\frac{\partial \chi}{\partial \mathbf{C}} = -\frac{1}{Z} \left( (M_j + Z) \otimes (M_j + Z) + (M_k + Z) \otimes (M_k + Z) \right)
\]
\begin{align}
\chi \left[ \frac{\partial \lambda_j}{\partial Z} \right] &= \frac{1}{\lambda_j} \left( m_j + z \right) \quad \text{(A.15b)} \\
\frac{\partial^2 \lambda_j}{\partial Z \otimes \partial Z} &= \frac{1}{\lambda_j} C - \frac{1}{\lambda_j^2} C (M_j + Z) \otimes C (M_j + Z) \quad \text{(A.16a)} \\
\chi \left[ \frac{\partial^2 \lambda_j}{\partial Z \otimes \partial Z} \right] &= \frac{1}{\lambda_j} I - \frac{1}{\lambda_j^3} (m_j + z) \otimes (m_j + z) \quad \text{(A.16b)} \\
\frac{\partial \phi_{jk}}{\partial Z} &= \left( \frac{1}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_j^2} \right) C (M_j + Z) + \left( \frac{1}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_k^2} \right) C (M_k + Z) \quad \text{(A.17a)} \\
\chi \left[ \frac{\partial \phi_{jk}}{\partial Z} \right] &= \left( \frac{1}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_j^2} \right) (m_j + z) + \left( \frac{1}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_k^2} \right) (m_k + z) \quad \text{(A.17b)} \\
\frac{\partial^2 \phi_{jk}}{\partial Z \otimes \partial Z} &= \left( \left( 3 \frac{\phi_{jk}}{\lambda_j^3} - \frac{2}{\lambda_j^2 \lambda_k} \right) C (M_j + Z) + \left( \frac{\phi_{jk}}{\lambda_j^3 \lambda_k^2} - \frac{\lambda_j^2 + \lambda_k^2}{\lambda_j^3 \lambda_k^2} \right) C (M_k + Z) \right) \otimes C (M_j + Z) \\
&\quad + \left( \left( 3 \frac{\phi_{jk}}{\lambda_k^3} - \frac{2}{\lambda_j \lambda_k^2} \right) C (M_k + Z) + \left( \frac{\phi_{jk}}{\lambda_j \lambda_k^3} - \frac{\lambda_j^2 + \lambda_k^2}{\lambda_j \lambda_k^3} \right) C (M_j + Z) \right) \otimes C (M_k + Z) \\
&\quad + \left( \frac{2}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_j^2} - \frac{\phi_{jk}}{\lambda_k^2} \right) C \quad \text{(A.18a)} \\
\chi \left[ \frac{\partial^2 \phi_{jk}}{\partial Z \otimes \partial Z} \right] &= \left( \left( 3 \frac{\phi_{jk}}{\lambda_j^3} - \frac{2}{\lambda_j^2 \lambda_k} \right) (m_j + z) + \left( \frac{\phi_{jk}}{\lambda_j^3 \lambda_k^2} - \frac{\lambda_j^2 + \lambda_k^2}{\lambda_j^3 \lambda_k^2} \right) (m_k + z) \right) \otimes (m_j + z) \\
&\quad + \left( \left( 3 \frac{\phi_{jk}}{\lambda_k^3} - \frac{2}{\lambda_j \lambda_k^2} \right) (m_k + z) + \left( \frac{\phi_{jk}}{\lambda_j \lambda_k^3} - \frac{\lambda_j^2 + \lambda_k^2}{\lambda_j \lambda_k^3} \right) (m_j + z) \right) \otimes (m_k + z) \\
&\quad + \left( \frac{2}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_j^2} - \frac{\phi_{jk}}{\lambda_k^2} \right) I \quad \text{(A.18b)}
\end{align}
\[
\frac{\partial^2 \lambda_j}{\partial Z \otimes \partial C} = \frac{1}{2\lambda_j} \left( (1 \otimes (M_j + Z)) + (1 \otimes (M_j + Z))^T \right) - \frac{1}{2\lambda_j^2} C(M_j + Z) \otimes (M_j + Z) \otimes (M_j + Z) \tag{A.19a}
\]

\[
\chi \left[ \frac{\partial^2 \lambda_j}{\partial Z \otimes \partial C} \right] = \frac{1}{2\lambda_j} \left( (1 \otimes (m_j + z)) + (1 \otimes (m_j + z))^T \right) - \frac{1}{2\lambda_j^2} C(m_j + z) \otimes (m_j + z) \otimes (m_j + z) \tag{A.19b}
\]

\[
\frac{\partial^2 \phi_{jk}}{\partial Z \otimes \partial C} = \left( \left( \frac{3\phi_{jk}}{2\lambda_j} - \frac{1}{2\lambda_j^2 \lambda_k} \right) C(M_j + Z) + \left( \frac{\phi_{jk}}{2\lambda_j^2 \lambda_k^2} - \frac{1}{2\lambda_j^2 \lambda_k} \right) C(M_k + Z) \right) \otimes (M_j + Z) \otimes (M_j + Z) \\
+ \left( \left( \frac{3\phi_{jk}}{2\lambda_k} - \frac{1}{2\lambda_j \lambda_k} \right) C(M_k + Z) + \left( \frac{\phi_{jk}}{2\lambda_j^2 \lambda_k^2} - \frac{1}{2\lambda_j \lambda_k} \right) C(M_k + Z) \right) \otimes (M_j + Z) \otimes (M_k + Z) \\
- \frac{1}{2\lambda_j \lambda_k} \left( \frac{1}{\lambda_j} C(M_j + Z) + \frac{1}{\lambda_k} C(M_k + Z) \right) \otimes ((M_j + Z) \otimes (M_k + Z) + (M_k + Z) \otimes (M_j + Z)) \\
+ \frac{1}{2} \left( \frac{1}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_j^2} \right) \left( (1 \otimes (M_j + Z)) + (1 \otimes (M_j + Z))^T \right) \\
+ \frac{1}{2} \left( \frac{1}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_k^2} \right) \left( (1 \otimes (M_k + Z)) + (1 \otimes (M_k + Z))^T \right) \tag{A.20a}
\]

\[
\chi \left[ \frac{\partial^2 \phi_{jk}}{\partial Z \otimes \partial C} \right] = \left( \left( \frac{3\phi_{jk}}{2\lambda_j} - \frac{1}{2\lambda_j^2 \lambda_k} \right) (m_j + z) + \left( \frac{\phi_{jk}}{2\lambda_j^2 \lambda_k^2} - \frac{1}{2\lambda_j^2 \lambda_k} \right) (m_k + z) \right) \otimes (m_j + z) \otimes (m_j + z) \\
+ \left( \left( \frac{3\phi_{jk}}{2\lambda_k} - \frac{1}{2\lambda_j \lambda_k} \right) (m_k + z) + \left( \frac{\phi_{jk}}{2\lambda_j^2 \lambda_k^2} - \frac{1}{2\lambda_j \lambda_k} \right) (m_j + z) \right) \otimes (m_j + z) \otimes (m_k + z) \\
- \frac{1}{2\lambda_j \lambda_k} \left( \frac{1}{\lambda_j} (m_j + z) + \frac{1}{\lambda_k} (m_k + z) \right) \otimes ((m_j + z) \otimes (m_k + z) + (m_k + z) \otimes (m_j + z)) \\
+ \frac{1}{2} \left( \frac{1}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_j^2} \right) \left( (1 \otimes (m_j + z)) + (1 \otimes (m_j + z))^T \right) \\
+ \frac{1}{2} \left( \frac{1}{\lambda_j \lambda_k} - \frac{\phi_{jk}}{\lambda_k^2} \right) \left( (1 \otimes (m_k + z)) + (1 \otimes (m_k + z))^T \right) \tag{A.20b}
\]
Formulas A.19a and A.20a were derived with the help of the following identity:

\[
\frac{\partial C(M + Z)}{\partial C} = \frac{\partial}{\partial C_{kl}} \left[ C_{ji} (M_i + Z_i) \right] e_j \otimes e_k \otimes e_l
\]

\[
= \frac{\partial}{\partial C_{kl}} \left[ \frac{1}{2} (C_{ji} + C_{ij}) (M_i + Z_i) \right] e_j \otimes e_k \otimes e_l
\]

\[
= \frac{1}{2} (\delta_{jk} \delta_{il} + \delta_{ik} \delta_{jl}) (M_i + Z_i) e_j \otimes e_k \otimes e_l
\]

\[
= \frac{1}{2} \left( \delta_{jk} (M_l + Z_l) + \delta_{jl} (M_k + Z_k) \right) e_j \otimes e_k \otimes e_l
\]

\[
= \frac{1}{2} \left( 1 \otimes (M + Z) + (1 \otimes (M + Z))^T \right)
\]

where the symmetry of the right Cauchy-Green tensor \( C_{ij} = C_{ji} \) was used. This relation is important. If it is not used the result gets unsymmetrical with respect to the indices of \( C_{kl} \).
### A.6 Some data on SCSi

Table A.1: The following table presents some data about SCSi. Values were taken out of several sources.

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Analytical dependance</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Geometry</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice constant of a unit cell [19]</td>
<td>( a )</td>
<td></td>
<td>5.431E-10 m</td>
</tr>
<tr>
<td>Bond length [19]</td>
<td>( R_0 )</td>
<td>( \sqrt{3}/4a )</td>
<td>2.352E-10 m</td>
</tr>
<tr>
<td>Bonding angle [19]</td>
<td>( \theta )</td>
<td>( \arccos \left[-\frac{1}{3}\right] )</td>
<td>109.471 °</td>
</tr>
<tr>
<td>Side-length of a Si-Si(_4) tetraeder [19]</td>
<td>( \sqrt{2}/2a )</td>
<td></td>
<td>3.840E-10 m</td>
</tr>
<tr>
<td>Si-atoms per volume [19]</td>
<td>( n )</td>
<td>( 10/a^3 )</td>
<td>1.037E+5 mol/m(^3)</td>
</tr>
<tr>
<td>Volume of the PUC</td>
<td>( V_{PUC} )</td>
<td>( a^3/4 )</td>
<td>40.048E-30 m(^3)</td>
</tr>
<tr>
<td><strong>Physical properties</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Density [19]</td>
<td>( \rho )</td>
<td></td>
<td>2329.0028 kg/m(^3)</td>
</tr>
<tr>
<td>Kleinman parameter [20]</td>
<td>( \zeta )</td>
<td></td>
<td>0.73 -</td>
</tr>
<tr>
<td>Elastic constants of second order (adiabatic) [21][[?]]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( C_{11} )</td>
<td></td>
<td>165.64(165.773) GPa 1.03(1.035) eV/Å(^3)</td>
<td></td>
</tr>
<tr>
<td>( C_{12} )</td>
<td></td>
<td>63.94(63.924) GPa 0.40(0.399) eV/Å(^3)</td>
<td></td>
</tr>
<tr>
<td>( C_{44} )</td>
<td></td>
<td>79.51(79.619) GPa 0.50(0.497) eV/Å(^4)</td>
<td></td>
</tr>
<tr>
<td>( C_{34}^0 ) [1]</td>
<td></td>
<td>111 GPa 0.69 eV/Å(^4)</td>
<td></td>
</tr>
<tr>
<td><strong>Phonon modes</strong> [16]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LTO((\Gamma))</td>
<td></td>
<td></td>
<td>15.53 THz</td>
</tr>
<tr>
<td>LOA((X))</td>
<td></td>
<td></td>
<td>12.32 THz</td>
</tr>
<tr>
<td>TO((X))</td>
<td></td>
<td></td>
<td>13.90 THz</td>
</tr>
<tr>
<td>TA((X))</td>
<td></td>
<td></td>
<td>4.49 THz</td>
</tr>
</tbody>
</table>
A.7 The subroutine UMAT

SUBROUTINE UMAT(STRESS, STATEV, DDSDDE, SSE, SPD, SCD, RPL,
1 DSDDEDT, DRPLDE, DRPLDT, STRAN, DSTRAN, TIME, DTIME, TEMP,
2 DTEMP, PREDEF, DPRED, MATERL, NDI, NSHR, NTENS,
3 NSTATV, PROPS, NPROPS, COORDS, DROT, PNEWDT,
4 CELENT, DFRD0, DFRD1, NOEL, NPT, KSPT,
5 KSLAY, KSTEP, KINC)

INCLUDE 'ABA_PARAM.INC'

CHARACTER*8 MATERL
DIMENSION STRESS(NTENS), STATEV(NSTATV), DDSDDE(NTENS,NTENS),
1 DSDDEDT(NTENS), DRPLDE(NTENS), STRAN(NTENS), DSTRAN(NTENS),
2 DFRD0(3,3), DFRD1(3,3), TIME(2), PREDEF(1), DPRED(1),
3 PROPS(NPROPS), COORDS(3), DROT(3,3)

C Definition of additional variables

C BEGIN OF THE MAIN ROUTINE
C------------------------------------------------------------------------
C Computations
C------------------------------------------------------------------------
RETURN
END
C END OF THE ROUTINE
C----------------------------------------------------------------------
A.7.1 **ABAQUS CAE dialogs**

Figure A.1: This figures show the dialog in ABAQUS CAE that are necessary to define a user defined material model. In the Property module one chooses as material options 'User Material' where also the material parameters can be defined, (a). Additionally the option 'Depvar' must be enabled, here the number of solution dependant state variables can be set, (b). In the Job module the file with the subroutine UMAT has to be selected, (c).
A.8 Verification of the elastic and stiffness moduli

Figure A.1: These three models were used to determine the elastic moduli $E_{<100>}$, $E_{<110>}$ and $E_{<111>}$ of the MEAM material. A cube with side length $l = 1$ is subjected to tension, its sides are free to contract. In model (a) the material is oriented in direction of the $x$-axis, the change gives the elasticity in $<100>$ direction, $E_{<100>}$. In model (b) the orientation of the material was redefined in direction of the face-diagonal. Here $\frac{\partial \sigma_{xx}}{\partial \varepsilon_{xx}}$ gives the elasticity $E_{<110>}$. Model (c) was used to determine the elasticity $E_{<111>}$ by redefining the material orientation along the room-diagonal.
Figure A.2: Models (a) and (b) were used to determine the stiffness moduli $C_{11}$, $C_{12}$ and $C_{44}$. In model (a) the cube with side length $l = 1$ is subjected to tension in $x$-direction. Its sides are confined, i.e. they can not contract. The change $\frac{\partial \sigma_{xx}}{\partial \varepsilon_{xx}}$ gives under these conditions the stiffness $C_{11}$, on the other hand the change $\frac{\partial \sigma_{yy}}{\partial \varepsilon_{xx}}$ gives the stiffness $C_{11}$. For the determination of $C_{44}$ the cube is sheared $y$-direction, the upper and lower faces are fixed in $z$-direction (b). Under this deformation the change $\frac{\partial \sigma_{xy}}{\partial \gamma_{xy}}$ is equal the stiffness $C_{44}$. 
A.9 Mathematical derivations

A.9.1 Derivation #1

Equations (2.44b-d) on page 24 can be written in a way that shows directly the \( \cos(\theta) \)-dependance of this terms. In order to do this, three intermediate results are presented here:

\[
\sum_{\alpha} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} \rho_{ij} \right)^2 = \sum_{j \neq i} (x_{ij} \cdot \rho_{ij}) \cdot \sum_{k \neq i} (x_{ik} \cdot \rho_{ik}) = \sum_{j,k} \rho_{ij} \rho_{ik} x_{ij} \cdot x_{ik} = \sum_{j,k} \rho_{ij} \rho_{ik} \cos(\theta_{jk}) \tag{A.21}
\]

\[
\sum_{\alpha,\beta} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} x_{ij}^{(\beta)} \rho_{ij} \right)^2 = \left( \sum_{j \neq i} x_{ij} \otimes x_{ij} \rho_{ij} \right) : \left( \sum_{k \neq i} x_{ik} \otimes x_{ik} \rho_{ik} \right) = \sum_{j,k} (x_{ij} \cdot x_{ik})^2 \rho_{ij} \rho_{ik} = \sum_{j,k} \rho_{ij} \rho_{ik} \cos^2(\theta_{jk}) \tag{A.22}
\]

\[
\sum_{\alpha,\beta,\gamma} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} x_{ij}^{(\beta)} x_{ij}^{(\gamma)} \rho_{ij} \right)^2 = \left( \sum_{j \neq i} x_{ij} \otimes x_{ij} \otimes x_{ij} \rho_{ij} \right) : \left( \sum_{k \neq i} x_{ik} \otimes x_{ik} \otimes x_{ik} \rho_{ik} \right) = \sum_{j,k} (x_{ij} \cdot x_{ik})^3 \rho_{ij} \rho_{ik} = \sum_{j,k} \rho_{ij} \rho_{ik} \cos^3(\theta_{jk}) \tag{A.23}
\]

where \( x_{ij}^{(\alpha)} \) is the \( \alpha \)-component of vector \( x_{ij} \)

\[
x_{ij} = \frac{r_j - r_i}{\|r_j - r_i\|}
\]
This allows a redefinition of equations (2.44b-d):

\[
\rho^{(1)}_i = \sum_{\alpha} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} \rho_{ij}^{a(1)} [r_{ij}] \right)^2 = \sum_{j,k} \rho_{ij}^{a(1)} [r_{ij}] \rho_{ik}^{a(1)} [r_{ik}] \cos(\theta_{jk}) \quad (A.24a)
\]

\[
\rho^{(2)}_i = \sum_{\alpha,\beta} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} x_{ij}^{(\beta)} \rho_{ij}^{a(2)} [r_{ij}] \right)^2 - \frac{1}{3} \left( \sum_{j \neq i} \rho_{ij}^{a(2)} [r_{ij}] \right)^2 = \sum_{j,k} \rho_{ij}^{a(1)} [r_{ij}] \rho_{ik}^{a(1)} [r_{ik}] \cos^2(\theta_{jk}) - \frac{1}{3} \left( \sum_{j \neq i} \rho_{ij}^{a(2)} [r_{ij}] \right)^2 \quad (A.24b)
\]

\[
\rho^{(3)}_i = \sum_{\alpha,\beta,\gamma} \left( \sum_{j \neq i} x_{ij}^{(\alpha)} x_{ij}^{(\beta)} x_{ij}^{(\gamma)} \rho_{ij}^{a(3)} [r_{ij}] \right)^2 = \sum_{j,k} \rho_{ij}^{a(1)} [r_{ij}] \rho_{ik}^{a(1)} [r_{ik}] \cos^3(\theta_{jk}) \quad (A.24c)
\]
A.9.2 Derivation #2

It has to be shown that equation

\[ \Phi[r_1] = \sum_s \phi[a_s r_1] \frac{n_s}{n_1} \]

can be solved for \( \phi[a_s r_1] \) introducing a cutoff radius \( r_c \). \( r_1 \) is the first-neighbor distance, \( a_s \) the ratio of the \( s \)th neighbor distance to the 1th neighbor distance and \( n_s \) is the number of \( s \)th neighbors.

\[ \Phi[r_1] = \sum_s \phi[a_s r_1] \frac{n_s}{n_1} \]
\[ \Phi[r_1] = \phi[a_1 r_1] \frac{n_1}{n_1} + \sum_{s>1} \phi[a_s r_1] \frac{n_s}{n_1} = \phi[r_1] + \sum_{s>1} \phi[a_s r_1] \frac{n_s}{n_1} \quad (A.25) \]

where we get from

\[ \phi[r_1] = \Phi[r_1] - \sum_{s>1} \phi[a_s r_1] \frac{n_s}{n_1} \quad s \rightarrow k \]
\[ r_1 \rightarrow a_s r_1 \]
\[ \phi[a_s r_1] = \Phi[a_s r_1] - \sum_{k>1} \phi[a_k a_s r_1] \frac{n_k}{n_1} \quad (A.26) \]

Inserting equation (A.26) in (A.25)

\[ \Phi[r_1] = \phi[r_1] + \sum_{s>1} \phi[a_s r_1] \frac{n_s}{n_1} - \sum_{s,k} \phi[a_k a_s r_1] \frac{n_k n_s}{n_1^2} \]

leading to

\[ \phi[r_1] = \Phi[r_1] - \sum_{s>1} \phi[a_s r_1] \frac{n_s}{n_1} + \sum_{s,k} \phi[a_k a_s r_1] \frac{n_k n_s}{n_1^2} \]
\[ \phi[r_1] = \Phi[r_1] - \sum_{s>1} \phi[a_s r_1] \frac{n_s}{n_1} + \phi[a_2 r_1] \frac{n_2}{n_1^2} + 2\phi[a_{2a_3} r_1] \frac{n_2 n_3}{n_1^4} + \sum_{s,k>3} \phi[a_k a_s r_1] \frac{n_k n_s}{n_1^2} \quad (A.27) \]

Assuming \( \phi(a_k a_s r_1) \) small beyond \( r_c = a_2^2 r_1 \) so that it can be neglected last two terms in equation (A.27) can be omitted and \( r_c = a_2^2 r_1 < a_{2a_3} r_1 \).

\[ \phi[r_1] = \Phi[r_1] - \sum_{s>1} \phi[a_s r_1] \frac{n_s}{n_1} + \phi[a_2^2 r_1] \frac{n_2^2}{n_1^2} \]
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