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Development of thermodynamically admissible molecular-based models for entangled polymers

Author(s):
Fang, Jiannong

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Development of Thermodynamically Admissible Molecular-based Models For Entangled Polymers

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SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH

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Doctor of Natural Sciences

presented by
Jiannong Fang
born January 11th, 1969
citizen of P. R. China

accepted on the recommendation of
Prof. Dr. Hans Christian Öttinger, examiner
Prof. Dr. Jay D. Schieber, co-examiner
Dr. Martin Kröger, co-examiner

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Summary

The purpose of this thesis is to develop new thermodynamically admissible molecular-based models for entangled polymers, which should incorporate the important ingredients such as chain stretching, double reptation (DR), and convective constraint release (CCR), and avoid the independent alignment approximation (IAA). Under the guidance of the GENERIC formalism of nonequilibrium thermodynamics, two models, the “single-label” model and the “double-label” model, are proposed. In the single-label model, the effects of constraint releases (DR and CCR) are introduced through the stochastic force (noise term) in the time-evolution equation for the orientation of inner chain segments, while in the double-label model, they are incorporated through the diffusion coefficient of a new position label together with the random orientation boundary conditions.

Based on the stochastic interpretation of the resulting diffusion equations, corresponding efficient stochastic simulation algorithms are designed to simulate the rheological behavior of the two models in the nonlinear viscoelastic regime. In the linear viscoelastic regime, we derive analytical results for the relaxation modulus for the two models. The single-label model prediction is very similar to that of the double reptation idea, while the double-label model exactly recovers the double reptation result.

The two models are comprehensively investigated for transient and steady properties in single-step strain, double-step strain, shear, and extensional flows. Quantitative comparisons are made with experimental data of entangled polystyrene solution in shear flows. We find that both models are able to capture qualitatively, or quantitatively in some cases, almost all the nonlinear properties observed so far in shear-type flows for entangled polymers. Comparisons with two recently formulated molecular-based models in shear flows are also presented.

The double-label model for monodisperse entangled polymers is extended to include polydispersity by introducing a new structural variable, the species index of surrounding chains, and applying a random sampling procedure for it. Overall, the extended model is
not a superposition model in the sense that the diffusion equations for chains of different lengths are generally coupled, and the stress is no more a summation of contributions from independent species. In the linear viscoelastic regime, the extended model predicts the successful double-reptation mixing rule.

Notably, each model of ours is a thermodynamically consistent single-segment theory which has only few degrees of freedom. In the sense of considering the time and memory requirements for the computation, it is very suitable to utilize our models to simulate complex flows in computer modeling of polymer processing.
Zusammenfassung


Ausgehend von der stochastischen Interpretation der sich ergebenden Diffusionsgleichungen werden die korrespondierenden effizienten stochastischen Simulationsalgorithmen konstruiert, um schliesslich das rheologische Verhalten der beiden Modelle im nichtlinear viskoelastischen Bereich zu erhalten. Für den linear viskoelastischen Bereich werden hier für beide Modelle analytische Resultate für den Relaxationsmodul bereitgestellt. Während die Vorhersagen der zweifachen Reptationsidee (DR) durch das ‘single-label’-Modell bereits gut beschrieben werden, werden sie durch das ‘double-label’-Modell exakt reproduziert.

alle bisher bekannten nichtlinearen Fliesseigenschaften von verschlauften Polymeren in scherartigen Strömungen vorherzusagen vermögen. Alle Aussagen werden weiterhin mit Ergebnissen zweier kürzlich formulierter molekularer Modelle verglichen.


Es ist beachtenswert, dass jedes unserer Modelle eine thermodynamisch konsistente Ein-Segment-Theorie darstellt, die mit wenigen Freiheitsgraden auskommt. In Angesicht der günstigen Zeit- und Speichieranforderungen, die für die numerische Auswertung nötig sind, bieten sich die Modelle an, um im Rahmen der numerischen Modellierung komplexer Strömungen für die Polymerverarbeitung genutzt zu werden.
Chapter 1

Introduction

Over the last decade, the molecular-based approach to the simulation of polymeric flows has been becoming attractive and viable in the field of computational modeling of polymer processing. The goal of the approach is to supply new generation of CAD tools, in addition to the conventional methods, to find the optimum combination of flow geometry, polymer composition, and processing conditions for any given fabrication technique. The motivation for developing molecular-based approach is the following. First, the molecular-based approach gives more realistic predictions than the conventional CFD (Computational Fluid Dynamics) methods, in which the polymer contributions to the stress are obtained from the phenomenological models. These models can be interpreted within the scope of continuum mechanics and possess closed-form expressions either of the integral (such as K-BKZ equations) or differential (such as Phan-Thien-Tanner model) type. The development of CFD programs has reached a point where inaccuracies in predicting the flow of a polymer liquid can often be attributed to the inability of phenomenological models to represent the nonlinear viscoelastic properties adequately. The inability is due to the empirical nature of the models. All the relevant polymer physics have not been included in these empirical models, and the lack of an underlying molecular understanding hinders further improvements. Therefore, for the purpose of better modeling reality, the molecular-based approach is uniquely suited. Second, only the molecular-based approach can provide micro-level information on the polymers such as molecular stretching and orientation, which are responsible for many advanced mechanical and optical properties of the finished solid products. Overall, the molecular-base approach is more realistic and more powerful.

The task of developing the molecular-based approach consists of two strongly coupled aspects. One aspect is developing new flow simulation techniques which allow us to
use the molecular-based models (usually not closed) instead of the empirical models (closed-form equations). A state-of-the-art simulation technique in this field is the so-called micro-macro approach. In the micro-macro approach, one solves the macroscopic conservation equations by means of a grid-based numerical method, and uses a kinetic theory model rather than a constitutive equation to evaluate the polymer contribution to the stress. Clearly, this approach is much more demanding in computer resources than conventional methods. However, the simulation only solves given models which already constitute a coarse-grained representation of the real system. So, memory and time requirements are compatible with present computer-hardware resources, especially with the powerful parallel computers. An early micro-macro method [Fan (1989)] was based on the solution of the Fokker-Plank equation for the configurational distribution function of the polymer chains within a material point. This approach, however, is limited to kinetic theory models with a conformation space of small dimension. Brownian dynamics or stochastic simulation techniques provide a powerful alternative [Öttinger (1996)]. They draw on the mathematical equivalence between the Fokker-Planck equation and the Itô stochastic differential equation. The idea of combining a stochastic simulation of a kinetic theory model with the numerical solution of the conservation equations has been pioneered in [Öttinger and Laso (1992); Laso and Öttinger (1993)]. The approach was called CONNFFESSIT — Calculation Of Non-Newtonian Flow: Finite Element & Stochastic Simulation Techniques. This approach uses standard finite element techniques for solving the balance equations but replaces the constitutive equation with stochastic simulations of polymer dynamics. In CONNFFESSIT, the polymer contribution to the stress tensor is determined from a stochastic simulation of an ensemble of model molecules from whose configurations the polymer stress can be computed as an ensemble average. In order to achieve this, a large number of model molecules is thrown into the flow region, and their dynamics is simulated together with the time evolution of the velocity field obtained by the finite element method. The CONNFFESSIT philosophy has been applied and further developed in [Feigl et al. (1995); Hua and Schieber (1996); Laso et al. (1997); Bell et al. (1997); Hua and Schieber (1998b)]. Second-generation micro-macro methods, with much improved numerical properties due to variance reduc-
tion, have been proposed recently for computing 2d transient flows. They are referred to as Brownian Configuration field (BCF) [Hülsen et al. (1997); Öttinger et al. (1997); van Heel et al. (1999); Fan et al. (1999)] and Lagrangian Particle [Gallez et al. (1999); Wapperom et al. (2000)] methods. In the BCF approach, the collection of individual model molecules is replaced by an ensemble of configuration fields, representing the internal degrees of freedom of the polymers. These configuration fields are convected and deformed by the flow and are subjected to Brownian motion. Due to the strong spatial correlation of stress fluctuations introduced by the idea, dramatic variance reduction can be achieved. Another important feature of the method is that the configurations are defined at every point of the domain, thus avoiding the difficulties associated with the particle tracking in CONNFFESSIT method. In this sense, the BCF method is a Eulerian description of the same problem. Although the implementation of the second-generation micro-macro methods is currently limited to rather elementary kinetic theory models, their potential range of applications is quite wide indeed.

Another aspect, on which this thesis rests, is the development of molecular-based models which are easily tractable for simulations by the micro-macro approach mentioned above. Here, we will focus on the models for polymer melts, since in most polymer processing operations such as injection molding, film blowing, and extrusion, the polymers are in the molten state. A widely applied class of molecular-based models for concentrated polymer solutions and melts relies on the notion of reptational motion [de Gennes (1971)]. The first reptation theory for melts was elaborated by Doi and Edwards (1978a, 1978b, 1978c, 1979) who extended the reptation idea to a tube idea in order to describe the viscoelastic behavior of entangled polymers in the presence of ‘obstacles.’ Within the tube and reptation pictures, the complex entanglement interaction between polymer chains has been treated in a rather direct approach, i.e. each chain in the polymer system is equivalent to a chain restricted to one dimensional motion (so called “reptation”) in a confining tube, except for its two ends which can move in any possible direction. In addition to the reptation mechanism, Doi and Edwards originally assumed instantaneous and complete chain retraction, affine tube deformation by the flow, and independent alignment of tube segments. By doing so, they obtained a closed-form con-
stitutive equation which only involves the second moment of the orientation vector for a tube segment. A more general reptation-based model was derived systematically from kinetic theory by Curtiss and Bird (1981a, 1981b).

For highly entangled, linear polymers, the original Doi-Edwards (DE) model has been extended to incorporate chain contour length fluctuations [Doi (1983); Ketzmerick and Öttinger (1989)] and constraint release due to the motions of the surrounding chains (so called “double reptation”) [Tsenoglou (1987); des Cloizeaux (1988)]. The combination of these two effects leads to a refined description of the linear viscoelastic properties [O’Connor and Ball (1992)], however, the model is much less successful for the nonlinear properties. The major experimental observations that the original DE theory fails to describe in the nonlinear regime are the following:

1. There exist irreversible effects in double-step strain experiments with flow reversal [Osaki and Kurata (1980); Osakia et al. (1981); Venerus and Kahvand (1994); Brown and Burghardt (1996)].

2. Over a wide range of shear rates \( \dot{\gamma} \) above the inverse disentanglement time \( 1/\tau_d \), the steady shear stress is nearly constant for very highly entangled melts or solutions or increases slowly with shear rate for less highly entangled ones. The first normal stress difference \( N_\parallel \) increases more rapidly with shear rate than does the shear stress over the same range of shear rates. The slope of \( N_\parallel \) versus \( \dot{\gamma} \) increases as the molecular weight decreases [Bercea et al. (1993); Mead and Larson (1990); Kahvand (1995)].

3. The steady-state shear viscosity of different molecular weights merge into a single curve in the high shear rate, power-law regime [Stratton (1966)].

4. The shear stress \( \tau_{xy} \) shows transient overshoots in the start-up of steady shear flow at low shear rates. The strain \( \gamma_o \) at which the maximum in the overshoot occurs increases with shear rate at high rates [Pearson et al. (1989); Menezes and Graessley (1982); Kahvand (1995)].
5. The first normal stress difference exhibits transient overshoots in the start-up of steady shear flow at moderate shear rates [Pearson et al. (1989); Menezes and Graessley (1982); Kahvand (1995)].

6. The rate of stress relaxation following cessation of steady shear flow is shear rate dependent [Attané et al. (1985); Menezes and Graessley (1982); Kahvand (1995)].

7. The steady-state extinction angle decreases more gradually with shear rate than predicted by the DE model [Mead and Larson (1990); Kahvand (1995)].

8. The transient extinction angle shows an undershoot at the start-up of steady shear at high shear rates; it also shows an immediate undershoot when the shear rate is suddenly decreased after a steady state has been reached, finally it reaches a higher steady-state value [Mead (1996)].

In order to improve the situation, many attempts of modifying the original DE model have been made during the last years. Several physical effects have been found to be important for more realistic modelling of nonlinear properties of entangled polymers. A short summary of the important effects found so far is given in the following five subsections.

1. Avoiding independent alignment (IA)

Recognizing that the large discrepancy between model prediction and experimental data in double step strain with flow reversal is caused by the IA approximation, Doi (1980a, 1980b) and Doi and Edwards (1986) made a detailed analysis for this situation and tried to derive a constitutive equation without using the IA approximation. Again, the instantaneous-chain-retraction assumption was employed in their derivation. It was shown that the model is able to correct the previous discrepancy whenever the time interval between the two applied step strains is much larger than a characteristic time $\tau_s$, called the retraction time. Marrucci (1986) and Marrucci and Grizzuti (1986) also
showed that the model without IA predicts the Weissenberg effect correctly. In an attempt to find a thermodynamically admissible formulation, the reptation model without IA has been reformulated by Öttinger and Beris (1999) in the GENERIC formalism of nonequilibrium thermodynamics [Grmela and Öttinger (1997); Öttinger and Grmela (1997)] (GENERIC is an acronym for “general equation for the nonequilibrium reversible-irreversible coupling”). The model has been shown to be thermodynamically consistent after modifying the production term and introducing an additional term in the extra stress tensor. A consistent model with a uniform monomer distribution along the chain was proposed by Öttinger (1999b).

2. Double reptation

Tsenoglou (1987) and des Cloizeaux (1988) derived a successful mixing rule for polydisperse melts based on the idea of “double reptation” which represents the relaxation mechanism for the tube that do not arise from motion of the probe chain, but rather motions of the surrounding chains. Öttinger (1994) has considered a reptation model in which this additional constraint release mechanism is mimicked through a noise term in the time-evolution equation for the orientation of inner chain segments. By doing so, the idea of double reptation has been extended to the nonlinear regime. The model predicts an improved power-law index of $-4/3$ for the steady-state viscosity in shear flow instead of $-3/2$ for the DE model. However, the shear stress vs. shear rate curve still exhibits a maximum when only double reptation is considered.

3. Chain stretching

Marrucci and Grizzuti (1988) extended the DE model to allow for chain stretching and predicted steady-state properties. An effect is predicted to result in elongational flows, giving rise to an expected upturn of the elongational viscosity, but surprisingly, there is no effect for steady shear flows, in particular, the extended model does not improve the quality of the model prediction for the power-law index of the steady-state shear viscosity. Later, Pearson et al. (1991) studied the same type of model with chain stretching in transient situations. They found that both the shear stress and the first nor-
mal stress difference overshoot in the start-up of steady shearing flows and the times required to reach these maxima are independent of the shear rate. Mead and Leal (1995) and Mead et al. (1995) presented a comprehensive study of the DE model by including chain stretching and a nonlinear finitely extensible spring law. Numerical predictions were given for steady two-dimensional flows with a continuously varying degree of extensional and shear character. The results revealed that significant steady state stretch is predicted as the flow becomes increasingly extensional in character.

Although chain stretching is important for correcting some of the failings such as an overshoot in $N_1$, it doesn’t solve a long-standing problem in the DE model, namely, the excessive shear thinning of the viscosity at high shear rates (associated with a maximum in shear stress followed by a region in which shear stress decreases with shear rate asymptotically as $\dot{\gamma}^{-0.5}$, which leads to constitutive instabilities in shear flow). The reason for this problem is that, in fast shear flow, the model predicts that the tube segments become highly oriented in the flow direction and hence present a very slim profile to the flow. As a result, the flow “loses its grip” on the molecules, leading to anomalously low friction and hence low viscosity.

4. Convective constraint release (CCR)

Marrucci (1996) and Ianniruberto and Marrucci (1996) proposed a convective constraint release mechanism (CCR) which removes the problem just mentioned above. They proposed a model for which, under flow conditions, relaxation of chain orientation occurs by two mechanisms. One of them is ordinary diffusion (reptation and double reptation) due to thermal motion, which of course takes place also in the absence of flow. The second mechanism is CCR, i.e. the topological obstacles on a probe chain are renewed through the relative motion among chains due to chain retraction. In fast flow situations, this mechanism leaves the chain much more free to relax than is possible only by the previously described mechanism and hence prevents the tube segments from becoming highly oriented in the flow direction.
5. Anisotropic tube cross sections

Ianniruberto and Marrucci (1998) introduced the idea that during deformation an initial circular tube cross section may become elliptical. They derived the corresponding expression for the stress tensor, but did not present a time-evolution equation for the tube cross section in flow. It was shown that the idea of anisotropic tube cross section has an important influence on the ratio of normal-stress difference in shear flow. In view of the well know intimate relation between the time evolution of the structural variables and the stress tensor expression implied by various approaches to nonequilibrium thermodynamics, Öttinger (1999a) developed a thermodynamically admissible reptation model with anisotropic tube cross section and the constraint release mechanisms associated with “double reptation” and “CCR”. For that model, he worked out relationships between the ratio of normal-stress differences and the mean-square curvature of the tube cross section in shear flow.

Very recently, reptation models incorporating all the well-established phenomena (except for anisotropic tube cross sections) have been formulated by two groups, based on a full-chain stochastic approach suitable for computer simulations by Hua and Schieber (1998a) and Hua et al. (1998, 1999) and on rather complicated coupled integral-differential equations by Mead et al. (1998). It is encouraging that these reptation models can quite successfully reproduce the experimentally observed rheological behavior in a large number of flow situations.

The main subject of this thesis is to develop new thermodynamically admissible reptation models for melts or entangled solutions of linear polymer molecules by using the GENERIC formalism of nonequilibrium thermodynamics and give comprehensive evaluations of the models by comparing with experiments and other models. We here pursue the idea of capturing as many as possible of the physically relevant aspects mentioned above in a minimal setting (few degrees of freedom) and possessing easy numerical tractability for the micro-macro flow simulation techniques. In Chapter 2, we begin with a brief introduction to the theory of GENERIC. The classical hydrodynamics is then reformulated in the GENERIC formalism in order to not only show a concrete example, but also establish a base for the next section. After that, guided by the GENERIC formalism
on the one hand and the physical ideas of the reptation picture on the other hand, two new reptation models incorporating double reptation, convective constraint release, and chain stretching, while avoiding the IA approximation are developed and discussed in detail for monodisperse entangled linear polymers. Finally, all the time-evolution equations for the two models are listed. In Chapter 3, stochastic interpretations of the models developed in Chapter 2 are first described. Then, numerical schemes are designed to simulate the rheological behaviors of the models based on the stochastic interpretations. The simulation procedures are given in detail in the last section of the chapter. Analytical results for the linear viscoelastic properties and a comprehensive evaluation of the two models in shear and extensional flows are given in Chapter 4. Both qualitative predictions and quantitative comparisons with experiments and the two above-mentioned alternative molecular-based models are presented there. Afterwards, one of our models is extended to account for polydispersity in Chapter 5. A non-superposition mixing rule in the limit of linear viscoelasticity is derived in that chapter. Chapter 6 summarizes the work and points out more advanced applications and further developments.
Chapter 2
Model formulation

In this chapter, the GENERIC modeling approach is applied to develop new thermodynamically admissible reptation models for monodisperse entangled linear polymers. First of all, an introduction to the theory of GENERIC is given in Section 2.1. In Section 2.2, the classical hydrodynamics is reformulated in the GENERIC formalism in order to not only show a concrete example, but also establish a base for the next section. Guided by the GENERIC formalism on the one hand and the physical ideas of the reptation picture on the other hand, two models incorporating double reptation (DR), convective constraint release (CCR), and chain stretching, while avoiding the IA approximation are developed and discussed in detail in Section 2.3. Finally, all the time-evolution equations for the two models are compiled and listed in Section 2.4.

2.1 Introduction to GENERIC

Complex fluids such as polymeric liquids, dispersions, emulsions etc. have various internal microstructures of their own, which are subjected to change under flow and give extra stress contributions. Conventional approaches for the modeling of complex fluids out of equilibrium are based on the conservation laws for the mass, momentum, and energy, and the stress-strain relationships through phenomenological constitutive equations or molecular models derived from kinetic theory. In order to check if the second law of thermodynamics is satisfied, one formulates an additional balance equation for the entropy density and identifies the local entropy production. Unlike the well-established equilibrium thermodynamics which has become an indispensable tool in engineering sci-
ences, the usefulness of nonequilibrium thermodynamics to the modeling of complex fluids is not generally accepted. This is due to a lack of a well-defined, systematic, and practical methodology for treating nonequilibrium processes. However, today, the problem is being solved under the development of a new general formalism for nonequilibrium systems [Grmela and Öttinger (1997); Öttinger and Grmela (1997); Öttinger (1998)]. It is called GENERIC which is an acronym for general equation for the nonequilibrium reversible-irreversible coupling. The proposed general time-evolution equation for nonequilibrium systems can be written in the form

\[
\frac{dx}{dt} = L(x) \cdot \frac{\delta E(x)}{\delta x} + M(x) \cdot \frac{\delta S(x)}{\delta x},
\]

(EQ 2.1)

which is supplemented by the complementary degeneracy requirements

\[
L(x) \cdot \frac{\delta S(x)}{\delta x} = 0,
\]

(EQ 2.2)

and

\[
M(x) \cdot \frac{\delta E(x)}{\delta x} = 0.
\]

(EQ 2.3)

Here \(x\) represents a set of independent state variables (containing the hydrodynamic fields and additional structural variables for a complete description of complex fluids for example), and the real-valued functionals \(E(x)\) and \(S(x)\) are the total energy and entropy expressed in terms of the state variables \(x\). The matrix \(L(x)\) is antisymmetric and satisfies the Jacobi identity, while the matrix \(M(x)\) is symmetric and positive-semidefinite. If we introduce the Poisson bracket associated with \(L(x)\) and the dissipative bracket associated with \(M(x)\) as the following:

\[
\{A, B\} = \frac{\delta A}{\delta x} \cdot L(x) \cdot \frac{\delta B}{\delta x}
\]

(EQ 2.4)
2.1 Introduction to GENERIC

and

\[ [A, B] = \frac{\delta A}{\delta x} M(x) \cdot \frac{\delta B}{\delta x}, \]  

(EQ 2.5)

then, in terms of these brackets, the antisymmetry property of \( L \) can now be stated as

\[ \{A, B\} = -\{B, A\}, \]  

(EQ 2.6)

the Jacobi identity is given by

\[ \{A, \{B, C\}\} + \{B, \{C, A\}\} + \{C, \{A, B\}\} = 0 \]  

(EQ 2.7)

for arbitrary functionals \( A, B \) and \( C \). The symmetry property of \( M \) can be formulated as

\[ [A, B] = [B, A], \]  

(EQ 2.8)

and the positive-semidefinite nature of \( M \) is equivalent to

\[ [A, A] \geq 0 \]  

(EQ 2.9)

for all functionals \( A \). For a summary, the full structure of GENERIC is given by Eq. (2.1) together with the six properties or requirements stated in Eq. (2.2), Eq. (2.3), Eq. (2.6), Eq. (2.7), Eq. (2.8), and Eq. (2.9). As \( x \) typically contains position-dependent fields, such as local mass, momentum and energy densities, the state variables are usually labeled by continuous (position) labels in addition to discrete ones. A matrix multiplication (indicated by the dots), often referred to as the application of linear operator, hence implies not only summations over discrete labels but also integrations over continuous labels, and \( \delta / \delta x \) typically implies functional rather than partial derivatives.

In the GENERIC framework, there are two separate generators for the reversible (generated by the energy \( E(x) \)) and irreversible (generated by the entropy \( S(x) \)) dynamics. The requirement that the gradient \( \delta S(x) / \delta x \) is in the null-space of \( L(x) \) expresses
the reversible nature of the $L$-contribution to the dynamics: the functional form of the entropy is such that it can not be affected by the operator generating the reversible dynamics. The requirement that the gradient $\delta E(x)/\delta x$ is in the null-space of $M(x)$ expresses the conservation of the total energy by the irreversible contribution to the dynamics. Both the complementary degeneracy requirements (2.2), (2.3) and the symmetry properties are very important for formulating proper $L$ and $M$ matrices when modeling concrete nonequilibrium problems [Ottinger and Grmela (1997)]. The Jacobi identity gives another important restriction on constructing the time-evolution equations [Edwards and Ottinger (1997); Ottinger and Beris (1999)]. The Jacobi identity amounts to the following evolution equation for Poisson brackets, 

$$\frac{d\{A, B\}}{dt} = \{\frac{dA}{dt}, B\} + \{A, \frac{dB}{dt}\} = \{\{A, B\}, E\},$$

for which only the reversible dynamics is considered. This expression reflects the time-structure invariance of the Poisson bracket, i.e., the matrix $L$ behaves as a ‘conserved’ quantity. It also implies that if two arbitrary functionals $A$ and $B$ are conserved in the reversible dynamics, then $\{A, B\}$ is also conserved.

Equation (2.1) and the chain rule lead to the following time-evolution of an arbitrary function $A$ in terms of the two separate generators $E$ and $S$:

$$\frac{dA}{dt} = \{A, E\} + [A, S]. \quad (EQ\ 2.10)$$

Applying this equation to $E$, together with the relation $\{E, E\} = 0$ (inferred from Eq. (2.6)) and $[E, S] = 0$ (inferred from Eq. (2.8) and Eq. (2.3)), gives the conservation law for the energy

$$\frac{dE}{dt} = 0. \quad (EQ\ 2.11)$$

On the other hand, equation (2.10), together with the relation $\{S, E\} = 0$ (inferred from Eq. (2.6) and Eq. (2.2)) and $[S, S] \geq 0$, guarantees that the entropy is a nondecreasing function of time.
These two results, namely, the first and second laws of thermodynamics, together with the time-structure invariance mentioned earlier and the Onsager relationships [Callen (1985), deGroot and Mazur (1984)] contained in the symmetry condition of $M$, are the key criteria for thermodynamic consistency. Therefore, in this sense, a model possessing the full structure of GENERIC is thermodynamically admissible. In practice, the time-evolution equations developed in the GENERIC formalism will yield physically meaningful (but not necessarily accurate) results for all types of problems.

The application of GENERIC to derive a thermodynamically admissible model for a given problem normally proceeds by the following steps:\(^1\)

1. Choose $x$, the set of independent state variables\(^\dagger\).

2. Formulate $E^\dagger$.

3. Formulate $S^\dagger$.

4. Determine the $L$ matrix by:
   
   (a) the transformation behavior of $x^\dagger$;
   
   (b) antisymmetry requirement;
   
   (c) $L \frac{\delta S}{\delta x} = 0$ (‘null space’ requirement);
   
   (d) the Jacobi identity.

5. Determine the $M$ matrix by:
   
   (a) determining the form of the energy dissipation\(^\dagger\);
   
   (b) symmetry requirement;
   
   (c) $M \frac{\delta E}{\delta x} = 0$ (‘null space’ requirement);

---

\(^{1}\) A superscript ($\dagger$) denotes a step that requires the input of physics.
(d) the positive-semidefinite nature.

The rather compact notation and the physical significance of all the GENERIC building blocks and steps should become entirely clear in the next two sections, when the formalism is applied in order to reformulate the time-evolution equations of classical hydrodynamics and to develop new reptation models for entangled polymers.

### 2.2 Reformulation of classical hydrodynamics

It is well known that the classical hydrodynamics can be represented by the following set of equations (the continuity equation, the Navier-Stokes equation, and the internal energy equation),

\[ \frac{\partial \rho}{\partial t} = \frac{\partial}{\partial r} \cdot (\rho \mathbf{v}), \]  
\[ \frac{\partial \mathbf{M}}{\partial t} = \frac{\partial}{\partial r} \cdot (\mathbf{v} \mathbf{M}) - \frac{\partial}{\partial r} \rho - \frac{\partial}{\partial r} \cdot \mathbf{\tau}, \]  
\[ \frac{\partial \varepsilon}{\partial t} = \frac{\partial}{\partial r} \cdot (\rho \varepsilon) - \frac{\partial}{\partial r} \cdot \mathbf{v} - \frac{\partial}{\partial r} \cdot f^\prime - \mathbf{\tau} : \frac{\partial}{\partial r} \mathbf{v}, \]

where \( \rho(r) \) is the mass density, \( \mathbf{M}(r) \) is the momentum density, and \( \varepsilon(r) \) is the internal energy density. The momentum density field is closely related to the velocity field \( \mathbf{v}(r) \), namely, by

\[ \mathbf{M}(r) = \rho(r) \mathbf{v}(r). \]

In Eq. (2.14), \( p \) is the pressure, and \( \mathbf{\tau} \) is the stress tensor which is determined by the Newton’s expression in terms of velocity gradients, the viscosity \( \eta \), and the dilatational viscosity (or second viscosity) \( \kappa \),
External forces have been neglected in the Navier-Stokes equation. In Eq. (2.15), we assume Fourier’s expression for the heat flux $j^i$ in terms of the temperature gradient and the thermal conductivity $\lambda T$.

$$j^i = -\lambda \frac{\partial T}{\partial r}.$$  \hspace{1cm} (EQ 2.18)

If the equilibrium equations of state $p = p(\rho, \varepsilon)$ and $T = T(\rho, \varepsilon)$ are known and if we make the "local equilibrium assumption" that the pressure and temperature fields can be obtained from these equilibrium relations by inserting the local mass and internal energy densities, then Eqs. (2.13)–(2.18) constitute a closed set of time-evolution equations.

The time-evolution equations for classical hydrodynamics can be rewritten in the GENERIC form [Öttinger and Grmela (1997)]. Here, we give the results directly. The state variables are

$$x = [p(r), M(r), \varepsilon(r)].$$ \hspace{1cm} (EQ 2.19)

One should notice that $x$ is a vector with five components ($M$ is vector field), each of which is labeled by a further continuous variable $r$. The total energy is given by

$$E = \int \left[ \frac{1}{2} \frac{M(r)^2}{p(r)} + \varepsilon(r) \right] d^3 r,$$ \hspace{1cm} (EQ 2.20)

which is the integral of the sum of the kinetic and the internal energy over the entire volume of the flow system. The entropy expression is obtained by the local equilibrium assumption

$$S = \int \delta(p(r), \varepsilon(r)) d^3 r,$$ \hspace{1cm} (EQ 2.21)
where the function \( s(\rho, \varepsilon) \) expresses the relationship between the densities of entropy, mass, and internal energy at equilibrium. By taking functional derivatives with respect to the state variables, the expressions for \( \delta E / \delta x \) and \( \delta S / \delta x \) are obtained as

\[
\frac{\delta E}{\delta x} = \begin{pmatrix}
\frac{\delta}{\delta \rho(\mathbf{r})} \\
\frac{\delta}{\delta M(\mathbf{r})} \\
\frac{\delta}{\delta \varepsilon(\mathbf{r})}
\end{pmatrix} E(\rho, M, \varepsilon) = \begin{pmatrix}
\frac{1}{2} v(\mathbf{r})^2 \\
v(\mathbf{r}) \\
1
\end{pmatrix},
\]

(EQ 2.22)

and

\[
\frac{\delta S}{\delta x} = \begin{pmatrix}
\frac{\mu(\mathbf{r})}{T(\mathbf{r})} \\
0 \\
\frac{1}{T(\mathbf{r})}
\end{pmatrix}.
\]

(EQ 2.23)

In Eq. (2.23), the local temperature \( T \) is defined by

\[
T(\mathbf{r}) = \left( \frac{\partial s(\rho, \varepsilon)}{\partial \varepsilon} \right)^{-1},
\]

(EQ 2.24)

and the local chemical potential \( \mu \) per unit mass by

\[
\frac{\mu(\mathbf{r})}{T(\mathbf{r})} = \frac{\partial s(\rho, \varepsilon)}{\partial \rho},
\]

(EQ 2.25)

both being functions of \( \mathbf{r} \) because they are evaluated at \( \rho(\mathbf{r}), \varepsilon(\mathbf{r}) \). The matrix \( L \) is given by
2.2 Reformulation of classical hydrodynamics

\[
L(x) = -\begin{bmatrix}
0 & \frac{\partial}{\partial r}\rho(r) & 0 \\
\rho(r)\frac{\partial}{\partial r} & \left[\frac{\partial}{\partial r}M(r) + M(r)\frac{\partial}{\partial r}\right]^T & \frac{\partial}{\partial r}\rho(r) + \frac{\partial}{\partial r}\rho(r) \\
0 & \frac{\partial}{\partial r}\varepsilon(r) + p(r)\frac{\partial}{\partial r} & 0
\end{bmatrix}, \quad (\text{EQ } 2.26)
\]

where the derivatives act on all terms to the right of them. It is straightforward to verify that the multiplication of \( L \) by \( \delta E/\delta x \) gives the reversible contributions to the dynamics which are those terms not involving the stress tensor \( \tau \) and the heat flux \( j^i \) in Eqs. (2.13), (2.14), and (2.15). Contrary, the irreversible contributions to the dynamics are those involving the stress tensor \( \tau \) and the heat flux \( j^i \), and are reproduced from \( M \cdot \partial S/\partial x \) by choosing the following \( M \) matrix

\[
M(x) = -\begin{bmatrix}
0 & 0 & 0 \\
0 & -\left(\frac{\partial}{\partial r}\eta T^r_r + \frac{1}{2} \frac{\partial}{\partial r}\eta \frac{\partial}{\partial r}\right)^T + \frac{2}{3} \frac{\partial}{\partial r} \kappa T^r_r + \frac{1}{2} \frac{\partial}{\partial r} \kappa \nabla \cdot \dot{\gamma} \\
0 & -\eta \dot{\gamma} \cdot \frac{\partial}{\partial r} + \kappa \nabla \cdot \dot{\gamma} \frac{\partial}{\partial r} + \frac{1}{2} \eta \dot{\gamma} \cdot \dot{\gamma} - \frac{\partial}{\partial r} \cdot \kappa T^r_r + \frac{1}{2} \kappa (\nabla \cdot \dot{\gamma})^2
\end{bmatrix}. \quad (\text{EQ } 2.27)
\]

In Eq. (2.27), the transport coefficient \( \hat{\kappa} \) is a combination of the viscosity \( \eta \) and the dilatational viscosity \( \kappa \),

\[
\hat{\kappa} = \frac{\kappa}{2} - \frac{\eta}{3}, \quad (\text{EQ } 2.28)
\]

and the tensor \( \dot{\gamma} \) is the symmetrized velocity gradient tensor

\[
\dot{\gamma}(r) = \frac{\partial}{\partial r} v(r) + \left[\frac{\partial}{\partial r} v(r)\right]^T. \quad (\text{EQ } 2.29)
\]

The symmetry properties of the matrix \( L \) in Eq. (2.26) and the matrix \( M \) in Eq. (2.27) can be verified after a matrix multiplication, and then integration by parts for each
term [see Eq. (2.6) and Eq. (2.8)]. The Jacobi identity [see Eq. (2.7)] can be verified for the matrix $L$ in Eq. (2.26). The matrix $M$ in Eq. (2.27) can be shown to be positive semidefinite [see Eq. (2.9)], so that we may call $M$ a metric matrix. The requirement that $\delta E/\delta x$ lies in the null space of $M$ [see Eq. (2.3)] is also satisfied. The matrix element of $M$ for classical hydrodynamics are proportional to $\eta$, $\kappa$, and $\lambda$, so that its relation to dissipative material properties and irreversible dynamics should be obvious. Another important cross relationship between the reversible and irreversible dynamics, stated in Eq. (2.2), remains to be checked for classical hydrodynamics:

$$L \cdot \frac{\delta S}{\delta x} = L(r) \cdot \begin{pmatrix} \mu(r) \\ -T(r) \\ -1 \\ 1 \end{pmatrix} = 0.$$  (EQ 2.30)

By using the explicit expression (26) for $L(r)$ we find the alternative formulation

$$\frac{\partial}{\partial r} \left( T(r) \frac{\varepsilon(r) - \mu(r)\rho(r) - T(r)s(r) + \rho(r) - 1}{T(r)} \right) = 0.$$  (EQ 2.31)

In view of our definitions for $p, T, s$, and $\mu$, this latter form of the condition follows immediately from the Gibbs-Duhem equation for the local equilibrium system.

2.3 GENERIC modeling of new reptation models

State variables

In order to describe the flow behavior of entangled linear polymers, it is necessary to include the hydrodynamic variables in the list of independent state variables. The variables used here are the same as those adopted in the above section, namely, the polymer mass density, $\rho(r)$, the momentum density, $M(r)$, and the internal energy density, $\varepsilon(r)$. 

20
For a complete description of complex fluids on a coarse-grained level, we need further, structural state variables. The appropriate choice of these structural state variables needs physical insight on the problem considered. Here, we fully rely on the well-established reptation picture for melts of linear polymer molecules [Doi and Edwards (1986)].

The reptation idea is depicted in Figure 2.1 where the dots represent other chains which, in that drawing, are assumed to be perpendicular to the plane. They are called ‘obstacles’. If we look the motion of one probe chain (the solid line) in a network of obstacles, it is obvious that the chain cannot move freely because they cannot pass through the obstacles. This constraint effectively confines each chain inside a tube-like region (the outline by dashed thin lines). It is easier for a polymer chain to move in the direction along its backbone than in the transverse direction, except for its two ends which can move in any possible direction. This type of motion was called reptation [de Gennes (1971)]. The centre line of such a tube-like region was called the primitive path (the dashed thick line). In the short time-scale the motion of the polymer is regarded as wriggling around the primitive path. On a longer time-scale, the conformation of the primitive path changes as the polymer moves, creating and destroying the ends of the primitive path. Since the primitive path at any moment represents the conformation of
the chain with the small-scale fluctuations omitted, we shall use the term ‘primitive chain’ to denote the dynamical equivalent of the primitive path. At this level of description, the details of the wriggling motion are irrelevant, and a simpler model could be made. Within this coarse-grained tube and reptation picture, there are two types of polymer relaxation. The first type is escape of a polymer from its tube by motion of the polymer itself. It includes all dynamic modes available to the single primitive chain in a tube—which due to its reptation—as well as other modes, such as fluctuations in contour length of the primitive chain. The second type is relaxation of a polymer chain by the motions of the surrounding polymers forming its tube. It includes the constraint release mechanisms such as DR and CCR which allow configurational relaxation to take place not only at the chain ends. In order to describe the stochastic effects involved in the dynamics of the primitive chain and the relaxation mechanisms, one introduces a configurational distribution function which, for nonhomogeneous flows, depends on the position \( r \). Well-established configurational variables appearing in the configurational distribution function of reptation models are a unit vector \( u \) and a label \( s \in [0, 1] \) [see Fig. 2.2], where \( u \) specifies the orientation of the tube or the primitive chain inside at the position \( s \) of the probe chain. The values \( s = 0 \) and \( s = 1 \) correspond to the chain ends, and we assume that \( s \) varies proportional to the contour length measured from one of the chain ends. We will keep this labeling rule, including the values 0 and 1 at the chain ends, even in the presence of chain stretching. It is clear that the first type of relaxation can be described by exploring proper dynamic equations for \( u \) and \( s \) supplemented by suitable initial and boundary conditions. Additionally, we introduce another label \( \xi \in [0, 1] \) to specify the position of a tube segment on the associated constraining chain which forms the tube [see Fig. 2.2]. The labeling rule for \( \xi \) is the same as that for \( s \). Whenever \( \xi \) moves out of \([0, 1] \), the associated tube segment is destroyed, or in other words, the constraint on the chain segment inside the tube is released and the configuration there will be relaxed. Therefore, the introduction of \( \xi \) offers a possibility to model the second type relaxation due to DR, CCR, and so on. At first view, it seems quite natural to introduce an orientation vector also for the constraining chain together with the second label \( \xi \), which may allow us a more elegant, consistent, and symmetric descrip-
2.3 GENERIC modeling of new reptation models

Although we don’t attempt to do so due to the following two reasons: 1. The key features of entangled linear polymers can be adequately represented by the present coarse-grained description, i.e. the tube or equivalently the primitive chain inside the tube. Hence only the dynamics of the primitive chain should be studied. Under this consideration no information on the constraining chain is necessary except for its position (specified by $\xi$ here) which may help to describe the second type relaxation of the primitive chain as mentioned above. 2. A reasonable physical argument for introducing an orientation vector for the constraining chain is rather difficult to establish, e.g. a new but ambiguous concept such as “crossed tubes” may occur. To conclude, we here consider the configurational distribution function $f(u, s, \xi, r)$. At any position $r$, we hence have a probability density in the configurational variables $u, s$ and $\xi$ which gives the joint probability for finding a tube segment at the position $(s, \xi)$ and with the orientation $u$. We choose the normalization condition $\int_0^1 \int_0^1 \int_0^1 f(u, s, \xi, r) d^3u ds d\xi = 1$, independent of position $r$, for the probability density $f(u, s, \xi, r)$ with $f \geq 0$.

In the original DE model, chain stretching was neglected. It has long been recognized that chain stretching is important at high shear rates (comparable to the reciprocal of the Rouse relaxation time of the molecule), in extensional flows, and for understanding very rapid double-step-strain deformations. We hence introduce a further variable, $\lambda(r)$, to account for the chain stretching, which is defined as the ratio between the contour length

![Figure 2.2: Illustration of the configurational variables for reptation models.](image-url)
of the primitive chain and the length at equilibrium. Instead of incorporating $\lambda$ into the list of arguments of the configurational distribution function and considering the contour length fluctuation effect, we prefer to keep it as a separate and deterministic variable. The reasons for doing so is the following. First, the overall chain stretch will not be affected by the local chain orientation at a specific position in the chain, so that there is no direct coupling between $\lambda$ on the one hand and $u$, $s$ and $\xi$ on the other hand. Second, although the contour length fluctuation can be modeled through proper noise effects, the structure of them is complicated and non-Markovian because they result from the many fluctuating modes of a one-dimensional Rouse chain in a tube [Doi (1983); Ketzmerick and Öttinger (1989)], so that any modeling of the noise effects on $\lambda$ on the diffusion-equation level would be very misleading. However, the additional relaxation mechanism for chain orientation caused by the contour length fluctuation can be modeled by either considering a proper diffusion function for the $s$ dynamics [Rusch et al. (1997)] or implicitly incorporating it into an integral-type model through the memory function [Fang et al. (1998)].

We now completed the first and important step of choosing the state variables $x$, which we can regard as the step of defining the level of description or the thermodynamic system that we want to investigate in this thesis,

$$x = [\rho(r), M(r), \varepsilon(r), f(u, s, \xi, r), \lambda(r)]. \tag{EQ 2.32}$$

According to the existing experience with reptation models, the choice of state variables in Eq. (2.32) would allow us to seize the important physical effects listed in Chapter 1, except for the anisotropic tube cross sections and the segment connectivity. The GENERIC building blocks we construct in the following will produce two new reptation models with the relevant physical effects incorporated in a thermodynamically admissible way. The models are guaranteed to give physically reasonable results. In Chapter 4, we show that all the important rheological properties (listed in Chapter 1) for entangled linear polymers can be explored by the models. On the other hand, detailed structure information, orientational correlations at different points along a chain, local chain
2.3 GENERIC modeling of new reptation models

dynamics, or any properties probing the segment connectivity are certainly beyond the range of phenomena accessible to us on the proposed level of description.

Energy

The total system energy is composed of the sum of the fluid’s kinetic and internal energy. It is assumed to have the following form:

\[ E = \int \left[ \frac{1}{2} \frac{M(r)^2}{\rho(r)} + \varepsilon(r) \right] d^3r. \]  

(EQ 2.33)

The internal energy density \( \varepsilon(r) \) here includes all the interactions between the atoms of all chains, as well as the kinetic energies associated with their motions with respect to the local fluid velocity, \( v(r) = \frac{M(r)}{\rho(r)} \). There are no further contributions to the energy in a entangled polymer system. Implicitly, it is assumed that all the interactions are on such a local scale that they are not affected by the polymer orientation on the scale of segments between entanglements, or by chain stretching. The functional derivative of the energy is given by

\[ \frac{\delta E}{\delta x} = \begin{pmatrix} \frac{1}{2} v(r)^2 \\ v(r) \\ 1 \\ 0 \\ 0 \end{pmatrix}. \]  

(EQ 2.34)

Entropy

The total system entropy is composed of the entropy associated with the very local arrangements and motions of atoms, with the configurational distribution function, and with the chain stretching. Thus, the following form is postulated for the total entropy:
Chapter 2 Model formulation

\[
S = \int s(\rho(r), \varepsilon(r)) - k_B \frac{N_A}{M} \rho(r) \Phi(\lambda(r)) \, \text{d}^3 r
- k_B Z N_A M \rho(r) \int_0^1 \int_0^1 \int_0^1 p(u, s, \xi, r) \ln p(u, s, \xi, r) \, \text{d}^3 u \, \text{d}^3 s \, \text{d}^3 \xi \, \text{d}^3 r
\]  
(EQ 2.35)

In writing this expression, we assumed that the local entropy contribution is described by a given function \( s = s(\rho, \varepsilon) \), which is expected to be similar to the entropy density of low-molecular-weight liquids. It is this function that can be used for introducing the concept of the absolute temperature defined by Eq. (2.24) and the chemical potential defined by Eq. (2.25). The second and third terms on the right side of Eq. (2.35) are the configurational entropy contributions per segment between entanglements due to stretching and orientation. The third one (\( p \ln p \) term) is clearly the contribution due to the configurational distribution function, where

\[
p(u, s, \xi, r) = \frac{f(u, s, \xi, r)}{\int_0^1 \int_0^1 \int_0^1 f(u', s', \xi', r) \, \text{d}^3 u' \, \text{d}^3 s' \, \text{d}^3 \xi'}
\]  
(EQ 2.36)

Using \( p \) instead of \( f \) is important in taking functional derivatives because, in considering variations; we otherwise would need to impose an explicit normalization constraint. Although the denominator in Eq. (2.36) is assumed to be equal to unity, we hence need to keep it in the definition of the entropy—it makes an important contribution to the functional derivative of \( S \) with respect to \( f \). Once all functional derivatives are taken, one can assume the normalization condition to be fulfilled, so that there is no need to distinguish between \( f \) and \( p \).

The parameters \( N_A, M, \) and \( Z \) in the prefactor of the \( p \ln p \) term in Eq. (2.35) are Avogadro’s number, the molecular weight of the polymers, and the number of entanglements per chain at equilibrium, respectively; \( k_B \) is Boltzmann’s constant. The prefactor reflects the extensive nature of the entropy, where each segment between entanglements makes a contribution. The number of entanglements is given by
where $M_e'$ is the average molecular weight between entanglement points along one chain. If we denote the value for polymer melts as $M_e$, then $M_e'$ for entangled polymer solutions can be estimated by using the relation $M_e' = M_e/\phi^{1/2}$, where $\phi$ is the volume fraction of polymer [Ferry (1980)]. In Eq. (2.35), the number density of polymers, $n_p$, has deliberately been expressed as $N_A\rho(r)/M$ in order to emphasize the extra occurrences of the state variable $\rho(r)$.

Finally, we consider the entropy due to chain stretching, the second term on the right side of Eq. (2.35), where $\Phi(\lambda)$ is the dimensionless entropy penalty for each chain deviating from the average equilibrium contour length, $\lambda = 1$. We propose the following functional form of $\Phi(\lambda)$,

$$
\Phi(\lambda) = -\frac{3}{2}Z\left[\ln \lambda^2 + (\lambda_{\text{max}}^2 - 1) \ln \frac{\lambda_{\text{max}}^2}{\lambda_{\text{max}}^2 - 1}\right],
$$

where $\lambda_{\text{max}}$ is the maximum possible stretching ratio of the contour length. For large extensions, we here assume the standard FENE type spring behavior (FENE is the acronym for finitely extensible nonlinear elastic), while for small extensions Hookean spring behavior is recovered. When $\lambda_{\text{max}} \to \infty$, we have $\Phi(\lambda) \approx -[\ln \lambda^2 + 1 - \lambda^2]$. The $\ln \lambda^2$ term ensures that the contour length is always positive.

The parameter $\lambda_{\text{max}}$ can be verified to be equal to the square root of $N_{KE}$ (the number of Kuhn steps per entanglement segment) based on the random-coil assumption for each entanglement segment at equilibrium, it is given by

$$
\lambda_{\text{max}} = \sqrt{N_{KE}} = \frac{d_e}{l_K},
$$

where $d_e$ is the average end-to-end distance of the entanglement segment at equilibrium and $l_K$ is the length of the Kuhn step (which is twice the persistence length). The values
of \( d_t \) and \( l_K \) for some polymer melts can be calculated from the relevant experimental data tabulated in the literature [Fetters et al. (1996)], where the values of \( M_e \) are also given. The value of \( l_K \) can be calculated from the characteristic ratio \( C_\infty \) by using the relationship

\[
C_\infty = \frac{l_K}{l} - 1, \tag{EQ 2.40}
\]

where \( l \) is the bond length [Flory (1988), p.111]. Based on these available data, the values of \( u_{\text{max}} \) for several important melts are given in Table 2.1.

**TABLE 2.1.** Values for the maximum possible stretching ratio \( u_{\text{max}} \) [via Eq. 2.39], the entanglement molecular weight \( M_e \), the average end-to-end distance of the entanglement segment at equilibrium \( d_t \), and the length of a Kuhn step \( l_K \) for three important melts at 140°C.

<table>
<thead>
<tr>
<th>Melts</th>
<th>( M_e ) (g mol(^{-1}))</th>
<th>( d_t ) (Å)</th>
<th>( l_K ) (Å)</th>
<th>( u_{\text{max}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>13000</td>
<td>76</td>
<td>16.2</td>
<td>4.7</td>
</tr>
<tr>
<td>HDPE</td>
<td>860</td>
<td>33</td>
<td>12.9</td>
<td>2.6</td>
</tr>
<tr>
<td>PP (atactic)</td>
<td>5400</td>
<td>61</td>
<td>10.7</td>
<td>5.7</td>
</tr>
</tbody>
</table>

For the following, it is very convenient to introduce an effective spring constant for deviations from the equilibrium contour length, associated with the derivative of \( \Phi(\lambda) \),

\[
c(\lambda) = \frac{3Z\lambda^2(\lambda + 1)}{\lambda(\lambda_{\text{max}}^2 - \lambda^2)}, \tag{EQ 2.41}
\]

which indicates that the spring force \( F(\lambda) \propto -c(\lambda)(\lambda - 1) \) vanishes at \( \lambda = 1 \), and diverges for \( \lambda \to 0 \) and \( \lambda \to \lambda_{\text{max}} \), respectively.

The functional derivative of the entropy is given by
2.3 GENERIC modeling of new reptation models

\[
\frac{\delta S}{\delta x} = \begin{pmatrix}
\frac{-\mu(r)}{T(r)} - k_B \frac{N_s}{M} \Phi(\lambda(r)) - k_B \frac{N_4}{M} H \\
0 \\
1 \\
-k_B Z_n(r) \ln f(u, s, \xi, r) - H \\
-k_B n_p(r) c(\lambda(r)) [\lambda(r) - 1]
\end{pmatrix}, \quad (EQ 2.42)
\]

where \( H = \int_0^R \int_0^R \int f(u', s', \xi', r) \ln f(u', s', \xi', r) d^3 u' d^3 s' d^3 \xi'. \)

**Poisson operator L**

To formulate the reversible dynamics, we can immediately fill in the well-known parts associated with the hydrodynamic variables \( \rho(r), M(r), \) and \( \varepsilon(r) \) to get

\[
L(x) = - \begin{bmatrix}
0 & \frac{\partial}{\partial r} \rho(r) & 0 & 0 & 0 \\
\rho(r) \frac{\partial}{\partial r} [M(r) + M(r) \frac{\partial}{\partial r}] & \varepsilon(r) \frac{\partial}{\partial r} - \frac{\partial}{\partial r} \cdot \tau(r) & L_{24} & L_{25} \\
0 & 0 & 0 & 0 & 0 \\
0 & L_{42} & 0 & 0 & 0 \\
0 & L_{52} & 0 & 0 & 0
\end{bmatrix}, \quad (EQ 2.43)
\]

where the matrix elements associated with the structure variables \( f(u, s, \xi, r) \) and \( \lambda(r) \) are left unspecified.

Construction of the \( L \) matrix (2.43) can be first focused on the second column of the matrix. The rest of the elements in the second row will be determined from the antisymmetry of the Poisson bracket. It is important to note that, according to the basic Eq. (2.1) and Eq. (2.34), the elements in the second column will be multiplied by \( \nu(r) \) from the right. Therefore, the first row immediately leads to the continuity equation (2.13). For the internal energy, a stress term, \( \tau(r) \), has been introduced in the third row (with the sign of a stress tensor rather than of a pressure tensor), because the changes of volume
and shape associated with the derivatives of \( v(r) \) affect the internal energy. For the momentum density in the second row, the convective behavior of a vector is taken into account.

By considering the convection behavior of \( f \) and \( \lambda \), we can similarly construct \( L_{42} \) and \( L_{52} \). Here, we begin with the construction of the simpler element \( L_{52} \). The tube is postulated to deform affinely with the macroscopic deformation. It can readily be shown [see Section 7.9 of Doi and Edwards (1986)] that the tangential velocity of the tube, relative to the center of the primitive chain, is the integrated projection of the transposed velocity gradient tensor onto \( uu \):

\[
v(n, t) = \mathbf{k}(t) : \int_0^n dn' u_n(n', \xi) u_n(n', \xi)
\]

where \( n \) is the curvilinear coordinate of a tube segment measured along the tube axis and \( \mathbf{k}(t) \) is the transposed velocity gradient tensor for the flow. From this equation we get

\[
\frac{DL}{Dt} = v(L/2, t) - v(-L/2, t) = L \mathbf{k}(t) : \int_0^1 ds u_n(s, \xi) u_n(s, \xi)
\]

where \( D/Dt \) is the material time derivative, \( L \) is the contour length of the primitive chain, and the transformation \( s = n'/L + 1/2 \) is applied. After \( L \) is normalized by its equilibrium value \( L_0 \) and the dyadic product \( uu \) at the point \( s \) is replaced by its average over the configuration distribution function at \( s \), the equation (2.45) gives

\[
\frac{D\lambda}{Dt} = \lambda \mathbf{k}(t) : \bar{\mathbf{t}}(t)
\]

with \( \lambda = L/L_0 \) and the symmetric second-moment tensor

\[
\bar{\mathbf{t}}(t) = \int_0^1 \int_0^1 uu f(u, s, \xi, r) d\xi ds d\eta.
\]
This average stretch arises from the hydrodynamic drag on a molecule by the mean-field friction of surrounding chains. Eq. (2.46) can be rewritten into the form

\[
\frac{\partial \lambda}{\partial t} = -\mathbf{v} \cdot \frac{\partial \lambda}{\partial r} + \lambda \mathbf{\tau} \cdot \frac{\partial}{\partial r} \mathbf{v},
\]  

(EQ 2.48)

from which we obtain by leaving out the vector \(\mathbf{v}\)

\[
L_{52} = \frac{\partial \lambda(r)}{\partial r} - \lambda(r) \mathbf{\tau}(r) \cdot \frac{\partial}{\partial r}.
\]  

(EQ 2.49)

In \(L_{42}\), we need to express the convection of the scalar configurational distribution function, the behavior of the configurational vector \(\mathbf{u}\) under flow, and the transformation rules of the position labels \(s\) and \(\xi\) due to convection. The standard co-rotational behavior of the orientation unit vector \(\mathbf{u}\) can be expressed in the form

\[
\dot{\mathbf{u}}_{\text{convect}} = \left(1 - \frac{\mathbf{uu}}{|\mathbf{u}|^2}\right) \cdot \mathbf{K} \cdot \mathbf{u}.
\]  

(EQ 2.50)

For obtaining the resulting changes in the position labels \(s\) and \(\xi\) due to convection, we simply assume that the convection has no influence on the labels [see Fig. 2.3], namely,

\[
\dot{s}_{\text{convect}} = 0 \quad \text{and} \quad \dot{\xi}_{\text{convect}} = 0.
\]  

(EQ 2.51)

This corresponds to a uniform stretching of the contour, and a uniform monomer distribution along the tube is maintained.

Keeping in mind that the matrix element \(L_{42}\) will be multiplied by \(\mathbf{v}(r)\) from the right, and that the convection terms (2.50) and (2.51) should appear in the corresponding first-order derivative term of a diffusion equation,

\[
\frac{\partial f}{\partial t} = -\mathbf{v} \cdot \frac{\partial f}{\partial \mathbf{r}} - \frac{\partial}{\partial \mathbf{u}} \cdot (\dot{\mathbf{u}}_{\text{convect}} f) - \frac{\partial}{\partial s} (\dot{s}_{\text{convect}} f) - \frac{\partial}{\partial \xi} (\dot{\xi}_{\text{convect}} f) + \cdots,
\]  

(EQ 2.52)
we can now write

\[ L_{42} = \frac{\partial f(u, s, \xi, r)}{\partial r} + \frac{\partial}{\partial u} \cdot f(u, s, \xi, r) \left( 1 - \frac{uu}{|u|^2} \right) u \cdot \frac{\partial}{\partial r}. \]  

(EQ 2.53)

The elements \( L_{24} \) and \( L_{25} \) are obtained from the antisymmetry of \( L \), the results are

\[ L_{24} = -\frac{\partial f(u, s, \xi, r)}{\partial r} \cdot \frac{\partial}{\partial r} \cdot u \left( 1 - \frac{uu}{|u|^2} \right) \cdot f(u, s, \xi, r) \cdot \frac{\partial}{\partial u}, \]  

(EQ 2.54)

and

\[ L_{25} = -\frac{\partial \lambda(r)}{\partial r} \cdot \frac{\partial}{\partial r} \cdot \tau(r) \lambda(r). \]  

(EQ 2.55)

So far, we have all the elements in the matrix \( L \) except for the stress tensor. By satisfying the degeneracy requirement (2.2), a total stress tensor consisting of three contributions is obtained,

\[ \tau = \tau_0 + \tau_1 + \tau_2, \]  

(EQ 2.56)

namely, the isotropic pressure implied by the entropy contribution similar to the one of a low-molecular-weight liquid, \( s = s(\rho, \varepsilon) \),

\[ \tau_0(r) = -(\mu \rho + Ts - \varepsilon) \mathbf{I}, \]  

(EQ 2.57)

the original Doi-Edwards contribution,

\[ \tau_1(r) = 3Zn_b k_b T \int_0^1 \int_0^1 uu f(u, s, \xi, r) d\xi ds d\xi, \]  

(EQ 2.58)

and a contribution associated with the chain stretching,
2.3 GENERIC modeling of new reptation models

\[ \tau_2(r) = c(\gamma)\beta(\gamma - 1)n_2k_BT \int_0^1 \int_0^1 uu f(u, s, \xi, r) d^3 u d^3 s d\xi. \]  

(EQ 2.59)

Finally, it can be shown that the Jacobi identity (2.7) is satisfied for the matrix \( L \) posed here.

**Friction matrix \( M \)**

In formulating the friction matrix \( M \), we again begin by filling in the hydrodynamic part, but neglecting the Newtonian terms (\( \eta = \kappa = 0 \)), typically associated with short time and length scales. The reason for doing so is that we are interested in the large stresses associated with entanglements in melts rather than in the much smaller purely viscous effects typical of fluids consisting of small molecules with short-range interactions. Under this consideration, the form of the matrix \( M \) reads

\[
M(x) = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & \lambda r T^2 \frac{\partial}{\partial r} & 0 & 0 \\
0 & 0 & M_{44} + M_{45} & M_{45} & M_{45} \\
0 & 0 & 0 & M_{54} & M_{55}
\end{bmatrix}. 
\]

(EQ 2.60)

In Eq. (2.60), the elements associated with the structural variables are left unspecified. To construct them, we have to consider the dissipative or irreversible effects on the structural variables. The physical effects to be included in \( M_{44} \) are (i) the diffusive reptation motion of a chain in a tube, and (ii) the constraint release mechanisms associated with double reptation and convective constraint release, which can be modeled as relaxation processes by either (a) introducing noise effects on the chain orientation vector \( u \) directly or (b) considering a “double diffusion” motion for \( \xi \) together with the random orientation boundary condition at \( \xi = 0 \) and 1. We hence write \( M_{44} \) for (a) as the following second-order differential operator,
where $\tau_d$ is the reptation time, and $D_u$ is the orientational diffusion coefficient or inverse relaxation time. We refer to this implementation as the **single-label model**, because finally only the position label $s$ is needed in this model, while another label $\xi$ is essentially irrelevant. For the implementation of DR and CCR by (b), $M_{44}$ can be written as

$$M_{44} = -\frac{1}{Zn_p k_B} \left( \frac{\partial}{\partial s} \frac{f}{\pi_d^2} \frac{\partial}{\partial s} + \frac{\partial}{\partial u} \cdot fD_u \left( 1 - \frac{uu}{|u|^2} \right) \frac{\partial}{\partial u} \right),$$  \hspace{1cm} (EQ 2.61)

where $D_{\xi}$ is the effective diffusion coefficient for $\xi$. We refer to this implementation as the **double-label model**, because both the position labels $s$ and $\xi$ are necessary for the modeling.

In the single-label model, the form of $D_u$ proposed here is

$$D_u = 1 \left[ \delta_1 \frac{1}{\tau_d} - \delta_2 \frac{\dot{\lambda}_{\text{dissip}}}{\lambda} H \left( -\frac{\dot{\lambda}_{\text{dissip}}}{\lambda} \right) \right],$$  \hspace{1cm} (EQ 2.63)

where $H(x)$ is the Heaviside step function [$H(x) = 1$ for $x \geq 0$, $H(x) = 0$ for $x < 0$], and $\dot{\lambda}_{\text{dissip}}$ is the dissipative contribution to the time-evolution equation for chain stretching [an explicit expression for it will be given in the next section]. The quantities $1/\tau_d$ and $-\dot{\lambda}_{\text{dissip}}/\lambda$ determine the rates of constraint release for probe chains due to the loss of entanglements caused by the reptation motion and the retraction of the surrounding chains, respectively. Hence, the $\delta_1$-term can be interpreted as representing “double reptation”, while the $\delta_2$-term can be regarded as the CCR mechanism. The prefactor $1/6$ is chosen such that, for $\delta_1 = 1$, the resulting relaxation mechanism from the $\delta_1$-term has exactly the same relaxation time as the dominating process in the original Doi-Edwards model i.e. $\tau_d$. Mead et al. (1998) showed that constraint release causes not only chain segments reorientation, but also contour length shortening; when the chain nears the unstretched status, constraint release is mainly manifested in chain segments reorienta-
tion; when the chain is highly stretched, constraint release is increasingly manifested in contour length shortening. Hence they introduced a switch function to apportion the effects of constraint release between contour length shortening and orientation relaxation. In other words, the constraint release rates (1/τ_d due to DR and −λ_dissip/λ due to CCR) are not fully contributed to the relaxation rate of chain orientation in general cases, their contributions depend on the stretch of the chain (fully contributed when λ → 1 and less contributed when λ → λ_{max}). This effect can be taken into account in our model here by assuming proper λ-dependent functions for the parameters δ_1 and δ_2. According to the above argument, the functions must be chosen in such a way that they approach unity when λ is near unity, and approach zero when λ is large. We will leave δ_1 and δ_2 as adjustable parameters with this general requirement on their possible forms. In Sec. 4.6, a simple form δ_1 = δ_2 = 1/λ is used, which gives a best overall fit to the available experimental data for the single-label model. The apportioning effect on stretching is not included in our models for the following reasons: 1. The way used by MLD to realize the effect is non GENERIC and it causes a non-physical prediction for the steady shear stress at high shear rate (see Fig. 4.29). 2. Although the effect could be roughly included by considering a λ-dependent stretching time in M55 (see later), it is difficult to fix a concrete form, and hence leads to another adjustable function. 3. Many tests show that it does not help a lot to improve the model predictions.

In the double-label model, D_5 is assumed to take the following form:

\[
D_5 = \frac{1}{\pi^2} \left[ \delta_1 \frac{1}{\tau_d} - \delta_2 \frac{\dot{\lambda}_{dissip}}{\lambda} H\left(\frac{\dot{\lambda}_{dissip}}{\lambda}\right) \right],
\]

(EQ 2.64)

where the first term is the diffusivity due to the reptation motion of the constraining chain, and the second term represents the mean-field convective contribution to the diffusivity for the constraining chain. Here we don’t expect the above-defined diffusion motion for the constraining chain is realistic, indeed, an enhanced reptative motion by CCR (the second term) is questionable. However, as mentioned early in this section, an accurate description of the dynamics for the constraining chain is not our goal here. The
important thing is that the double diffusion of $\epsilon$ with the diffusion coefficient defined by Eq. (2.64) plus the random orientation of $u$ on the two ends of $\epsilon$ results in an effective mimic of the additional relaxation mechanisms caused by double reptation and convective constraint release. This can be seen from the fact that the $\delta_1$-term with $\delta_1 = 1$ gives an additional relaxation process which is the same as the original Doi-Edwards model and the $\delta_2$-term with $\delta_2 = 1$ gives another one with the dominant relaxation rate determined by the chain retraction rate. Therefore we can consider the $\delta_1$-term and the $\delta_2$-term as representing DR and CCR, respectively. Again the parameters $\delta_1$ and $\delta_2$ here are $\lambda$-dependent functions which serve to adjust the constraint-release-induced relaxation rate of chain orientation according to the argument discussed above for the single-label model. For the double-label model, we find in Sec. 4.6, the form $\delta_1 = \delta_2 = 1/\lambda^2$ gives a better overall fit to the experimental data than does the form $\delta_1 = \delta_2 = 1/\lambda$.

Finally, we need to choose the matrix elements $M_{ij}$ in Eq. (2.60), which specify the contour length relaxation mechanism, and resulting dissipative effects on the configurational distribution function. We choose

$$M_{ss} = \frac{1}{3\tau_s Z n_s k_B}, \quad \text{(EQ 2.65)}$$

where $\tau_s$ is the Rouse time or “stretch time”. For simplicity, we here assume that the contour length relaxation has no influence on the label $\epsilon$, except for the implicit influence through the diffusion coefficient $D_{\epsilon}$ [Eq. (2.64)] in the double-label model. Under this consideration, when the contour length changes by relaxation, only two resulting effects will take place [see Fig. 2.3], one is the relabeling of $s$ for tube or chain segments, and another is the creation/destruction of configurations compensating for a possible loss/gain of configurations at the chain ends. These two effects are incorporated by choosing the rest of the elements $M_{ij}$ as the following:

$$M_{ss} = M_{55} \left\{ -\gamma_1 f + \frac{\partial}{\partial s} \left[ \gamma_2 \left( s - \frac{1}{2} \right) f \right] \right\}, \quad \text{(EQ 2.66)}$$
2.3 GENERIC modeling of new reptation models

Figure 2.3: Illustration of the transformation rule of the position label $s$ under convection and retraction, and the creation of configurations for compensating the loss of configurations at chain ends due to retraction.

\[ M_{34} = M_{55} \left\{ -\gamma_1 f - \gamma_2 \left( s' - \frac{1}{2} \right) f \frac{\partial}{\partial s'} \right\}, \]  

(EQ 2.67)

and

\[ M_{44} = M_{55} \left\{ -\gamma_1 f + \frac{\partial}{\partial s} \left[ \gamma_2 \left( s' - \frac{1}{2} \right) f \right] \right\} \left[ -\gamma_1 f - \gamma_2 \left( s' - \frac{1}{2} \right) f \frac{\partial}{\partial s'} \right], \]  

(EQ 2.68)

where the $\gamma_2$-term is a linear rescaling term proportional to $s - 1/2$, and $\gamma_1$-term is a creation/destruction term. Simple physical arguments will be used to determine the choice of $\gamma_1$ and $\gamma_2$ in the next section. The expression for $M_{34}$ [Eq. (2.67)] is obtained from Eq. (2.66) by using the symmetry of the matrix $M$, and the expression for $M_{44}$ [Eq. (2.68)] is chosen such that the positive-semidefiniteness of the matrix $M$ is guaranteed for $\tau_d > 0$, $\tau_s > 0$, $\delta_1 \geq 0$, $\delta_2 \geq 0$. By looking at the expression for $\delta E/\delta x$ in Eq. (2.34)
and the expression for $M$ in Eq. (2.60), it is easy to check out that the degeneracy requirement (2.3) is fulfilled. It must be pointed out that the independent alignment (IA) approximation is avoided by the presentation of the $\gamma_1, \gamma_2$-terms.

At this point, the formulation of our new reptation model that accounts for reptation motion, double reptation, convective constraint release, and chain stretching, and that avoids the independent alignment approximation, is completed. We have developed all the GENERIC building blocks, and we have verified all their required properties for the two versions of the model. Hence, they are thermodynamically admissible.

### 2.4 Time-evolution equations

By inserting the GENERIC building blocks developed in the last section into the fundamental time-evolution equation (2.1), we obtain all the model equations in a more familiar form. We first write down the explicit time-evolution equations for the double-label model.

For the hydrodynamic variables, we obtain the purely reversible continuity equation (2.13), the familiar momentum balance equation

$$\frac{\partial M}{\partial t} = \frac{\partial}{\partial r} \cdot (\nu M) + \frac{\partial}{\partial r} \cdot \tau, \quad (\text{EQ 2.69})$$

and the internal energy balance equation

$$\frac{\partial e}{\partial t} = -\frac{\partial}{\partial r} \cdot (\nu e) + \tau : \frac{\partial}{\partial r} v + \frac{\partial}{\partial r} \cdot \lambda_1 \frac{\partial T}{\partial r}, \quad (\text{EQ 2.70})$$

where the stress tensor $\tau$ is given by Eqs. (2.56)-(2.59).

In the following and next chapters, we assume that we consider the problem in a coordinate system moving with an arbitrary, given fluid particle, and we hence suppress the position argument. The equation for the chain contour length stretching and relaxation reads
2.4 Time-evolution equations

\[ \frac{D \lambda}{Dt} = \dot{\lambda}_{\text{tot}} = \dot{\lambda}_{\text{convect}} + \dot{\lambda}_{\text{dissip}}, \tag{EQ 2.71} \]

where the total stretching rate is split into convective and dissipative contributions,

\[ \dot{\lambda}_{\text{convect}} = \lambda \kappa : \tau, \tag{EQ 2.72} \]

and

\[ \dot{\lambda}_{\text{dissip}} = - \frac{1}{\tau_s} \frac{c(\lambda)}{3Z} (\lambda - 1) - \frac{\gamma_s}{3\tau_s} [1 - \bar{f}(0)]. \tag{EQ 2.73} \]

In Eq. (2.73), \( \bar{f}(0) \) is the value of the function \( \bar{f}(s) \) at \( s = 0 \). The definition of \( \bar{f}(s) \) is

\[ \bar{f}(s) = \int_0^s f(u, s, \xi, t) du d\xi, \tag{EQ 2.74} \]

which is the monomer density at position \( s \) of the tube. Eq. (2.73) tells us, on the time scale \( \tau_s \), not only deviations from the equilibrium contour length, but also deviations of the monomer density at the chain ends from the uniform monomer density cause contour relaxation. However we will find a little later the double-label model possesses a uniform monomer distribution along the tube, hence the latter term is absent, and so does the single-label model.

The diffusion equation for the configurational distribution function takes the form

\[ \frac{Df}{Dt} = - \frac{\partial}{\partial u} \left[ \left( 1 - \frac{uu}{u^2} \right) \kappa \cdot u f \right] - \frac{\partial}{\partial s} (s_{\text{tot}} f) - \gamma_i \dot{\lambda}_{\text{dissip}} f \]

\[ + \frac{1}{\pi \tau_s} \frac{\partial^2 f}{\partial s^2} + D_s \frac{\partial^2 f}{\partial \xi^2}, \tag{EQ 2.75} \]

with a dissipative drift contribution
which states there is only a rescaling of $s$ when the chain relaxes in the tube. In view of
keeping the range of $s$ fixed, we choose

\[ \gamma_2 = \frac{1}{\lambda}. \]  

(EQ 2.77)

The creation/destruction term \(-\gamma_1 \lambda \text{dissip} f\) in Eq. (2.75) compensates for configurations
lost or gained at the boundaries; this physical interpretation suggests

\[ \gamma_1 = \frac{\tilde{f}(0)}{\lambda}. \]  

(EQ 2.78)

For discussing the boundary conditions at the probe and surrounding chain ends, it is
useful to integrate the diffusion equation (2.75) to obtain

\[ \frac{D\tilde{f}}{Dt} = \frac{\partial}{\partial s} (\dot{s}_{\text{tot}} \tilde{f}) - \gamma_1 \lambda \text{dissip} \tilde{f} + \frac{1}{\pi \tau_s} \frac{\partial^2 \tilde{f}}{\partial s^2} + D_\xi \frac{\partial}{\partial \xi} \left[ \frac{\partial \tilde{f} d^4 u}{\partial \xi} \right]_0. \]  

(EQ 2.79)

Conservation of the total probability implies the boundary conditions

\[ \frac{\partial \tilde{f}(s)}{\partial s} \bigg|_{s=0} = \frac{\partial \tilde{f}(s)}{\partial s} \bigg|_{s=1} = 0 \quad \text{and} \quad \frac{\partial \tilde{f}(\xi)}{\partial \xi} \bigg|_{\xi=0} = \frac{\partial \tilde{f}(\xi)}{\partial \xi} \bigg|_{\xi=1} = 0, \]  

(EQ 2.80)

where \( \tilde{f}(\xi) = \int_0^1 \int f(u, s, \xi, t) d^4 u ds \). At the probe chain ends, we further impose random
orientation of \( u \) and random value of \( \xi \) by specifying the distribution

\[ f(u, s, \xi, t) = \tilde{f}(s) \frac{1}{4\pi} \delta(|u|-1), \quad s = 0, 1. \]  

(EQ 2.81)
At the surrounding chain ends, we further impose random orientation of $u$ and random value of $s$ by specifying the distribution

$$f(u, s, \xi, t) = \hat{f}(\xi) \frac{1}{4\pi} \delta(|u| - 1), \quad \xi = 0, 1. \quad \text{(EQ 2.82)}$$

It is important to note that, for the model proposed here, $\int f \, du = 1$ (hence $\hat{f}(s) = 1$ and $\hat{f}(\xi) = 1$) is the solution of the partial differential equation (2.79) with the boundary conditions (2.80). The model thus indeed possesses a uniform monomer distribution along the tube. In the model, the loss of configurations at the boundaries caused by a nonvanishing irreversible drift term, together with the creation term, avoids the IA approximation, and is crucial for obtaining irreversible effects in double-step strain experiments with flow reversal. It should be mentioned that, for a single-step strain, the results obtained from the model are the same as that from the DE model with IAA. This is due to the fact that we consider an extensible chain with a finite stretching time. It can be shown that results similar to that from the DE model without IAA are obtained by letting $\tau_s$ go to zero, i.e. assuming a rapid relaxation of chain stretching.

Now we compile all the corresponding equations for the single-label model, for which $\xi$ is irrelevant and hence can be eliminated. For the hydrodynamic variables, we obtain the same continuity equation (2.13), momentum balance equation (2.69), and internal energy balance equation (2.70) as the double-label model, except for the stress tensor $\tau$ [Eqs. (2.56)-(2.59)] where $\xi$ and the integration over $\xi$ should be canceled. The equation for the contour length stretching and relaxation takes the same form of Eq. (2.71). Again, $\xi$ should be dropped from all the related expressions where it occurs. The diffusion equation for the configurational distribution function takes the following form different from the double-label model, i.e.

$$\frac{Df}{Dt} = -\frac{\partial}{\partial u} \left[ \left(1 - \frac{uu}{|u|^2} \right) \cdot \kappa \cdot u \cdot f \right] - \frac{\partial}{\partial s}(\dot{s}_{\text{tot}}f) - \frac{\hat{\kappa}_{\text{dissip}}}{\lambda} f$$

$$+ \frac{1}{\pi^2 \tau_s \partial^2 s} \cdot \frac{\partial^2 f}{\partial s^2} + \frac{\partial}{\partial u} \cdot D_s \left(1 - \frac{uu}{|u|^2} \right) \cdot \frac{\partial}{\partial u} f \quad \text{(EQ 2.83)}$$
with $f = f(u, s, t)$. The corresponding boundary conditions for the above diffusion equation are

$$\frac{\partial \tilde{f}(s)}{\partial s} \bigg|_{s=0} = \frac{\partial \tilde{f}(s)}{\partial s} \bigg|_{s=1} = 0$$  \hspace{1cm} (EQ 2.84)

with $\tilde{f}(s) = \int f(u, s, t) d^3u$, and

$$f(u, s, t) = \frac{1}{4\pi} \delta(\|u\| - 1), \quad s = 0, 1.$$  \hspace{1cm} (EQ 2.85)

For both single-label model and double-label model, the plateau modulus $G_N^0$, to which $\tau_2$ does not contribute, is given by the Doi-Edwards result [see Sec. 4.1]

$$G_N^0 = \frac{3}{5} Z n_p k_B T.$$  \hspace{1cm} (EQ 2.86)

When $\lambda_{\text{max}}$ approaches infinity, we obtain the simple stress expression

$$\tau(r) = 5 G_N^0 \lambda^2 \int_0^1 \int_0^1 uu f(u, s, \xi, r) d^3uds d\xi$$  \hspace{1cm} (EQ 2.87)

for the double-label model and

$$\tau(r) = 5 G_N^0 \lambda^2 \int_0^1 uu f(u, s, r) d^3uds$$  \hspace{1cm} (EQ 2.88)

for the single-label model, which may be regarded as a manifestation of the stress-optic rule, see also Fuller (1995).

The single-label model has only four structural degrees of freedom, one from the position label $s$, two from the unit orientation vector $u$, and one from the chain stretching $\lambda$, while the double-label model has one more degree of freedom from the position label $\xi$. In this thesis, we assume $\tau_0/\tau_s = 3Z$. So, in addition to the plateau modulus
$G_N^0$ and the reptation time $\tau_4$, each model has four parameters ($Z$, $\delta_1$, $\delta_2$, $\lambda_{\text{max}}$) with the preferable values $Z \gg 1$ and $\lambda_{\text{max}} = 5$ for melts as motivated above. The parameters $Z$ and $\lambda_{\text{max}}$ depend on the chemistry of the polymer chain. The parameters $\delta_1$ and $\delta_2$ are $\lambda$-dependent functions with the required property, i.e. they approach unity when $\lambda$ is near unity, and approach zero when $\lambda$ is large.
Chapter 3

Stochastic simulation

In this chapter, stochastic interpretations of the two models developed in Chapter 2 are first described. Then, numerical schemes are designed to simulate the rheological behaviors of the models based on the stochastic interpretations. Finally, the simulation procedures are given in detail.

3.1 Stochastic model interpretations

For knowing the rheological behaviors of the two models developed in Chapter 2 in given homogeneous flows, only the equation (2.71) for the chain contour length \( \lambda \) and the diffusion equation (2.75) or (2.83) for the configurational distribution function \( f \) have to be solved. Among them, the most complicated equation clearly is the diffusion equation (2.75) or (2.83). Although the diffusion equation can be solved directly by numerical methods such as the finite element method, the finite difference method, the spectral method, and so on, it is very time-consuming to yield the full information about the distribution due to the fact that the equation is in a space of three or four dimensions. In view of the fact that \( f \) occurs in the time-evolution equations for the other state variables only through the second-moment tensors \( \tau \) and \( \bar{\tau} \), we here consider a possible strategy for simplifying the analysis of the diffusion equation for \( f \), namely, the stochastic simulation techniques described below. We will first take the double-label model as an example.

According to the theory of stochastic differential equations (SDEs), the diffusion equation (2.75), when ignoring the creation/destruction term discussed separately below, is equivalent to the following set of Itô SDEs for the stochastic processes \( u_t, s_t, \) and \( \xi_t, \)
Chapter 3 Stochastic simulation

\[ du_t = \left( 1 - \frac{u_i u_j}{|u|^2} \right) \cdot \mathbf{K} \cdot u_i \, dt, \quad (\text{EQ 3.1}) \]

\[ ds_t = \dot{s}_{\text{tot}} \, dt + \frac{1}{\tau_d} \sqrt{\frac{2}{\pi}} \, dW_t^s, \quad (\text{EQ 3.2}) \]

\[ d\xi_t = \sqrt{2D_{\xi}} \, dW_t^\xi, \quad (\text{EQ 3.3}) \]

where \( W_t^s \) and \( W_t^\xi \) are independent Wiener processes. The mentioned equivalence means that the average of an arbitrary function \( X(u, s, \xi) \), evaluated as an integral with the solution \( f \) of the diffusion equation at the time \( t \), can be obtained as the expectation of the stochastic process \( X(u_t, s_t, \xi) \),

\[ \int_0^t \int_0^1 \int_0^1 X(u, s, \xi) f(u, s, \xi, t) \, du \, ds \, d\xi = \langle X(u_t, s_t, \xi) \rangle. \quad (\text{EQ 3.4}) \]

This provides a powerful alternative, the stochastic simulation techniques, to resolve the problem. Instead of solving the diffusion equation (2.75), the SDEs (3.1)-(3.3) are numerically integrated to yield an ensemble of trajectories from which one can evaluate averages. In principle, one can also obtain information about the distribution by dividing the configuration space into cells and counting the number of trajectories which assume values in each cell. However, in a high-dimensional configuration space, for any reasonable approximation to the distribution function the number of cells would be so large that most cells would be unoccupied, hence the full distribution cannot be determined efficiently by this way.

One should note that Eqs. (3.1)-(3.3) are independent from each other. Nevertheless, there exists couplings between the processes \( u_t, s_t \) and \( \xi_t \) resulting from the boundary conditions (2.81) and (2.82) and the creation/annihilation term in the diffusion equation (2.75), which need to be discussed for obtaining a full equivalence between diffusion equations and SDEs. Whenever \( s_t \) reaches the boundaries 0 or 1, \( u_t \) and \( \xi_t \) must be replaced by a random unit vector and a random number within \([0,1]\), respectively.
Whenever $\xi_\gamma$ reaches the boundaries 0 or 1, $u_\gamma$ and $s_\gamma$ must also be replaced by a random unit vector and a random number within $[0,1]$, respectively. Actually, there is a non-zero drift through the boundaries of $s_\gamma$ which is exactly compensated by the creation/destruction term in the diffusion equation. Therefore, and in view of Eq. (2.80), the configurations diffusing through the boundaries are reflected back into the range of allowed $s$ and $\xi$ values.

For the single-label model, we can establish a similar stochastic interpretation of the model. Correspondingly, the Itô SDE for the stochastic processes $u_\gamma$ [Eq. (3.1)] is replaced by

$$
\frac{du_\gamma}{dt} = \left(1 - \frac{u_\gamma u_\gamma}{|u_\gamma|^2}\right) \cdot \kappa \cdot u_\gamma - 2D_a u_\gamma \right) dt + \sqrt{2D_a \left(1 - \frac{u_\gamma u_\gamma}{|u_\gamma|^2}\right)} \cdot dW_t
$$

where the three components of the vector $W_t$ are independent Wiener processes. The SDE for $s_\gamma$ is also given by Eq. (3.2), and the SDE for $\xi_\gamma$ is no more present. In the next section, we will design numerical schemes to simulate the SDEs together with the boundary conditions and the creation/destruction term.

### 3.2 Numerical schemes

In a stochastic simulation, the expectation $\langle \ldots \rangle$ in Eq. (3.4) is calculated as an ensemble average from a number of realizations, $\{u'_\gamma, s'_\gamma, \xi'_\gamma\}$, of the stochastic processes $u_\gamma$, $s_\gamma$ and $\xi_\gamma$, namely,

$$
\langle X(u_\gamma, s_\gamma, \xi_\gamma) \rangle = \frac{1}{N_{\text{sample}}} \sum_{i=1}^{N_{\text{sample}}} X(u'_\gamma, s'_\gamma, \xi'_\gamma),
$$

where $N_{\text{sample}}$ is the number of realizations or trajectories. These realizations are propagated as follows. First, the drift in Eq. (3.2) is treated by a deterministic method. Given an $s_\gamma$ value at time $t$, the intermediate value after this treatment is
\[ s_i' = s_i + \dot{s}_{\text{tot}}(t) \Delta t. \]  

(EQ 3.7)

If there is a net flux of configurations out of the interval \([0,1]\) \(\lambda_{\text{dissip}}(t) < 0\), the lost configurations \(s_i' \notin [0, 1]\) are randomly replaced by existing ensemble members; if there is a net flux of configurations into the interval \([0,1]\) \(\lambda_{\text{dissip}}(t) > 0\), the \(s\) values of the gained configurations are set in equal distance from the two outerest positions of \(\{s_i'\}\) to the corresponding chain ends, meanwhile the \(u\) vectors are randomly oriented and the \(\xi\) values are randomly selected from \([0,1]\) (only for the double-label model) according to the boundary conditions. The number of the gained configurations, \(\lambda_{\text{destruction}}\), is equal to the integer part of \(\lambda_{\text{simple}}\lambda_{\text{dissip}}\Delta t/\lambda\). In order to keep the ensemble size constant in the latter case, \(\lambda_{\text{destruction}}\) configurations are randomly selected from the existing ensemble members between the two outerest positions and discarded. This first step takes care of both the drift in Eq. (3.2) and the creation/destruction term in the diffusion equation. In the next step, we construct the new configurations at time \(t + \Delta t\) as follows:

\[ s_i^{\text{new}} = s_i' + \frac{1}{\sqrt{4 \pi \Delta t}} e^{-\frac{(s_i')^2}{4\Delta t}}, \]  

(EQ 3.8)

\[ \xi_i^{\text{new}} = \xi_i + \sqrt{2D_\xi} \Delta W_i^\xi, \]  

(EQ 3.9)

\[ u_i' = u_i + \mathbf{K} \cdot u_i \Delta t + \sqrt{2D_u} \Delta W_i^u, \]  

(EQ 3.10)

\[ \mathbf{u}_i^{\text{new}} = \frac{u_i'}{|u_i'|}, \]  

(EQ 3.11)

where \(\Delta W_i^\gamma, \Delta W_i^\xi\) and the three components of the vector \(\Delta W_i^\gamma\) are independent random numbers with mean zero and variance \(\Delta t\), Eq. (3.9) should be eliminated for the single-label model, and the noise term in Eq. (3.10) should vanish for the double-label model. If \(s_i^{\text{new}}\) leaves the interval \([0,1]\), it will be reflected back into it. Upon any reflection, a new random unit vector \(\mathbf{u}_i^{\text{new}}\) and a new uniform random number \(\xi_i^{\text{new}}\) (only for the double-
3.2 Numerical schemes

label model) are chosen according to the boundary condition (2.81). For the double-label model, if $\xi^{\text{new}}$ leaves the interval $[0,1]$, it will also be reflected back into it. Upon any reflection, a new random unit vector $u^{\text{new}}_i$ and a new uniform random number $s^{\text{new}}_i$ are chosen according to the boundary condition (2.82). For both single-label and double-label model, the chain-contour-length stretching ratio $\lambda$ at time $t + \Delta t$ is obtained as

$$\lambda^{\text{new}} = \lambda + \left[ \dot{\lambda}_{\text{convect}}(t) + \dot{\lambda}_{\text{dissip}}(t) \right] \Delta t.$$  \hspace{1cm} \text{(EQ 3.12)}

Now, let’s check the convergence of the numerical scheme suggested above. It is known that the Euler scheme [Eq. (3.12)] for the deterministic differential equation (2.71) of chain stretching converges with order $\Delta t$. For the stochastic differential equation (3.5) of chain orientation, the weak convergence of the scheme [Eqs. (3.10) and (3.11)] is at least of order $\Delta t$. This can be shown as follows. To first order in $\Delta t$, one recovers the Euler scheme for the SDE (3.5) after expanding the denominator in (3.11) to second-order of

$$\Delta u_i = \kappa \cdot u_i \Delta t + \sqrt{2D_u} \Delta W_i.$$  \hspace{1cm} \text{(EQ 3.13)}

and using the multiplication table for reducing products of stochastic differentials given in Table 3.1 of Ref. [Öttinger (1996)]. Under suitable smoothness and growth conditions on the drift and diffusion coefficients, the first-order weak convergence can be rigorously established for the Euler scheme (see Theorem 14.5.1 of Ref. [Kloeden and Platen (1992)]). Hence the scheme [Eqs. (3.10) and (3.11)] is at least of order $\Delta t$ in weak convergence.

Finally, the convergence of the scheme [Eqs. (3.7) and (3.8)] for the $s$ dynamics described by the SDE (3.2) has to be checked. Although the scheme is a straightforward Euler discretization of the corresponding SDE, its convergence is of order $\sqrt{\Delta t}$. This is due to unobserved reflections at the boundaries [Strittmatter (1988)] which states that even if both $s^{\prime}_i$ and $s^{\text{new}}_i$ lie in the interval $[0,1]$, there is a certain non-zero probability that the process $s_i$ left the interval $[0,1]$ during the time step $\Delta t$. The probability for such
unobserved reflections is of order $\sqrt{\Delta t}$. Hence, the situation can occur that reflections that should trigger the process $u_i$ to start with a new random unit vector go unnoticed in a simulation with discrete time step. In order to obtain a higher-order ($\Delta t$) algorithm, we adopt the improved scheme [Öttinger (1989)] in which the effect of unobserved reflections is taken into account by choosing a new random unit vector $u_i^{\text{new}}$ with a certain probability $P_u$ even when no reflection at a boundary has been observed in the time step. The conditional probability $P_u$ for an unobserved reflection at $b = 0$ or $b = 1$ for given values of $s'_i$ and $s_i^{\text{new}}$ related by Eq. (3.8) is

$$P_u = \exp \left\{ -\pi^2 \frac{\tau_d}{\Delta t} (b - s'_i)(b - s_i^{\text{new}}) \right\}. \quad \text{(EQ 3.14)}$$

Obviously, this probability is exponentially small and hence completely negligible, except when the distance between the boundary $b$ and $s'_i$ is at most of order $\sqrt{\Delta t}$; for that reason, one needs to consider only one boundary in each small time step. The above treatment is also applied to the $\xi$ dynamics.

### 3.3 Simulation procedures

In order to calculate the statistical error of the results, we perform the same simulation procedure for a number of independent blocks ($N_{\text{block}}$). For each block, the algorithm for the double-label model is simulated in the following steps.

1. First, we make the time dimensionless by the characteristic time (reptation time) $\tau_d$. We start the simulation from the equilibrium state. So, for $i = 1, \ldots, N_{\text{sample}}$, $s_i$ and $\xi_i$ are chosen as random numbers from the interval $[0,1]$ according to the uniform distribution, $u_i$ is chosen as a random unit vector according to the uniform distribution, and $\lambda$ is set equal to 1.

2. During each time step, the new ratio of the chain contour length, $\lambda^{\text{new}}$, is first calculated according to Eq. (3.12).
(3) After step 2, Eq. (3.7) is solved to find the intermediate value \( s_i' \) for \( s_i \). Then the creation/destruction effect is simulated by the way described in Sec. 3.2.

(4) A new orientation vector \( \mathbf{u}_i^{\text{new}} \) is calculated according to Eqs. (10) and (11) for \( i = 1, \ldots, N_{\text{sample}} \).

(5) \( N_{\text{sample}} \) Gaussian random numbers that satisfy the distribution of \( \Delta W_i^a \) are created, and the equation (3.8) is solved to obtain \( s_i^{\text{new}} \) for \( i = 1, \ldots, N_{\text{sample}} \). If \( s_i^{\text{new}} \) leaves the interval \([0,1]\), it will be reflected back into it, that is, \( s_i^{\text{new}} \rightarrow -s_i^{\text{new}} \) for \( s_i^{\text{new}} < 0 \), and \( s_i^{\text{new}} \rightarrow 2 - s_i^{\text{new}} \) for \( s_i^{\text{new}} > 1 \). If \( s_i^{\text{new}} \) is in the interval \([0,1]\), then check whether there was an unobserved reflection according to the conditional probability \( P_u \). Upon any reflection, a new random unit vector \( \mathbf{u}_i^{\text{new}} \) and a new random number \( \xi_i \) are chosen.

(6) Solve the equation (3.9) to obtain \( \xi_i^{\text{new}} \) by the way similar to that in step 5. The reflect boundary condition is treated as in step 5. Upon any reflection, a new random unit vector \( \mathbf{u}_i^{\text{new}} \) and a new random number \( s_i^{\text{new}} \) are chosen.

(7) Calculate the stress tensor at present time

\[
\mathbf{\tau}^{\text{new}} = \mathbf{\tau}_1^{\text{new}} + \mathbf{\tau}_2^{\text{new}} \tag{EQ 3.15}
\]

\[
\mathbf{\tau}_1^{\text{new}} = 5G_N^0 \langle \mathbf{u} \mathbf{u}^{\text{new}} \rangle \tag{EQ 3.16}
\]

\[
\mathbf{\tau}_2^{\text{new}} = 5G_N^0 \frac{c(\lambda^{\text{new}})\lambda^{\text{new}}(\lambda^{\text{new}} - 1)}{3Z} \langle \mathbf{u} \mathbf{u}^{\text{new}} \rangle \tag{EQ 3.17}
\]

(8) Repeat the steps 2-7 until the specified number of time steps is reached.

A simulation procedure for the single-label model can be constructed by modifying the above procedure accordingly, i.e. eliminating the operations associated with the position label \( \xi \) and adding noise term to the orientation equation in step 4. For the results presented in the next chapter, we choose \( N_{\text{sample}} = 10^5 \) per block, \( N_{\text{block}} = 10 \), and the time step size such that the strain is a maximum of 0.02 per time step and the maximum of the time step is 0.01 for small deformation rates. In each block, transient values of the stresses are obtained in step 7 by ensemble average, and steady values of the stresses are
obtained by average over time after reaching steady state in addition to ensemble average at each time step. The relative statistical errors of the simulation data are within ±2%, except for those with very small absolute values (smaller than 10^{-3}) at the very beginning of the start-up of steady flows. There is no detectable difference in the results by increasing ensemble size or decreasing time step size.
Chapter 4
Model predictions

In this chapter, linear viscoelastic properties of the two thermodynamically consistent reptation models developed in Chapter 2 are discussed at first. Then numerical predictions of nonlinear properties are presented for single-step strain, double-step strain, shear and extensional flows. Comparisons with experimental data and two alternative molecular-based models are given in detail finally.

4.1 Linear viscoelasticity

Following the tradition of Doi (1980b), the models developed in Chapter 2 can be transformed into integral forms, based on which the linear viscoelastic properties can be obtained analytically. We first treat the double-label model. The procedure used in this section is a straightforward generalization of the methods used by Doi (1980b).

As is shown in Appendix, the diffusion equation (2.75) can be rewritten in the integral form

\[ f(u, s, \xi, t) = \int_{-\infty}^{\infty} \frac{\partial K(t, t', s, \xi)}{\partial t'} g(u, t, t') dt' \]  \hspace{1cm} (EQ 4.1)

where the orientation distribution function \( g(u, t, t') \) is a solution of the differential equation

\[ \frac{\partial g}{\partial t} = -\frac{\partial}{\partial u} \left[ \left( 1 - \frac{uu}{|u|^2} \right) \cdot \mathbf{k} \cdot ug \right] \] \hspace{1cm} (EQ 4.2)
Chapter 4 Model predictions

under the initial condition

\[ g(u, t', t') = \frac{1}{4\pi} \delta(|u| - 1). \]  

(EQ 4.3)

The integral kernel \( K(t, t', s, \xi) \) in Eq. (4.1) is a solution of the differential equation

\[
\frac{\partial K}{\partial t'} = -\frac{\partial}{\partial S}(\dot{S}_{\text{tot}} K) - \gamma_1 \dot{\lambda}_{\text{dissip}} K + \frac{1}{\pi \tau_\sigma} \frac{\partial^2 K}{\partial S^2} + D_\xi \frac{\partial^2 K}{\partial \xi^2}
\]  

(EQ 4.4)

with the initial condition

\[ K(t', t', s, \xi) = 1 \]  

(EQ 4.5)

and with the absorbing boundary conditions

\[ K(t, t', s, \xi)|_{S = 0} = K(t, t', s, \xi)|_{\xi = 0} = 0. \]  

(EQ 4.6)

Physically, \( K \) is the probability that a tube segment at time \( t \) is in a configuration with labels \( s \) and \( \xi \), and was created before \( t' \). From the above equations, one obtains

\[
\int X(u) f(u, s, \xi, t) d^3u = \int_{-\infty}^{\infty} \frac{\partial K(t, t', s, \xi)}{\partial t'} \langle X(u) \rangle_t dt'
\]

\[
= \langle X(u) \rangle_t - \int_{-\infty}^{\infty} K(t, t', s, \xi) \frac{\partial \langle X(u) \rangle_t}{\partial t'} dt'
\]  

(EQ 4.7)

where \( \langle X(u) \rangle_t \) indicates an expectation evaluated with the solution of Eq. (3.1) and the initial condition that \( u_t \) is given by a random unit vector.

In order to calculate the linear viscoelastic properties of the double-label model such as the dynamic viscosities, shear relaxation modulus, and viscometric functions at zero shear rate, it is sufficient to determine the probability \( K \) from Eq. (4.4) in the absence of flow, that is, for \( \lambda_c = 1 \) and \( \dot{\lambda}_{\text{tot}} = \dot{\lambda}_{\text{convect}} = \dot{\lambda}_{\text{dissip}} = 0 \). The leading-order predictions
result from the \( uu \) average in the stress tensor contribution given by Eq. (2.58). Under this consideration, we obtain from Eq. (4.7)

\[
\tau(t) = 3Zn_k T \left\{ \frac{1}{3} - \int_{-\infty}^{\infty} p(t, t') \frac{\partial \langle uu \rangle}{\partial t'} dt' \right\}, \tag{EQ 4.8}
\]

where \( p(t, t') = \int_0^t \int_{-\infty}^{\infty} K(t, t', s, \xi) ds d\xi \) and the probability \( K \) is now determined by the diffusion equation

\[
\frac{\partial K(t, t', s, \xi)}{\partial t} = \frac{1}{\pi^2 \tau_d} \frac{\partial^2 K(t, t', s, \xi)}{\partial s^2} + \frac{1}{\pi^2 \tau_d} \frac{\partial^2 K(t, t', s, \xi)}{\partial \xi^2}, \tag{EQ 4.9}
\]

with the initial condition Eq. (4.5) and the absorbing boundary conditions Eq. (4.6).

By following the same procedure as above, we obtain Eq. (4.8) also for the single-label model, where \( p(t, t') = \int_0^t K(t, t', s) ds \) and \( \langle uu \rangle \) indicates an expectation evaluated with the solution of Eq. (3.5) and the initial condition that \( u_{t'} \) is given by a random unit vector. The probability \( K \) here is determined by the diffusion equation

\[
\frac{\partial K(t, t', s)}{\partial t} = \frac{1}{\pi^2 \tau_d} \frac{\partial^2 K(t, t', s)}{\partial s^2}, \tag{EQ 4.10}
\]

with the initial condition \( K(t', t', s)|_{s=0,1} = 1 \) and the absorbing boundary conditions \( K(t', t', s)|_{s=0,1} = 0 \). The corresponding solution \( K(t, t', s) \) is well known [see Eq. (6.14) of Doi and Edwards (1986)]. After integrating the solution over \( s \), we have

\[
p(t, t') = p_{DE}(t-t') = \frac{8}{\pi^2} \sum_{n>0} \frac{1}{(2n+1)^2} \exp[-(2n+1)^2(t-t')/\tau_d], \tag{EQ 4.11}
\]

for the single-label model. It can be verified that \( K(t, t', s, \xi) = K(t, t', s)K(t, t', \xi) \) is the solution of the diffusion equation (4.9) with the initial condition (4.5) and the bound-
ary conditions (4.6). Therefore we obtain \( p(t, t') \) for the double-label model after integrating the solution over \( s \) and \( \xi \), that is

\[
p(t, t') = p_{DE}^2(t-t'). \tag{EQ 4.12}
\]

In order to obtain the linear viscoelastic properties by means of Eq. (4.8), one then still needs to construct a perturbation solution of Eq. (3.5) for small \( K \), from which the linear viscoelastic limit of the second moment \( \langle u,u \rangle_r \) can be found [see Sec. 14.5 of Bird et al. (1987)]. The results are

\[
\langle u,u \rangle_r = \frac{1}{3} + \frac{1}{5} \int_{t'}^t \gamma(t'') \exp[-(t-t'')/\tau_s] \, dt'' \tag{EQ 4.13}
\]

for the single-label model and

\[
\langle u,u \rangle_r = \frac{1}{3} + \frac{1}{5} \int_{t'}^t \gamma(t') \, dt' \tag{EQ 4.14}
\]

for the double-label model, where \( \gamma \) is the rate-of-strain tensor. Now, we can substitute these two expressions into the equation (4.8) to obtain the relaxation modulus

\[
G(t) = \frac{3}{5} Z n_p k_b T p_{DE}(t) \exp[-t/\tau_s] \tag{EQ 4.15}
\]

for the single-label model and

\[
G(t) = \frac{3}{5} Z n_p k_b T p_{DE}^5(t) \tag{EQ 4.16}
\]

for the double-label model. The plateau modulus \( G_N^{(d)} \) is hence the same for both models and is given by
4.2 Single-step strain

\[
G^0_\infty = G(0) = \frac{3}{2}Zn_pk_BT. \tag{Eq. 4.17}
\]

From the equation (4.16), we see that the double-label model exactly recovers the “double reptation” idea for the calculation of the relaxation modulus [see Eq. (6) of des Cloizeaux (1988)]. Therefore, the linear properties obtained from the double-label model are more realistic than the single-label model and Doi-Edwards predictions. However, both single-label and double-label models do not take into account the relaxation mechanism due to chain-length fluctuations, hence we cannot expect good quantitative predictions of linear properties of real entangled polymers. In the following sections, we focus entirely on the basic nonlinear behavior.

4.2 Single-step strain

For a single-step strain experiment, a step strain is assumed to be imposed instantaneously at time \( t = 0 \). The rheological quantity of interest is the stress relaxation following the step strain. The relaxation of shear stress, \( \tau_{xy} \), is described by the nonlinear relaxation modulus, \( G(t, \gamma) \), defined as

\[
G(t, \gamma) = \frac{\tau_{xy}}{\gamma}, \tag{Eq. 4.18}
\]

where \( \gamma \) is the magnitude of the imposed step strain. For most polymeric fluids, the nonlinear relaxation modulus is found to show separability into time- and strain-dependent parts over a wide range of strains:

\[
G(t, \gamma) = G(t)h(\gamma), \tag{Eq. 4.19}
\]

where \( h(\gamma) \) is the “damping function” representing the nonlinear part of the stress relaxation.
Results just after a single-step strain can be obtained analytically. However, we here perform the calculation numerically for the purpose of making a universal simulation code for both single-step and double-step strain experiments. In the numerical treatment of the step strain, the total shear step is divided into a number of small shear or time steps. For the results presented below, we use 100 time steps with $\Delta t = 10^{-5}$ and $\dot{\gamma} = \gamma/(100\Delta t)$ to mimic the step strain. There is no significant difference in the results by decreasing the time step length or increasing the number of small shear steps. In Fig. 4.1, we plot $G(t, \gamma)/G_N^0$ as functions of time predicted by the double-label model for several different magnitudes of strains. Not shown are the predictions by the single-label model which look very similar. We find that the shear stress relaxation exhibits two distinct regimes at early and long times for large strains. In these cases, the initial stress decay corresponds mostly to the chain retraction, and the decay at long times is mainly due to reptation of probe and surrounding chains. The results in Fig. 4.1 are qualitatively in agreement with the experimental data reported by Venerus and Kahvand (1994). The individual effect of chain retraction and reptation on stress relaxation is clear if one looks at the curve of $G(t, \gamma)/G_N^0$ divided by the damping function $h(\gamma)$ as shown in Fig. 4.2 using the same set of data as in Fig. 4.1. It reveals that the separability is observed after a certain time, $t/\tau_d = 0.2$, which is roughly four times the retraction time $\tau_r$. A curve similar to Fig. 4.2 has also been obtained from the full-chain simulations by Hua and Schieber (1998a).
4.2 Single-step strain

FIG. 4.1. Shear stress relaxation as functions of dimensionless time predicted by the double-label model for several different magnitude of strains: \( \gamma = 0.5, 1, 2, 4 \) and 8. The parameter values used are \( Z = 7 \), \( \lambda_{\text{max}} = 21 \), and \( \delta_1 = \delta_2 = 1/\kappa^2 \).

FIG. 4.2. Shear stress relaxation divided by the damping function as functions of dimensionless time using the same set of simulation data as in Fig. 4.1. The parameter values used are the same as for Fig. 4.1.
4.3 Double-step strain

For a double-step strain experiment, a strain of $\gamma_1$ is imposed at time $t = 0$, followed by a strain of $\gamma_2$ after a waiting time $t_w$. The second step strain considered here is in a direction opposite to the first ($\gamma_2 < 0$). The simulation results of the shear stress relaxation following the double-step strain are presented in Fig. 4.3 and 4.4 for the single-label and double-label model, respectively. The magnitude of the two strains chosen here are $\gamma_1 = 4$ and $\gamma_2 = -2$. We find that the double-label model predicts sign changes and smooth overshoots over a certain range of values of $t_w$, which is in a manner similar to that observed experimentally [see Fig. 8 of Venerus and Kahvand (1994)], while the single-label model does not predict such behaviors. For a further analysis of the results, we introduce the critical waiting time, $t_w$, at which the shear stress following the second step strain starts to change sign, and the half linear relaxation time, $t_h$, at which $G(t_h) = G(0)/2$ in linear viscoelasticity. For the double-label model, we obtain $t_w = 0.1 \tau_d$, which is close to $t_h = 0.15 \tau_d$ obtained from Eq. (4.16). For the single-label model, we have $t_w = 0.04 \tau_d$, which is much smaller than $t_h = 0.25 \tau_d$ obtained from Eq. (4.15), while the same type of double-step strain experiment by Venerus and Kahvand (1994) shows $t_w = t_h$. The differences between the two model predictions is due to the different implementations of the relaxation mechanisms (DR and CCR). To reveal how the different implementations make the differences on $t_w$, we study two corresponding simple models, the original DE model and the rigid dumbbell model. During the waiting time period, the orientation of $\mathbf{u}$ in the former either stays as it was just after the first step strain or is randomly chosen when $s$ reaches the chain ends, while in the latter it is no more the case because the orientation is relaxed through the stochastic force. It is then clear that for the former $t_w = t_h$, because at the time $t_h$ ($p_{DE}(t_h) = 0.5$), half of the orientations are in the state corresponding to the first step strain (+4) and half of them are in equilibrium, after the second step strain (-2), the two parts will be in the states corresponding to the step strains +2 and -2, respectively, so totally the stress is zero. For the latter, the simulation results show that at the time $t_h$ ($\exp(-t_h/\tau_d) = 0.5$), the stress is relaxed to a value around half of the value just after the first step strain (+4), but after the
second step strain (-2), the stress becomes negative instead of zero, and $t_w$ is shifted to a value around 0.32 $t_d$. We can conclude that the double-label model is preferable in describing the double-step strain experiments. However, good quantitative predictions can be only achieved by taking into account the real relaxation modulus.

**FIG. 4.3.** Shear stress relaxation following double-step strain with $\gamma_1 = 4$ and $\gamma_2 = -2$ for several different values of $t_i$ predicted by the double-label model. The curves from up to down correspond to $t_i/t_d = 0.05, 0.1, 0.2, 0.4$, and 0.8. The parameter values used are the same as for Fig. 4.1.
FIG. 4.3. Shear stress relaxation following double-step strain with $\gamma_1 = 4$ and $\gamma_2 = -2$ for several different values of $t_1$ predicted by the single-label model. The curves from up to down correspond to $t_1/\tau_d = 0.02, 0.03, 0.04, 0.05, 0.1, 0.2, \text{and } 0.4$. The parameter values used are the same as for Fig. 4.1.

4.4 Shear flows

Shear flows are important in many polymer processing operations, for example, in injection molding and extrusion. Shear flows in the nonlinear regime are among the flow fields where the Doi-Edwards (DE) model is least successful. The major failures of the DE model in describing experimental observations in shear flows are listed in Chapter 1. The essential feature of shear flows is that it is possible to identify a one-parameter family of material surfaces that slide relative to one another without stretching. A homogeneous simple shear flow, for which these material surfaces are planes, is given by a velocity field

$$v_x = \dot{\gamma} y, \quad v_y = 0, \quad v_z = 0,$$

(EQ 4.20)
4.4 Shear flows

where the shear rate $\dot{\gamma}$ can be a function of time. For this flow, the transposed velocity gradient tensor $\mathbf{K}$ is

$$
\mathbf{K} = \begin{bmatrix}
0 & \dot{\gamma}(t) & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix} \tag{EQ 4.21}
$$

For steady shear flow the shear rate is independent of time. For this type of flow, the stress tensor can be fully characterized by three material functions depending only on the shear rate, they are viscosity,

$$
\eta(\dot{\gamma}) = \frac{\tau_{xy}(\dot{\gamma})}{\dot{\gamma}}, \tag{EQ 4.22}
$$

first-normal-stress coefficient,

$$
\Psi_1(\dot{\gamma}) = \frac{[\tau_{xx}(\dot{\gamma}) - \tau_{yy}(\dot{\gamma})]/\dot{\gamma}^2}{\dot{\gamma}}, \tag{EQ 4.23}
$$

and second-normal-stress coefficient,

$$
\Psi_2(\dot{\gamma}) = \frac{[\tau_{yy}(\dot{\gamma}) - \tau_{zz}(\dot{\gamma})]/\dot{\gamma}^2}{\dot{\gamma}}. \tag{EQ 4.24}
$$

An example of a time-dependent shear flow is the start-up of steady shear flow in which the fluid is at rest for $t<0$ and in a state of flow described by (4.20) for $t>0$. Then, for $t>0$, the stress growth coefficients $\eta^+$, $\Psi_1^+$, and $\Psi_2^+$ depending on time and shear rate are defined by

$$
\eta^+(t, \dot{\gamma}) = \frac{\tau_{xy}(t, \dot{\gamma})}{\dot{\gamma}}, \tag{EQ 4.25}
$$

$$
\Psi_1^+(t, \dot{\gamma}) = \frac{[\tau_{xx}(t, \dot{\gamma}) - \tau_{yy}(t, \dot{\gamma})]/\dot{\gamma}^2}{\dot{\gamma}}, \tag{EQ 4.26}
$$

$$
\Psi_2^+(t, \dot{\gamma}) = \frac{[\tau_{yy}(t, \dot{\gamma}) - \tau_{zz}(t, \dot{\gamma})]/\dot{\gamma}^2}{\dot{\gamma}}.
$$
\[ \Psi^2(t, \dot{\gamma}) = \frac{\tau_{yy}(t, \dot{\gamma}) - \tau_{zz}(t, \dot{\gamma})}{\dot{\gamma}^2}. \quad (\text{EQ 4.27}) \]

The reverse experiment is cessation of a steady shear flow at time \( t = 0 \). For \( t > 0 \) the stress decay coefficients \( \eta^-, \Psi^1, \) and \( \Psi^2 \) are again defined by

\[ \eta^-(t, \dot{\gamma}) = \frac{\tau_{xy}(t, \dot{\gamma})}{\dot{\gamma}}, \quad (\text{EQ 4.28}) \]

\[ \Psi^1(t, \dot{\gamma}) = \frac{\tau_{xx}(t, \dot{\gamma}) - \tau_{yy}(t, \dot{\gamma})}{\dot{\gamma}^2}, \quad (\text{EQ 4.29}) \]

\[ \Psi^2(t, \dot{\gamma}) = \frac{\tau_{yy}(t, \dot{\gamma}) - \tau_{zz}(t, \dot{\gamma})}{\dot{\gamma}^2}. \quad (\text{EQ 4.30}) \]

Numerical predictions of these material functions in shear flows for the two models developed in Chapter 2 by using the simulation algorithm implemented in Chapter 3 are presented in the following subsections. The results given here for all type of shear flows are not sensitive to the finite extensibility parameter \( \lambda_{\text{max}} \). In most cases, the predictions by the two models are similar, hence we only discuss the double-label model, unless there are significant differences between the two models. The parameter values \( Z = 7, \lambda_{\text{max}} = 21, \) and \( \delta_1 = \delta_2 = 1/\lambda^2 \) are used for most of the cases, otherwise to be mentioned.

**A. Start-up of steady shear flow**

Fig. 4.5 shows the growth of the dimensionless shear viscosity for several dimensionless shear rates predicted by the double-label model. The linear viscoelastic limit forms an upper envelope for all the shear rates, and the transient overshoots occur at medium and high shear rates. The growth of the dimensionless first-normal-stress coefficient and second-normal-stress coefficient predicted by the double-label model with the same parameters are plotted in Fig. 4.6 and 4.7, respectively. The overshoot in \( \Psi^1 \) occurs at a higher shear rate than the viscosity \( \eta^+ \) does, while the overshoot in \( -\Psi^2 \) occurs at the same shear rate as the viscosity does for the overshoot. The behavior of all these overshoots is qualitatively in agreement with many experimental findings. The results
obtained from the single-label model are qualitatively different from the double-label
model predictions at high shear rates, i.e., the former predicts transient undershoots in
shear stress and narrower overshoots. A comparison illustrating the differences is shown
in Fig. 4.8. These undershoots are also reported by the experimental work [Kahvand
(1995)] and the full-chain simulations [Hua et al. (1999)]. The differences between the
two model predictions concerning the undershoots are due to the different implementa¬
tions of DR and CCR, and they are closely related to the differences to be discussed in
the subsection D.

B. Cessation of steady shear flow

In Fig. 4.9 we plot the relaxation of the shear stress, normalized by the corresponding
steady value, after cessation of steady shear flow. The model parameters are the same as
above. Three cases with the dimensionless steady shear rate $\dot{\gamma} \tau_s = 0.1, 1, \text{and } 10$ are
shown. The stress relaxation rate increases with the increasing previous shear rate. Later
in the relaxation process, at $t \gg \tau_s$, the relaxation rate is governed only by the reptation
process and constraint release due to double reptation. This behavior is in accordance
with the experimental results [Attané et al. (1985); Kahvand (1995); Menezes and
Graessley (1982)].

C. Steady shear flow

In Fig. 4.10a-c, we plot the steady-state values of the shear stress $\tau_{xy}$ and the first-
normal-stress difference $N_1 = \tau_{xx} - \tau_{yy}$ for $Z = 7, 20,$ and $40$ (corresponding to
$\tau_d/\tau_s = 21, 60, \text{and } 120$). As in the DE model, in each case, there is the expected linear
viscoelastic regime at low shear rate, $\dot{\gamma} \leq 1/\tau_d$, in which $\tau_{xy} \propto \dot{\gamma}$ and $N_1 \propto \dot{\gamma}^2$. However,
the predictions of the double-label model at shear rates in excess of $1/\tau_d$ are very differ¬
ten from $\tau_{xy} \propto \dot{\gamma}^{-0.5}$ predicted by the DE theory. The shear stress increases slightly with
shear rate for $Z = 7$ or is nearly constant for $Z = 20$ and $40$ over a wide range of shear
rates, and the range becomes ever wider as $\tau_d/\tau_s$ increases. When the shear rate exceeds
$10/\tau_s$, there tends to be a second Newtonian regime. From the figure, we also find that
$N_1$ increases more rapidly with shear rate than does $\tau_{xy}$ over the same range of shear rate
and the slope of $N_1$ versus $\dot{\gamma}$ increases as $Z$ decreases. The results in Fig. 4.10a-c are in remarkably good agreement with the experimental results [Bercea et al. (1993); Mead and Larson (1990); Kahvand (1995)]. The predictions of the steady shear stress obtained by the two models are compared in Fig. 4.11 for $Z = 7$. One can see that the single-label model predicts a slight decrease of the shear stress in the range mentioned above and the minimum value is about 10% less than the value at the local maximum near $\dot{\gamma} = 1/\tau_d$.

We compare the viscosity curves for two different numbers of entanglements in Fig. 4.12 using the same set of data as in Fig. 4.10b-c, in order to resolve the effect of molecular weight on viscosity. As a basis for comparison, we assume that the reptation time scales like $\tau_d \propto M^3$. It turns out that the steady-state viscosity of two different molecular weights coincides in the power-law region, in agreement with the behaviour observed in experiments [Stratton (1966)] and, e.g., molecular dynamics simulations [Kröger et al. (1993)].

We examine the behavior of the steady-state shear stress and its dependence on the choice of our model parameters in more detail in order to understand how to avoid the prediction of an instability region as mentioned in Chapter 1. From Fig. 4.13, we see that the inclusion of chain stretching alone yields the onset of an upturn of the shear stress at high shear rates, but the prediction of the power-law index is worse (this is due to avoiding IAA by drift and creation terms leads to less segment orientation when chain tends to be stretched at intermediate shear rates). When double reptation is considered, the situation is improved. After CCR is added, the maximum in the steady-state shear stress disappears and the model predicts a slight increasing of shear stress over a wide range of shear rates, which is also observed in the experiments of entangled polymer solutions [Mead and Larson (1990); Kahvand (1995)]. We thus confirm the previous conclusion that the CCR effect is critical for predicting the right shape of the shear stress curve.

D. Transient extinction angle

The extinction angle $\chi$ is given by $(1/2) \arctan(2 \tau_{xy}/N_1)$. In Fig. 4.14 we show the transient extinction angle predicted by the two models in the start-up of shear flow.
followed by a stepdown in shear rate. For the single-label model, the extinction angle shows a pronounced undershoot at the start-up of flow with the first shear rate and an immediate very small undershoot at the inception of the lower shear rate before reaching a higher steady-state value, while the double-label model predicts nonoccurrence of the first undershoot but a pronounced second undershoot. In Fig. 4.15 we plot the transient extinction angle for the reverse case (steady state followed by a stepup in shear rate). It shows that the double-label model predicts a pronounced overshoot just after the stepup, while the single-label model predicts a very small one. Pronounced over- and undershoots just after the step-change and less pronounced undershoots at the start-up are reported by experiments [see Fig. 2 of Mead et al. (1998)] and the full-chain simulations [see Fig. 11 of Hua et al. (1999)]. The differences between the two model predictions are again due to the different implementations of DR and CCR. For the single-label model, the occurrence of the first undershoot is a consequence of its nontrivial prediction of the transient noise [see Fig. 4.16] and the delicate competition between the increase and decrease effects on the extinction angle caused respectively by the noise and the flow. The same picture with the role of the noise replaced by the double diffusion [see Fig. 4.16] exists for the double-label model. Hence the nonexistence of the undershoot for the double-label model may be due to the fact that the change of the noise has an immediate impact on the orientation, while the change of the double diffusion coefficient has a gradual impact on the orientation because of the indirect action through the boundary conditions.
FIG. 4.5. Dimensionless shear viscosity as function of dimensionless time after start-up of steady shear flow for several different dimensionless shear rates predicted by the double-label model. The curves from up to down correspond to $\gamma \tau_d = 0.6, 1.5, 6, 15, 60, 150,$ and $600$.

FIG. 4.6. Dimensionless first-normal-stress coefficient as function of dimensionless time after start-up of steady shear flow for several different dimensionless shear rates predicted by the double-label model. The curves from up to down correspond to the shear rates as for Fig. 4.5.
4.4 Shear flows

FIG. 4.7. Dimensionless \((-\Psi_2^2)\) as function of dimensionless time after start-up of steady shear flow for several different dimensionless shear rates predicted by the double-label model. The curves from up to down correspond to \(\gamma^d = 1.5, 6, 15, 60, 150,\) and 600.

FIG. 4.8. Dimensionless shear stress as function of dimensionless time after start-up of steady shear flow for \(\gamma^d = 150\) predicted by the single-label model and the double-label model.
FIG. 4.9. Relaxation of the shear stress reduced by its value at steady state as a function of dimensionless time, after cessation of steady shear flow for three dimensionless shear rates predicted by the double-label model. The shear rate is labeled nearby the corresponding curve.

FIG. 4.10. Steady-state values of the dimensionless shear stress and first-normal-stress difference as functions of dimensionless shear rate predicted by the double-label model for $Z = 7, 20, \text{ and } 40$. The other parameter values are set to $\delta_1 = \delta_2 = 1/\lambda^2$ and $\lambda_{\text{max}} = 10$. 
FIG. 4.11. Steady-state values of the dimensionless shear stress and first-normal-stress difference as functions of dimensionless shear rate predicted by the single-label model and the double-label model for $Z = 7$, $S_1 = S_2 = 1/\kappa^2$, and $\lambda_{\text{max}} = 21$.

FIG. 4.12. Steady-state shear viscosity versus shear rate for $Z = 20$ and $Z = 40$ using the same set of data as in Fig. 4.10b-c. The curves are scaled using the assumption that $\tau_d \propto Z^\gamma$. 
FIG. 4.13. Steady-state values of the dimensionless shear stress as functions of dimensionless shear rate predicted by the DE model, the double-label model without constraint release effects ($\delta_1 = 0$, $\delta_2 = 0$), the double-label model with DR effect ($\delta_1 = 1/\lambda^2$, $\delta_2 = 0$), the double-label model with DR and CCR effects ($\delta_1 = \delta_2 = 1/\lambda^2$). The other parameters of the double-label model are set to $Z = 7$ and $\lambda_{\text{max}} = 21$.

FIG. 4.14. Time-dependent extinction angle as a function of dimensionless time after start-up of steady shear flow and attainment of steady state followed by a stepdown in dimensionless shear rate predicted by the single-label model and the double-label model.
4.4 Shear flows

**FIG. 4.15.** Time-dependent extinction angle as a function of dimensionless time after start-up of steady shear flow and attainment of steady state followed by a step up in dimensionless shear rate predicted by the single-label model and the double-label model.

**FIG. 4.16.** The orientational diffusion coefficient in the single-label model and the double diffusion coefficient in the double-label model as functions of dimensionless time after start-up of steady shear flow with the shear rate $\dot{\gamma}_d = 150$. 

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4.5 Extensional flows

Rather general extensional flows of incompressible liquids are given by the velocity field

\[ v_x = \dot{\varepsilon} x, \quad v_y = m\dot{\varepsilon} y, \quad v_z = -(1 + m)\dot{\varepsilon} z, \quad (\text{EQ 4.31}) \]

where the largest principal strain rate \( \dot{\varepsilon} \) (\( \dot{\varepsilon} > 0 \)) and the ratio of the second largest and largest principal strain rates \( m \) (\( -1/2 \leq m \leq 1 \)) can be functions of time. Extensional flows are found in many polymer processing operations such as fiber spinning, film blowing, and sheet stretching. The transposed velocity gradient tensor \( \mathbf{K} \) of extensional flows is

\[ \mathbf{K} = \begin{bmatrix} \dot{\varepsilon} & 0 & 0 \\ 0 & m\dot{\varepsilon} & 0 \\ 0 & 0 & -(1 + m)\dot{\varepsilon} \end{bmatrix}. \quad (\text{EQ 4.32}) \]

For extensional flows, one needs only two normal stress differences to characterize the experimentally observable part of the stress tensor completely. For steady extensional flows, the strain rate \( \dot{\varepsilon} \) and the parameter \( m \) are independent of time. The two experimentally accessible normal stress differences can be characterized by the extensional viscosities \( \mu_1 \) and \( \mu_2 \):

\[ \mu_1 = \frac{\tau_{xx} - \tau_{zz}}{2(2 + m)\dot{\varepsilon}}, \quad (\text{EQ 4.33}) \]

\[ \mu_2 = \frac{\tau_{yy} - \tau_{zz}}{2(1 + 2m)\dot{\varepsilon}}. \quad (\text{EQ 4.34}) \]

The above definitions of the extensional viscosities have been chosen such that for a Newtonian liquid \( \mu_1 = \mu_2 = \eta \). In the same way as for simple shear flow one can
investigate time-dependent stress growth and stress decay at start-up and cessation of steady shear-free flows of the form (4.31). The corresponding stress growth and decay coefficients are denoted by $\mu_1^+ (t, \dot{\varepsilon}, m)$ and $\mu_2^+ (t, \dot{\varepsilon}, m)$.

Several special steady or time-dependent extensional flows are obtained for particular choices of the parameter $m$, namely, simple (or uniaxial) extension ($m = -1/2$), equibiaxial extension ($m = 1$), and planar extension ($m = 0$). For equibiaxial extension, the extensional viscosities $\mu_1$ and $\mu_2$ are equal; for simple extension, $\mu_2$ is undefined. For these extensional flows, the rheological properties predicted by the two models are again quite similar in most cases. Therefore in this section only the results obtained by the double-label model and the different results obtained by the single-label model are presented.

We show the steady-state uniaxial extensional viscosity $\mu_1$ as function of extensional rate predicted by the double-label model in Fig. 4.17. One observes four regimes of extension rate: i) a low rate region, $\dot{\varepsilon} < 1/\tau_i$, where the extensional viscosity is a constant equal to one third of the Trouton value; ii) an intermediate region, $1/\tau_i \leq \dot{\varepsilon} \leq 1/\tau_s$, in which the extensional viscosity is extension thinning, scaling as $\dot{\varepsilon}^{-1}$; iii) a high rate region, $\dot{\varepsilon} > 1/\tau_s$, where the extensional viscosity increases with increasing strain rate; and iv) a very high rate region, where the viscosity reaches another constant value due to the finite extensibility of the chain. The same conclusion for the first three regimes has been drawn by Mead et al. (1998). The single-label model predicts an additional region v) between i) and ii), $0.1/\tau_i \leq \dot{\varepsilon} \leq 1/\tau_i$, where the viscosity shows a weak extension hardening induced by orientation and the maximum factor above the first constant region is around 1.05 [see Fig. 4.18]. Regime v) is caused by the constraint releases (DR and CCR) implemented by adding noise on $u$ orientation directly. Accordingly, it is not predicted by the DE theory. Because of the lack of experimental data on monodisperse, linear entangled polymers, these unusual predictions have not yet been fully established. Two of the few works showing a pronounced regime v) were performed by Munstedt and Laun (1981) and Ferguson et al. (1997). The first of these papers stated that two of the four HDPE investigated in their study do not show a maximum of the steady-state elongational viscosity; for the others it is less pronounced than in the case of branched LDPE.
In Fig. 4.19 we plot the transient elongational viscosity as a function of time in the start-up of uniaxial extensional flow. After the extensional rate exceeds $1/\tau_s$, the viscosity shows strain-hardening behavior and finally saturates because of the finite chain stretchability. To study the strain-hardening property of our model in detail, a “strain-hardening parameter” vs. Hencky strain at the extensional rate of 100 is plotted in Fig. 4.20. The strain-hardening parameter is defined as the ratio of the strain rate-dependent nonlinear elongational viscosity to the strain rate-independent linear elongational viscosity at the same time [Koyama and Ishizuka (1983)]. The figure reveals that the first departure from linearity occurs at a Hencky strain value around 0.5, fully in accord with the experimentally observed value by Takahashi et al. (1999). Fig. 4.21 shows the influence of the maximum stretch $\lambda_{\text{max}}$ on the transient uniaxial extensional viscosity. An increase of $\lambda_{\text{max}}$ does not affect the occurrence of strain-hardening, but postpones the saturation and increases the saturation value. Not shown are the predictions of the steady-state and transient viscosity in equibiaxial extension, which have qualitative shapes similar to those seen in the uniaxial extension, except that it is ‘softer’ and less strain-hardening than uniaxial extension [Nishioka et al. (2000)]. Simulations of planar extension of our model are also performed. The steady-state planar viscosity $\mu_1$ (direction of extension) and $\mu_2$ (neutral direction) are plotted in Fig. 4.22. The viscosity $\mu_2$ decays much faster than the $\mu_1$ does in the intermediate region, $1/\tau_d \leq \dot{\varepsilon} \leq 1/\tau_s$, and there is no regime v) for both of them. In Fig. 4.23 we show the transient viscosity $\mu_2^{\tau}$ (not shown is the $\mu_1^{\tau}$, which is similar to the transient viscosity in uniaxial extension). The model predicts overshoots at medium and high extensional rates.
4.5 Extensional flows

FIG. 4.17. Steady-state values of the dimensionless uniaxial extensional viscosity as function of dimensionless extensional rate predicted by the double-label model with $Z = 20$, $\lambda_{\text{max}} = 10$, and $\delta_1 = \delta_2 = 1/\lambda^2$.

FIG. 4.18. Steady-state values of the dimensionless uniaxial extensional viscosity as function of dimensionless extensional rate predicted by the single-label model with $Z = 20$, $\lambda_{\text{max}} = 10$, and $\delta_1 = \delta_2 = 1/\lambda^2$. 
Chapter 4 Model predictions

FIG. 4.19. Dimensionless uniaxial extensional viscosity versus dimensionless time after start up of steady uniaxial elongation for several different dimensionless elongational rates predicted by the double-label model with the same parameter values as for Fig. 4.17.

FIG. 4.20. The strain-hardening parameter as a function of the Hencky strain for the dimensionless elongational rate $\dot{\varepsilon} \tau_d = 150$ predicted by the double-label model with the same parameter values as for Fig. 4.17.
FIG. 4.21. Dimensionless uniaxial extensional viscosity versus dimensionless time after start-up of steady uniaxial elongation for $\varepsilon \tau_d = 150$ predicted by the double-label model with three different values of $\lambda_{\text{max}}$. The other parameter values are the same as for Fig. 4.17.

FIG. 4.22. Steady-state values of the dimensionless planar extensional viscosity $\mu_1$ and $\mu_2$ as functions of dimensionless extensional rate predicted by the double-label model with the same parameter values as for Fig. 4.17.
4.6 Comparisons with experimental data and other models

In this section, we compare our models with experimental data and two alternative molecular-based models. The experimental data used for comparison is from Kahvand (1995) which were also used by Hua et al. (1999). The test fluid is a solution in tricresyl phosphate of nearly monodisperse polystyrene with a molecular weight $M_w$ of $1.9 \times 10^6$ (polydispersity index of 1.2) at a polymer density of 0.135 g/cm$^3$. This fluid has a zero-shear-rate viscosity $\eta_0$ of $6.8 \times 10^3$ Pa s and a zero-shear-rate first normal stress coefficient $\Psi_{1,0}$ of $2.0 \times 10^5$ Pa s$^2$. The longest relaxation time and the average number of entanglement of the fluid are estimated to be 15 s and 7 respectively. Correspondingly, for our models we will use $Z = 7$ and $\lambda_{\text{max}} = 21$. The latter corresponds to $N_{K_B} = 441$ [see Eq. (2.39)]. This value of $N_{K_B}$ (the number of Kuhn steps per entanglement segment) is calculated by dividing the molecular weight per entanglement segment ($M_w/Z \approx 2.7 \times 10^5$ here) by the molecular weight per Kuhn step (its value calculated from the data on PS melts in Table 2.1 is about 590, which corresponds to about 6 mono-
mers per Kuhn step). Note that, the results given here are not sensitive to finite extensibility. The parameters \( \tau_d \) and \( G_N^0 \) are chosen in such a way that the cross point of the steady shear stress and first-normal-stress difference curves is predicted correctly. For the single-label model, we obtain \( \tau_d = 15 \text{ s} \) and \( G_N^0 = 1160 \text{ Pa} \). For the double-label model, we obtain \( \tau_d = 18 \text{ s} \) and \( G_N^0 = 1260 \text{ Pa} \) (the larger values here are due to the double-diffusion implementation of DR). The parameters \( \delta_1 \) and \( \delta_2 \) are assigned as \( \delta_1 = \delta_2 = 1/\lambda \) for the single-label model and \( \delta_1 = \delta_2 = 1/\lambda^2 \) for the double-label model. The two \( \lambda \)-dependent functions satisfy the general requirement mentioned in Sec. 2.3, and they are obtained respectively by a best overall fit to the experimental data, especially the overshoots of shear stress at the start-up of steady shear flow. The above sets of parameter values for the two models are used for all the cases. In addition to the comparisons with the experimental data, comparisons with the two other models are also presented. These two models are the full chain simulation model by Hua and Schieber (1998a), Hua et al. (1999), and the simplified (S-) form of the theory by Mead, Larson and Doi (1998). Here, we shall denote them as “FCS” model and “MLDS” model, respectively. For the FCS model, the simulations were done by J. Neergaard and coworkers, with the parameter \( b = 3N_K/(N-1) = 150 \), where \( N_K \) denotes the number of Kuhn steps per chain and \( N \) is the number of beads for the FCS model (comp. Tab. 4.1). The chosen value is more reasonable than the value \( b = 25 \) used by Hua et al. (1999), while the other parameters are kept the same. The former value of \( b \) corresponds to 150 Kuhn steps per entanglement, or 17 monomers per Kuhn step. This value of monomers per Kuhn step is larger than the value we estimated above. However, as for our model, the results given here for the FCS model are not affected significantly by choosing an even larger value of \( b \). For the MLDS model in which double reptation is not taken into account, one may regard \( \tau_d \) and \( \tau_s \) both as adjustable parameters. The values \( \tau_d = 9 \text{ s} \), \( \tau_d/\tau_s = 10 \), and \( G_N^0 = 800 \text{ Pa} \) are obtained by a best overall fit to the available experimental data, where the exponential switch function is used. For \( \tau_d/\tau_s = 3Z = 21 \) the fit would deteriorate considerably. Prior to further discussion of the different models, we refer to Table 4.1 for a characterization of the four models: FCS, MLDS and the two models under study.
A. Start-up of steady shear flow

In Fig. 4.24 we compare the double-label model predictions to the experimental data for the transient growth of the shear viscosity for several shear rates. Actually the model is able to capture the features of the data quantitatively. The predictions of different models for the same property are plotted in Fig. 4.25 where only the curves for the highest shear rate are shown because all the models give similar results for the two lower shear rates. It turns out that the FCS model overpredicts the overshoot and captures the undershoot, the single-label model predicts a narrower overshoot with precise magnitude and a sharper undershoot, while the double-label model and the MLDS model predict the magnitude of the overshoot precisely, but do not predict an undershoot. Comparisons between the double-label model predictions and the experimental data are also made for the first-normal-stress difference coefficient $\Psi_1$ in Fig. 4.26. Here, the double-label model underpredicts the magnitude of the overshoot at the highest shear rate. Not shown are the predictions by the other three models, they are very comparable with the double-label model for the two lower shear rates. For the highest rate, again the FCS model overpredicts the overshoot, the MLDS model gives a fit similar to the double-label model, and the overshoot predicted by the single-label model is narrower and smaller than that predicted by the double-label model. In Fig. 4.27 we plot the magnitude of the strain $\gamma_p$ at which the maximum in the overshoot of the shear stress occurs as functions of shear rate predicted by the models and the experiment. It appears that the values of $\gamma_p$ stay nearly constant at low shear rates and increase with increasing shear rate at high rates. Here, the predictions by all the models are qualitatively in agreement with the experimental data, but the FCS model, the MLDS model and the double-label model overpredict at high rates, while the single-label model gives better but underpredictive results. Not shown are the model predictions and the experimental data of $\gamma_p$ for the first-normal-stress difference, which have a qualitative shape similar to that seen in Fig. 4.27 but differ approximately by a factor of 2.
4.6 Comparisons with experimental data and other models

B. Cessation of steady shear flow

In Fig. 4.28 we plot the relaxation of the shear stress, normalized by its initial value, after cessation of steady shear flow for two shear rates. All the model predictions (not shown are the predictions by MLDS and the single-label model which are close to the double-label model results) compare rather well with the experimental data. The stress relaxation rate increases with increasing previous shear rate. Later in the relaxation process, at times much larger than \( \tau_s \), the relaxation rate is governed only by the reptation process and constraint release due to double reptation (represented by a smaller value of \( \tau_d \) in the MLDS model). This behavior is also in accordance with other experimental results [Attané et al. (1985); Menezes and Graessley (1982)].

C. Steady shear flow

In Fig. 4.29 the steady-state values of the shear stress \( \tau_{xy} \) and the first normal stress difference \( N_1 \) are plotted as functions of shear rate. The double-label model predictions for the shear stress are in good agreement with the experimental data over the whole range of shear rates, while the single-label model and the FCS model predict a slight decrease of the shear stress over a range of shear rates that extends from roughly \( \dot{\gamma} \approx 0.3 \, \text{s}^{-1} \) to \( \dot{\gamma} \approx 2 \, \text{s}^{-1} \) for which the MLDS model predicts a slight increase which is consistent with the experimental data. This new observation of the MLDS model may be attributed to the fact that we use a relatively small ratio \( \tau_d / \tau_s = 10 \) here. Over the same range of shear rates, all the model predictions for the first normal stress difference \( N_1 \) increase gradually with shear rate, which are consistent with the experimental data. For the shear stress at shear rates after the range, the single-label model predicts an increase, the double-label model and the FCS model show a lesser increase which is also observed experimentally, while the MLDS model gives a decrease. This decreasing behaviour of MLDS is caused by the exponential switch function used and the additional term accounting for the CCR effect in the equation for stretch.
D. Steady extinction angle

In Fig. 4.30 we show the steady-state extinction angle as a function of shear rate. Obviously, in our models, CCR and double reptation prevent the chain segments from aligning with flow dramatically at high shear rates, and thus solve the overestimated steady shear orientation problem of the original DE model. The predictions of the FCS model, the MLDS model, and our models compare very favorably with the experimental results at shear rates below 10 s\(^{-1}\). After that, the predictions of the FCS model, the MLDS model, and the double-label model go back to the DE model predictions, which the single-label model gives better but still underpredictive results. This means that all the models still have the over-orientation problem at very high shear rates. To solve the problem, new physical mechanism should be explored and incorporated into the models. A first guess for that is the unsteady rotation of chains which may act to increase the steady (time-averaged) extinction angle at high shear rates. For the FCS model, in which the tumbling effect just mentioned has already existed, the reorientation algorithm for constraint release may profit from an adjustment by taking into account the effect.
### TABLE 4.1. Characterization of the three models discussed in this section.

<table>
<thead>
<tr>
<th>Model</th>
<th>FCS</th>
<th>MLDS</th>
<th>Our models</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameters</td>
<td>adjustable</td>
<td>The plateau modulus $G_N^0$, the reptation time $\tau_d$, and the Rouse time $\tau_s$ (fit from nonlinear data)</td>
<td>The plateau modulus $G_N^0$ and the reptation time $\tau_d$ (fit from nonlinear data)</td>
</tr>
<tr>
<td></td>
<td>fixed by the chemistry of the polymer or physical arguments</td>
<td>The number of entanglements per chain $Z$, the Kuhn step length $\alpha_K$, and the number of Kuhn steps per chain $N_K$</td>
<td>None</td>
</tr>
<tr>
<td>Physical effects incorporated and corresponding mathematical means</td>
<td>Reptation</td>
<td>* Incorporated into a set of Langevin equations for the chain motion</td>
<td>* The second term in the equation for the tube survival probability, Eq. 10 of the reference for MLDS</td>
</tr>
<tr>
<td></td>
<td>Avoiding IÅ approximation</td>
<td>* As for reptation plus an equation for the tube motion</td>
<td>Not considered</td>
</tr>
<tr>
<td></td>
<td>Chain stretching</td>
<td>* As for avoiding the IÅ approximation</td>
<td>* The equation for stretch, Eq. 12 of the reference</td>
</tr>
<tr>
<td></td>
<td>Double reptation</td>
<td>* By a random, instantaneous constraint release algorithm</td>
<td>Not considered</td>
</tr>
<tr>
<td></td>
<td>Convective constraint release (CCR)</td>
<td>* As for double reptation</td>
<td>* The term with the “switch” function in Eq. 10 and the last term in Eq. 12 of the reference</td>
</tr>
<tr>
<td></td>
<td>Chain-length breathing and segment connectivity</td>
<td>* Incorporated into a set of Langevin equations for the chain motion</td>
<td>Not considered</td>
</tr>
</tbody>
</table>

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FIG. 4.24. Transient growth of normalized viscosity as function of time under start up of steady shear flow for three different shear rates predicted by the double-label model (lines) and experiment (symbols).

FIG. 4.25. Transient growth of normalized viscosity as functions of time under start up of steady shear flow for $\gamma = 10$ s$^{-1}$ predicted by different models and experiment.
4.6 Comparisons with experimental data and other models

**FIG. 4.26.** Transient growth of normalized first-normal-stress difference coefficient as functions of time under start up of steady shear flow for three different shear rates predicted by the double-label model (lines) and experiment (symbols).

**FIG. 4.27.** Magnitude of the strain $\gamma_p$ at which the maximum in the stress overshoot occurs as functions of shear rate for shear stress under start up of steady shear flow predicted by different models and experiment.
**FIG. 4.28.** Relaxation of the shear stress reduced by its value at steady state as a function of time after cessation of steady shear flow for two different shear rates predicted by experiment and different models.

**FIG. 4.29.** Steady-state values of shear stress and first-normal-stress difference as functions of shear rate predicted by different models and experiment.
FIG. 4.30. Steady-state extinction angle as a function of shear rate predicted by different models and experiment.
Chapter 5

Extension to polydispersity

In this chapter, the double-label model for monodisperse melts is extended to incorporate polydispersity. After the section of introduction, the formulation of the extended model is given in section 5.2. In section 5.3, we obtain linear viscoelastic properties of the model from the memory-integral expression of the stress tensor.

5.1 Introduction

In most applications, polymers possess certain molecular weight distributions; they are “polydisperse” rather than “monodisperse”. Polydispersity has an enormous effect on the rheological behavior of polymeric systems. Developing molecular-based models able to predict the influence of polydispersity on macroscopic properties is relevant from a theoretical standpoint, but also has implications in tailoring polymer properties with respect to processability. The polydispersity effects have been included in the Doi-Edwards model by superposition (so called “simple reptation”) [Doi and Edwards (1986)]. The Curtiss-Bird (CB) model [Curtiss and Bird (1981a, 1981b)] has been extended to polydisperse mixtures by summing up contributions from the various species of molecules [Bird et al. (1987)]. The solution for each species has the same form as that for the monodisperse fluid, i.e., it is still a superposition method. The extended CB theory has been used to make extensive comparisons with experimental data for polydisperse melts [Schieber et al. (1986); Schieber (1987a, 1987b)].

For the regime of linear viscoelasticity, the Doi-Edwards (DE) model has been extended to incorporate constraint release effects due to the reptation motion of the surrounding chains (so called “double reptation”) [Tsengoglou (1987); des Cloizeaux
Chapter 5 Extension to polydispersity

The double-reptation idea is very successful in describing linear properties of polydisperse melts. Öttinger (1994) has considered a modified reptation model in which the idea of double reptation has been extended to the nonlinear regime and a nontrivial mixing rule for polydisperse melts has been suggested.

In the previous chapters, two new thermodynamically admissible reptation models, the single-label model and the double-label model, for monodisperse linear entangled polymers have been developed under the guidance of GENERIC and evaluated by stochastic simulation. The two models incorporate chain stretching, double reptation, and convective constraint release (CCR) mechanisms, while avoiding the independent alignment (IA) approximation. In the next sections, we will extend the double-label model to polydisperse melts by applying the modeling procedure suggested by Öttinger (1994). The extension work can be done similarly for the single-label model. The formulation of the model is given in section 5.2. In section 5.3, we derive a memory-integral expression for the stress tensor from which the predictions for the influence of polydispersity on the relaxation modulus and the zero-shear-rate viscosity is obtained.

5.2 Model development

The polydisperse melt is modeled as a system of entangled, interacting primitive chains, each chain of species \( \alpha \) having a molecular weight \( M_\alpha \) with certain mass fraction. In order to describe the flow behavior of the fluid, it is necessary to include the hydrodynamic variables in the list of independent state variables. The variables used here are the same as those adopted in Chapter 2, namely, the polymer mass density, \( \rho(r) \), the momentum density, \( M(r) \), and the internal energy density, \( \varepsilon(r) \).

For a complete description of such a complex fluid on a coarse-grained level, we need further structural state variables. The appropriate choice of these structural state variables needs physical insight into the problem considered. Here, we will choose them mainly based on the structural state variables chosen for monodisperse systems and by taking into account the polydispersity effect. For the same reasons stated in Chapter 2
and keeping in consistent with the monodisperse case, we here choose, for each species \( \alpha \), a configurational distribution function \( f_{\alpha} \) and the stretch ratio of chain contour length \( \lambda_{\alpha} \) as the structural state variables which, for nonhomogeneous flows, both depend on the position \( r \). Inherited from the previous double-label model for monodisperse entangled polymers, configurational variables appearing in the configurational distribution function should contain a unit vector \( u \), a label \( s \in [0, 1] \), and a label \( \xi \in [0, 1] \), where \( u \) specifies the orientation of the segment at the cross point \((s, \xi)\) by the probe chain of species \( \alpha \) and a surrounding chain. The values \( s = 0 \) and \( s = 1 \) correspond to the ends of the probe chain, similarly, \( \xi = 0 \) and \( \xi = 1 \) correspond to the ends of the surrounding chain. For polydisperse melts, the species indexes of the surrounding chains associated with a probe chain of species \( \alpha \) are no more the same as that of the probe chain, instead, they are subjected to randomness due to polydispersity. For the purpose of having information on the fact and having the possibility of including the resulting influences on the probe chain dynamics, we here introduce an additional configurational variable \( \beta \) (an integer) which specifies the species of the surrounding chain at the position \((s, \xi)\). In conclusion, we here consider the configurational distribution functions \( f_{\alpha}(u, s, \xi, \beta, r) \) with \( \alpha = 1, \ldots, N_s \), where \( N_s \) is the total number of species contained in the polydisperse system. We choose the normalization condition

\[
\sum_{\beta} \int_{s} \int_{\xi} f_{\alpha}(u, s, \xi, \beta, r) d^3u ds d\xi = 1, \tag{EQ 5.1}
\]

independent of position, for each probability density \( f_{\alpha}(u, s, \xi, \beta, r) \) with \( f_{\alpha} \geq 0 \).

In summary, the state variables \( x \) chosen for the description of the polydisperse melts are the following

\[
x = [\rho(r), M(r), \varepsilon(r), \{f_{\alpha}(u, s, \xi, \beta, r), \lambda_{\alpha}(r)\}_{\alpha = 1, \ldots, N_s}], \tag{EQ 5.2}
\]

which is a natural extension of that for monodisperse melts with introduction of an additional configurational variable \( \beta \), the species index of surrounding chains associated with each probe chain of a given species.
The development of the time-evolution equations for the state variables can be done by mimicking the same procedure and methodology as discussed in Chapter 2 for the monodisperse systems. In order to avoid repetitive works, only the necessary modifications to the original development will be pointed out. Indeed, the derivation of the time-evolution equations for the hydrodynamic variables is kept the same as the earlier derivation for monodisperse melts, except for the stress tensor which now must account for polydispersity; the modeling of the time-evolution equations for the structural state variables of each species $\alpha$ is independent from each other (no interactive terms needed) and hence is a duplication of the monodisperse modeling for each, but with an additional treatment of the new configurational variable $\beta$.

We begin with the first major change to the original GENERIC building blocks: the total entropy, which is important for the determination of the stress tensor. For the chosen level of description, there can be entropy associated with the very local arrangements and motions of atoms, with the configurational distribution function of each species, and with the chain stretching of each species. We here write the total entropy as a summation of all the contributions with each taking the same form as the corresponding contribution in monodisperse systems, namely,

$$S(x) = \int s(\rho(r), \varepsilon(r)) - \sum_{\alpha} k_B n^0_{\alpha} \Phi(\nu_{\alpha}(r))$$

$$- \sum_{\alpha} k_B Z_{a} n^0_{a} \sum_{\beta} \int_{0}^{1} \int_{0}^{1} p_{\alpha}(u, s, \xi, \beta, r) \ln p_{\alpha}(u, s, \xi, \beta, r) d^3u ds d\xi d\beta.$$

(EQ 5.3)

In writing this expression, we assumed that the local entropy contribution is described by a given function $s = s(\rho, \varepsilon)$, which is expected to be similar to the entropy density of low-molecular-weight liquids. The contribution due to the configurational distribution function of each species has the typical Boltzmann form $(-k_B \int p_{\alpha} \ln p_{\alpha})$, where

$$p_{\alpha}(u, s, \xi, \beta, r) = \frac{f_{\alpha}(u, s, \xi, \beta, r)}{\sum_{\beta'} \int_{0}^{1} \int_{0}^{1} f_{\alpha'}(u', s', \xi', \beta', r) d^3u' ds' d\xi' d\beta'}. $$

(EQ 5.4)
5.2 Model development

Using $p_a$ instead of $f_a$ is important in taking functional derivatives [see Chapter 2]. The parameters $k_B$, $Z_a$, and $n_p^a$ in the prefactor of the $p_a \ln p_a$ term in Eq. (5.3) are Boltzmann’s constant, the number of entanglements per chain of species $\alpha$ at equilibrium which is given by $M_a/M_e$ ($M_e$ is the average molecular weight between entanglement points along one chain assumed to be independent of the species), and the number density of polymers of species $\alpha$, respectively.

In Eq. (5.3), $\Phi(\lambda_a)$ is the dimensionless entropy penalty for each chain of species $\alpha$ deviating from the average equilibrium contour length ($\lambda_a = 1$), and it takes the following form [see Chapter 2]

$$\Phi(\lambda_a) = \frac{3}{2} Z_a \left[ \ln \lambda_a^2 + (\lambda_{\max}^2 - 1) \ln \frac{\lambda_{\max}^2 - \lambda_a^2}{\lambda_{\max}^2 - 1} \right]$$  \hspace{1cm} (EQ 5.5)

where $\lambda_{\max}$ is the maximum possible stretching ratio of the chain contour length which is equal to the square root of the number of Kuhn steps per entanglement, independent of the species. For the following, it is very convenient to introduce, for each species, an effective spring constant for deviations from the equilibrium contour length, associated with the derivative of $\Phi(\lambda_a)$.

$$c(\lambda_a) = \frac{3Z_a\lambda_{\max}^2(\lambda_a + 1)}{\lambda_a(\lambda_{\max}^2 - \lambda_a^2)}.$$  \hspace{1cm} (EQ 5.6)

We now consider necessary modifications of the Poisson bracket $L$ and the friction matrix $M$ due to the introduction of the new configurational variable $\beta$. Since introducing such a variable is just to describe the randomness of surrounding chains due to polydispersity, it is reasonable to assume that at equilibrium $\beta$ is randomly chosen according to the actual mass fraction of chains; it does not diffuse; and it is not convected by flow. Under these assumptions, there are no additional convection and diffusion terms for $\beta$ in $L$ and $M$, respectively. Nevertheless, $\beta$ possesses a dynamics through the boundary condition of the final diffusion equation [see Eqs. (5.17) and (5.18)], namely, whenever the $s$ or $\xi$ reaches the two ends (0 and 1), the $\beta$ should be randomly selected according to a
proper distribution, e.g. the actual mass fraction of chains adopted here (when the state is far from equilibrium, it may profit from an adjustment of the distribution by taking into account the actual chain lengths).

Finally, the important change to the friction matrix $M$ due to polydispersity is the diffusion coefficient of $\xi$, which is assumed to be determined by the static (molecular weight or reptation time) and dynamic (chain retraction rate) properties of the surrounding chains. In the previous modeling of monodisperse melts in Chapter 2, all chains had the same molecular weight, they carried the same index of species, and the diffusion coefficient of $\xi$ was given by Eq. (2.64). For polydisperse melts, for a given probe chain of species $\alpha$, the diffusion coefficient of $\xi$ should be changed to the following form accordingly,

$$D^\xi(\beta) = \frac{1}{\pi^2} \left[ \delta_1 \frac{1}{\tau^\beta} - \delta_2 \frac{\lambda^\beta_{\text{dissip}}}{\lambda^\beta_{\text{dissip}}} H\left( -\frac{\lambda^\beta_{\text{dissip}}}{\lambda^\beta_{\text{dissip}}} \right) \right]$$

(EQ 5.7)

with $\delta_1 = \delta_2 = 1/\lambda^2_\alpha$, where $\beta$ is the species index of the surrounding chains and $H(x)$ is the Heaviside step function. The $\delta_1$ -term is interpreted as representing “double reptation”, and the $\delta_2$ -term triggers the CCR mechanism. Here, $\delta_1$ and $\delta_2$ do not depend on $\beta$, i.e. the surrounding chain properties, because of the reason for introducing them [see Chapter 2].

As a result of these modifications, the final time-evolution equations to be presented below for the structural state variables of each species have the same overall forms as those for the monodisperse fluid given in Chapter 2 with changes in notations and modifications on the boundary conditions at the chain ends.

For each species, the equation for the chain contour length stretching and relaxation reads

$$\frac{D\lambda^\alpha}{Dt} = \dot{\lambda}^\alpha_{\text{convect}} + \dot{\lambda}^\alpha_{\text{dissip}},$$

(EQ 5.8)
where $D/Dt$ is the material time derivative, and the total stretching rate is split into convective and dissipative contributions,

$$
\dot{\lambda}_{\text{convect}} = \lambda_{\alpha} \mathbf{k} : \bar{\mathbf{\tau}}_{\alpha}, \tag{EQ 5.9}
$$

and

$$
\dot{\lambda}_{\text{dissip}} = -\frac{1}{\tau_{\alpha}} \frac{c(\lambda_{\alpha})}{3Z_{\alpha}} (\lambda_{\alpha} - 1), \tag{EQ 5.10}
$$

where $\mathbf{k}$ is the transpose of the velocity gradient tensor, $\bar{\mathbf{\tau}}_{\alpha}$ is the symmetric second-rank orientation (alignment) tensor defined by

$$
\bar{\mathbf{\tau}}_{\alpha} = \sum_{\beta} \int_{0}^{1} d\xi \int_{0}^{1} ds \int d^4u f_{\alpha}(u, s, \xi, \beta, r) uu, \tag{EQ 5.11}
$$

for the chains of species $\alpha$. In Eq. (5.10), $\tau^{\alpha}_{s}$ denotes the characteristic stretching time for the chains of species $\alpha$.

The diffusion equation for the configurational distribution function of the chains of species $\alpha$ takes the form

$$
\frac{Df_{\alpha}}{Dt} = -\frac{\partial}{\partial u} \left[ \left( 1 - \frac{uu}{u^2} \right) \mathbf{k} : \mathbf{u} f_{\alpha} \right] - \frac{\partial}{\partial s} (S_{\text{rot}} f_{\alpha}) - \frac{\dot{\lambda}_{\text{dissip}}}{\lambda_{\alpha}} f_{\alpha}
+ \frac{1}{\pi^2 \tau_{d}^2} \frac{\partial^2 f_{\alpha}}{\partial^2 s} + D^{\alpha}_{z}(\beta) \frac{\partial^2 f_{\alpha}}{\partial^2 \xi}, \tag{EQ 5.12}
$$

where the equation of change for the position label $s$ reads

$$
S_{\text{rot}} = -\frac{1}{\lambda_{\alpha}} \left( s - \frac{1}{2} \right) \dot{\lambda}_{\text{dissip}}. \tag{EQ 5.13}
$$
In Eq. (5.12), \( \tau_0^\alpha \) stands for the reptation time of the probe chain of species \( \alpha \). Conservation of the total probability for each species implies the boundary conditions

\[
\frac{\partial \tilde{\mathcal{J}}_\alpha}{\partial s}\bigg|_{s=0} = \frac{\partial \tilde{\mathcal{J}}_\alpha}{\partial s}\bigg|_{s=1} = 0 \text{ and } \frac{\partial \tilde{\mathcal{J}}_\alpha}{\partial \xi}\bigg|_{\xi=0} = \frac{\partial \tilde{\mathcal{J}}_\alpha}{\partial \xi}\bigg|_{\xi=1} = 0, \tag{EQ 5.14}
\]

where

\[
\tilde{\mathcal{J}}_\alpha = \sum_\beta \int_0^1 \int_0^1 \int_0^1 \int_0^{2\pi} f_\alpha(u, s, \xi, \beta, r) d^3u d\xi. \tag{EQ 5.15}
\]

and

\[
\hat{\mathcal{J}}_\alpha = \sum_\beta \int_0^1 \int_0^1 \int_0^1 \int_0^{2\pi} \hat{f}_\alpha(u, s, \xi, \beta, r) d^3u ds. \tag{EQ 5.16}
\]

At the probe chain ends, we assume random orientation of \( u \) and random selection of the position label \( \xi \) and the species index \( \beta \) of the surrounding chain by specifying the distribution

\[
f_\alpha(u, s, \xi, \beta, r) = \frac{1}{4\pi} w_\beta \delta(|u| - 1), \quad s = 0, 1, \tag{EQ 5.17}
\]

where \( w_\beta \) is the mass fraction of the chains of species \( \beta \). At the surrounding chain ends, we impose random orientation of \( u \) and random selection of the position label \( s \) and the species index \( \beta \) by specifying the distribution

\[
f_\alpha(u, s, \xi, \beta, r) = \frac{1}{4\pi} w_\beta \delta(|u| - 1), \quad \xi = 0, 1. \tag{EQ 5.18}
\]

The extra stress tensor consists of two contributions, \( \tau = \tau_1 + \tau_2 \), where \( \tau_1 \) is associated with the original Doi-Edwards contribution:
5.2 Model development

\[ \tau_1(r) = \sum_{\alpha} 3Z_n n_p^\alpha k_B T \sum_{\beta} \int_0^1 d\xi \int_0^1 d\eta \int_0^1 d\eta' u u f_\alpha(u, s, \xi, \beta, r) d^3 u d s d \xi. \]  

(EQ 5.19)

The contribution \( \tau_2 \) associated with the chain stretching takes the form

\[ \tau_2(r) = \sum_{\alpha} c(\lambda_\alpha) \lambda_\alpha (\lambda_\alpha - 1) n_p^\alpha k_B T \sum_{\beta} \int_0^1 d\xi \int_0^1 d\eta \int_0^1 d\eta' u u f_\alpha(u, s, \xi, \beta, r) d^3 u d s d \xi. \]  

(EQ 5.20)

At this point, the extension of the double-label model to polydisperse mixtures is complete. The variation of the time coefficient \( \tau_d^* \) with \( Z_n \) depends on the choice of model. The Curtiss-Bird theory states

\[ \tau_d^* \propto Z_n^{1+b} Z_\alpha^2, \]  

(EQ 5.21)

where \( Z_n \) is the number-average number of entanglements and \( b \) is a chain constraint exponent, while the Doi-Edwards theory uses

\[ \tau_d^* \propto Z_{\alpha}^2. \]  

(EQ 5.22)

In this paper, the relationship \( \tau_d^*/\tau_s^* = 3Z_\alpha \) is assumed. The remaining model parameter \( \lambda_{\text{max}} \) is set to the preferable value, \( \lambda_{\text{max}} \approx 5 \) for melts, as motivated in Chapter 2.

In the presented model, the time-evolution equations of each species keep the same structure as the double-label model equations for the monodisperse case discussed in Chapter 2, except for two aspects: i) a new variable “species index” \( \beta \) has been introduced, but no additional terms for it (no convection and no diffusion), and ii) randomness with given distribution now enters the diffusion coefficient of \( \xi \). Since these two aspects have no influence on the GENERIC structure such as degeneracy properties and a valid Jacobi identity, the thermodynamic admissibility of the model for monodisperse melts is inherited by the extended model. Notice further, that the new variable \( \beta \) possesses a dynamics through the boundary conditions (5.17) and (5.18), namely, whenever the \( s \) or \( \xi \) reaches the two ends (0 and 1), the \( \beta \) should be randomly selected. GENERIC
in its present form does not provide a route to judge about the structure of boundary conditions.

In the nonlinear regime, all the time-evolution equations are coupled with each other due to the form of the diffusion coefficient \( D_{\xi}(\beta) \) [Eq. (5.7)]. Hence, the solution for each species cannot be obtained from the one for a monodisperse fluid by replacing \( \tau_d \) by \( \tau_d^n \), which is the case for the superposition models such as the extended DE model and the extended CB model. Even if the CCR mechanism is removed from our model, as a result, the time-evolution equations for chains of different species can be solved independently, it is still impossible to obtain the overall solution by the superposition method just mentioned, in view of the existence of the parameter \( \tau_d^n/\tau_s^n = 3Z_x \) which actually affects the amount of chain stretching and the parameter \( \tau_d^\beta \) with given distribution in \( D_{\xi}(\beta) \).

### 5.3 Linear viscoelasticity

In order to calculate the linear viscoelastic properties of the model polydisperse system, we again formulate the extra stress tensor in the form of a memory-integral expression. By following the same procedure as for the monodisperse system [see Sec. 4.1] and taking into account that the species index \( \beta \) is a random number with a given distribution (the mass fraction), we obtain

\[
\tau(t) = \sum_a \sum_\beta 3Z_x w_a^\beta w_b T \left\{ \frac{1}{3} \int_{-\infty}^{t} p_a(t-t') p_b(t-t') \frac{\partial \langle \mathbf{u}_a \mathbf{u}_b \rangle}{\partial t'} dt' \right\}, \tag{EQ 5.23}
\]

where \( p_a(t-t') \) and \( p_b(t-t') \) are given by Eq. (4.11) with \( \tau_d \) there replaced by \( \tau_d^n \) and \( \tau_d^\beta \), respectively. The linear viscoelastic limit of the second moment \( \langle \mathbf{u}_a \mathbf{u}_b \rangle \) is given by Eq. (4.14). After substituting these expressions into the equation (5.23), one obtain the relaxation modulus.
5.3 Linear viscoelasticity

\[ G(t) = \sum_{\alpha} \sum_{\beta} \frac{3}{5} Z_\alpha n_\alpha^\alpha w_\beta k_B T \rho_\alpha(t) p_\beta(t), \]  
\text{(EQ 5.24)}

from which the plateau modulus \( G_N^0 \) can be deduced:

\[ G_N^0 = G(0) = \sum_{\alpha} \frac{3}{5} Z_\alpha n_\alpha^\alpha k_B T. \]  
\text{(EQ 5.25)}

The normalized relaxation modulus then reads

\[ \frac{G(t)}{G_N^0} = \sum_{\alpha} \sum_{\beta} w_\alpha w_\beta \rho_\alpha(t) p_\beta(t) = \left( \sum_{\alpha} w_\alpha \rho_\alpha(t) \right)^2. \]  
\text{(EQ 5.26)}

Form the above equation, we see that the extended model exactly predicts the successful “double reptation mixing rule” for polydisperse melts in the limit of linear viscoelasticity [see Eq. (6) of des Cloizeaux (1988)]. The viscosity and the first-normal-stress coefficient at zero shear rate can be obtained from the relaxation modulus by the formulas

\[ \eta_0 = \int_0^\infty G(t) dt \quad \text{and} \quad \psi_{1,0} = 2 \int_0^\infty t G(t) dt, \]  
respectively.
Chapter 6

Conclusions

In this thesis, two new thermodynamically admissible reptation models for entangled polymers, the single-label model and the double-label model, that include chain stretching, double reptation (DR), and convective constraint release (CCR), and that avoid the independent alignment approximation (IAA) are developed within the molecular-based picture of the system under consideration and under the guidance of the GENERIC formalism of nonequilibrium thermodynamics. In the single-label model, the effects of constraint releases (DR and CCR) are introduced through the stochastic force (noise term) in the time-evolution equation for the orientation of inner chain segments, while in the double-label model, they are incorporated through the diffusion coefficient of the second label $\xi$ together with the random orientation boundary conditions.

Based on the stochastic interpretation of the resulting diffusion equations, corresponding efficient stochastic simulation algorithms are designed to simulate the rheological behaviors of the two models in the nonlinear viscoelastic regime. In the linear viscoelastic regime, we derive analytical results of the relaxation modulus for the two models. The single-label model prediction is very similar to that predicted by double reptation idea, while the double-label model exactly recovers the double reptation result.

The two models are comprehensively investigated for transient and steady properties in single-step strain, double-step strain, shear, and extensional flows. Quantitative comparisons are made with experimental data of entangled polystyrene solution in shear flows. We find that both models are able to capture qualitatively, or quantitatively in some cases, almost all the nonlinear properties observed so far in shear-type flows for entangled polymers. The double-label model is qualitatively better than the single-label model in describing the shear stress relaxation after double-step strain (e.g. sign change and overshoot) and the steady-state values of stress in shear flow (e.g. slowly increasing
of shear stress for lowly entangled polymers). However, the double-label model does not predict the transient undershoots in shear stress and extinction angle after start-up of steady shear flow. Exploration of possible reasons for this shortcoming of the theory will be left to future work.

Comparisons with two recently formulated molecular-based models, FCS [Hua and Schieber (1998a)] and MLDS [Mead et al. (1998)], in shear flows are also presented. It turns out that our models and the two models are competitive with each other; in many cases, they show similar behaviors. Very detailed comparisons are given in Sec. 4.6 and Fang et al. (2000). All the models have the negative feature that, if the model parameters are chosen to capture the transient phenomena satisfactorily, then the predicted steady-state extinction angles in shear flow are too small at very high shear rates. Removing this drawback from our models remains a topic of future work.

For extensional flows, our models exhibit unusual predictions. In order to confirm all the model predictions, further measurements of the stress for ideal samples (linear, monodisperse, entangled polymers) in various extensional flows are required. There are difficulties in performing this kind of experiments: a monodisperse polymer is usually sold in powder form, which is often more difficult to shape into bubble free samples than granules; the polymer breaks at much lower Hencky strains and is less homogeneous than an industrial melt [Schweizer (1999)].

In addition to the plateau modulus $G_N^0$ and the reptation time $\tau_d$, each model of ours has two basic parameters, namely $Z$, the number of entanglements per chain which is proportional to the molecular weight (and can be expressed in terms of the Rouse and reptation time), and the maximum stretch $\lambda_{\text{max}}$, being equal to the square root of the number of Kuhn steps per entanglement segment. The remaining two model parameters $\delta_1, \delta_2$ have been introduced but actually assigned with the values $\delta_1 = \delta_2 = 1/\lambda^2$ for the double-label model and $\delta_1 = \delta_2 = 1/\lambda$ for the single-label model.

Notably, each model of ours is a thermodynamically consistent single-segment theory which has only few degrees of freedom (four for the single-label model and five for the double-label model). In the sense of considering the time and memory requirements for the computation, it is very suitable to utilize our models to simulate complex flows.
by using the CONNFFESSIT idea [Laso and Öttinger (1993)]. Up to our present knowledge, variance reduction techniques [Hulsen et al. (1997); Öttinger et al. (1997); van Heel et al. (1999); Gallez et al. (1999); Bonvin and Picasso (1999)] may not be directly applied to the models. The dynamics for the position label $s$ - and in particular its jump events upon touching the chain ends - depend on the local value for the macroscopic velocity gradient such that a synchronization of trajectories by cancellation of fluctuations is prevented at first glance.

The double-label model for monodisperse entangled polymers is extended to include polydispersity by introducing a new structural variable, the species index $\beta$ of surrounding chains, and applying the random sampling procedure for it. Overall, the extended model is not a superposition model in the sense that the time-evolution equations for chains of different lengths are generally coupled, and the stress is no more a summation of contributions from independent species. In the linear viscoelastic regime, the extended model predicts the successful double-reptation mixing rule.
Appendix
Proof of Eq. (4.1)

We will show that Eq. (4.1) is a solution of Eq. (2.75) satisfying the boundary conditions (2.81) and (2.82). The proof given below is simpler and more general than the similar one given by Doi (1980b). Integrating Eq. (4.1) by parts, we get

\[ f(u, s, \xi, t) = K(t, t, s, \xi)g(u, t, t) - \int_{-\infty}^{t} K(t, t', s, \xi) \frac{\partial g(u, t', t')}{\partial t'} dt'. \]  \hspace{1cm} (EQ 1)

Using the initial conditions (4.3) and (4.5) for \( K \) and \( g \), we obtain

\[ f(u, s, \xi, t) = \frac{1}{4\pi} \delta(|u|-1) - \int_{-\infty}^{t} K(t, t', s, \xi) \frac{\partial g(u, t', t')}{\partial t'} dt'. \]  \hspace{1cm} (EQ 2)

Now it is obvious that \( f(u, s, \xi, t) \) satisfies Eqs. (2.81) and (2.82) because of the boundary conditions for \( K(t, t', s, \xi) \) [Eq. (4.6)]. To prove it also satisfies Eq. (2.75), we differentiate Eq. (2) with respect to \( t \), getting

\[
\frac{df}{dt} = -K(t, t, s, \xi) \left[ \frac{\partial g(u, t', t')}{\partial t'} \right]_{t' \rightarrow t} - \int_{-\infty}^{t} K(t, t', s, \xi) \frac{\partial g(u, t', t')}{\partial t'} dt' 
- \int_{-\infty}^{t} K(t, t', s, \xi) \frac{\partial}{\partial t'} \left[ \frac{\partial g(u, t', t')}{\partial t} \right] dt'.
\]  \hspace{1cm} (EQ 3)

Each term in the right-hand side of Eq. (3) can be rewritten as follows:
Appendix Proof of Eq. (4.1)

the first term  
\[
= \left[ \frac{\partial g(u, t, t')}{\partial t'} \right]_{t'=t} = \left[ \frac{\partial g(u, t, t')}{\partial t} \right]_{t'=t} 
= \left( -\frac{\partial}{\partial u} \cdot \left( 1 - \frac{uu}{|u|^2} \right) \cdot \mathbf{k} \cdot u \right) \left( \frac{1}{4\pi} \delta(|u| - 1) \right),
\]  
\text{(EQ 4)}

the second term  
\[
= -\int_{-\infty}^{\infty} \left( \frac{\partial}{\partial s} s_{tot} - \gamma_1 \dot{x}_{\text{dissip}} + \frac{1}{\pi \tau_e \bar{s}} \frac{\partial^2}{\partial s^2} + \frac{D_1}{\xi_1^2} \frac{\partial^2}{\partial \xi^2} \right) \text{K} \frac{\partial g}{\partial t} \text{dt}'
\]
\[
= \left( \frac{\partial}{\partial s} s_{tot} - \gamma_1 \dot{x}_{\text{dissip}} + \frac{1}{\pi \tau_e \bar{s}} \frac{\partial^2}{\partial s^2} + \frac{D_1}{\xi_1^2} \frac{\partial^2}{\partial \xi^2} \right) f
= \left( \frac{\partial}{\partial s} s_{tot} - \gamma_1 \dot{x}_{\text{dissip}} + \frac{1}{\pi \tau_e \bar{s}} \frac{\partial^2}{\partial s^2} + \frac{D_1}{\xi_1^2} \frac{\partial^2}{\partial \xi^2} \right) f
\text{(EQ 5)}

the third term  
\[
= \int_{-\infty}^{\infty} K(t, t', s, \xi) \frac{\partial}{\partial t'} \left[ \left( -\frac{\partial}{\partial u} \cdot \left( 1 - \frac{uu}{|u|^2} \right) \cdot \mathbf{k} \cdot u \right) g(u, t, t') \right] \text{dt}'
\]
\[
= \left( -\frac{\partial}{\partial u} \cdot \left( 1 - \frac{uu}{|u|^2} \right) \cdot \mathbf{k} \cdot u \right) \left( \frac{1}{4\pi} \delta(|u| - 1) \right)
\text{(EQ 6)}
\]

Summation of Eqs. (4), (5), and (6) gives the right-hand side of Eq. (2.75). A similar proof can be readily performed for the single-label model.
Bibliography


Flory, P. J., Statistical Mechanics of Chain Molecules (Hanser, Munich, 1988).


Bibliography


