doi:10.2533/chimia.2011.223 Chimia 65 (2011) 223–227

Systematic Coarse Graining Flowing Polymer Melts: Thermodynamically Guided Simulations and Resulting Constitutive Model

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§SCS Metrohm Prize for best oral presentation

Abstract: Complex fluids, such as polymers, colloids, liquid-crystals *etc.*, show intriguing viscoelastic properties, due to the complicated interplay between flow-induced structure formation and dynamical behavior. Starting from microscopic models of complex fluids, a systematic coarse-graining method is presented that allows us to derive closed-form and thermodynamically consistent constitutive equations for such fluids. Essential ingredients of the proposed approach are thermodynamically guided simulations within a consistent coarse-graining scheme. In addition to this new type of multiscale simulations, we reconstruct the building blocks that constitute the thermodynamically consistent coarse-grained model. We illustrate the method for low-molecular polymer melts, which are subject to different imposed flow fields like planar shear and different elongational flows. The constitutive equation for general flow conditions we obtain shows rheological behavior including shear thinning, normal stress differences, and elongational viscosities in good agreement with reference results.

Keywords: Computer simulations · Constitutive equations · Polymer melts · Shear flow

Introduction

The viscoelastic flow properties of polymer melts play an important role in many industrial processes, like film-blowing, injection molding, *etc.* Shear thinning, strain hardening, normal stress effects are examples of such effects, that are absent in simple liquids.[1] Atomistic or other microscopic models of polymer melts provide a more or less accurate description of polymer's equilibrium and thermodynamic properties, although present-day computational power only allows the study of rather moderate chain lengths.[2] Concerning dynamical properties and in particular dynamics out of equilibrium (as typically occurs in flows), the situation is dramatically different. Due to the enormous gap in time scales between microscopic motions (typical vibration of carbon–carbon bonds takes femtoseconds) and macroscopically relevant flow time scale (typically between microseconds and minutes) direct, brute-force approaches by nonequilibrium molecular dynamics simulations are necessarily limited not only to short chains but also to rather high flow rates.[3–5]

Since most microscopic details are irrelevant for the macroscopic flow behavior, semi-phenomenological constitutive equations have been proposed that directly describe macroscopic quantities of interest.[1,6] The constitutive equations therefore do not suffer from the inherent limitations of microscopic simulations. On the other hand, these equations contain several phenomenological parameters that can be used to fit experimental data but that often lack a clear microscopic interpretation. This deficiency makes it difficult to investigate the influence of microscopic structures and chain architecture on macroscopic (flow) properties. Understanding this relation, however, is very important in designing new polymer materials. Ideally, one would like to derive closed-form constitutive equations for a given polymer melt, with a clear identification of material parameters that enter the constitutive equations.

We here propose a method that is able to tackle exactly this issue by combining a thermodynamically consistent coarse graining approach based on projection operators with newly designed hybrid simulations.[7,8] Our approach is embedded in a general framework of nonequilibrium thermodynamics,[9] which emphasizes the building blocks of dynamical equations: energy and entropy as generators of reversible and irreversible dynamics, respectively, as well as a Poisson and a friction matrix. Having established the building blocks on the coarse-grained level numerically, we obtain explicit analytical expressions for the coarse-grained model in a reconstruction step, which allows the formulation of closed-form constitutive equations.[10] We discuss the form of these equations, which are generalizations of well-accepted constitutive equations that have been proposed in the literature on semi-phenomenological grounds. Furthermore, we obtain numerical values of the material parameters for the specific polymer melt under study.

Methods

Microscopic Model and Simulations

On a microscopic level, polymer melts are described as a system of interacting

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particles, where the interactions contain bonded as well as non-bonded (like excluded volume) potentials. We here employ a bead-spring model of polymer melts that has been used extensively in the past in molecular dynamics simulations in order to study various polymer properties.[11] Also rheological properties of this model have been investigated by nonequilibrium molecular dynamics simulations, mostly in planar shear and uniaxial elongational flows.[3–5] In this model, excluded volume interactions between all particles are described by a purely repulsive Lennard-Jones potential. In addition, bonded interactions are modeled by finitely-extendable nonlinear elastic (FENE) spring forces. We study the system at the same density and temperature as was done in previous studies. We follow common practice and report all quantities in reduced Lennard-Jones units. For polyethylene, for example, the corresponding reference values are 5.3 Å, 1.8 ps, 0.07 mPa·s for the units of length, time, viscosity, respectively.[4] According to classical mechanics, the dynamics of the system is given by Hamilton's equation of motion. In order to perform simulations at a fixed temperature T, these equations are supplemented by a thermostat, which we choose as simple velocity rescaling.[2,3] Since the trajectories of all particles have to be integrated in time numerically, this brute force approach becomes computationally very expensive for long chain lengths and at small flow rates. Fig. 1 shows snapshots of this model system obtained by long molecular dynamics simulations for a system containing 50 chains of $N = 20$ beads each. Periodic boundary conditions are used in order to minimize finite-size effects.

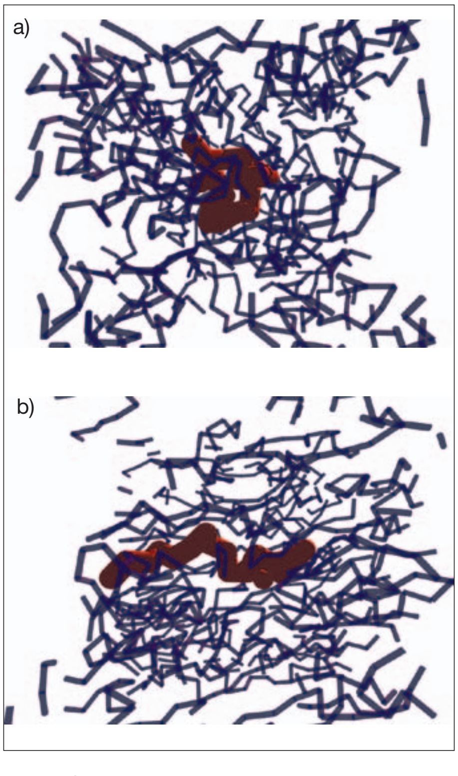

Fig. 1. Snapshot of chain configurations for a polymer melt of length $N = 20$. Panels (a) and (b) correspond to equilibrium conditions and planar shear flow of rate $\gamma = 0.05$. For better visibility, only one chain is highlighted while the others are shown in reduced size. Chain stretching under shear flow is clearly visible.

Thermodynamically Consistent Coarse Graining

Macroscopic properties evolve on time scales that are much longer than microscopic motions, like the fast bond vibrations. Therefore, molecular simulations are ideally suited for studying short-time-small-scale phenomena but very inefficient when used to directly address macroscopic properties. A first and essential ingredient of any coarse-graining procedure is the identification of a set of collective (macroscopic) variables in terms of the underlying microscopic model.[12] Under equilibrium conditions, different coarse-graining approaches have been proposed, where the coarse-grained levels range from superatoms containing only a few microscopic atoms or particles up to the continuum scale.[13] For dynamical and especially flow phenomena, most of these approaches face some serious difficulties.[14] Here, we attempt to derive constitutive equations and therefore want to coarse grain over entire chains. Out of equilibrium, the gyration tensor $x = (1/N)\ \Sigma_j (r_j - r_{\mathrm{cm}})(r_j - r_{\mathrm{cm}})$ is a convenient measure for the average deformation and stretching of the polymers.[15] The position of the N monomers and their center of mass are denoted by r_j and r_{cm}, respectively. The well-known gyration radius R_{G} is contained in the trace of the matrix x, $R_{\mathrm{G}}^2 = \mathrm{tr}\ x$. We aim at a closed-form description of the polymer melt and its dynamics in term of the gyration tensor only. Other configuration tensors can be chosen as well (*e.g.* the second rank tensor formed by the end-to-end vector), but the gyration tensor seems to be particularly well suited for the present case.[7] From previous work, it is known that the polymer contribution to the stress tensor can be expressed in terms of x by $\sigma = -2nTx\cdot\delta S/\delta x$, where n and T denotes the polymer density and temperature, respectively.[9,16] Therefore, although many microscopic details are no longer accessible, knowledge of x provides not only some information on the nonequilibrium structure on the coarse-grained scale but also on the rheology. Crucial to a thermodynamically consistent coarse-graining scheme is a clear separation of time scales between the microscopic and chosen coarse-grained (macroscopic) level.[12,17] Given this separation of time scale holds, the dynamical equations for the macroscopic variables take the GENERIC form[9,16]

$$x_{(1)} = M(x)\cdot\frac{\delta S}{\delta x} \qquad (1)$$

where $x_{(1)}$ denotes the upper-convected derivative of x, $S(x)$ the macroscopic entropy, and M a symmetric, positive semi-definite friction matrix, describing viscous dissipation, diffusion, and other irreversible relaxation processes. From projection operator derivation of Eqn. (1), the friction matrix is given by a generalized Green-Kubo formula $M = 1/2\tau_{\mathrm{s}} <\Delta\Pi\Delta\Pi>$, where $\Delta\Pi$ denote the fast fluctuations of the instantaneous gyration tensor components.[9] The time τ_{s} should be chosen larger than the time scale of the fast motions but shorter than the slow dynamics of the macroscopic variables. The existence of such a separating time scale is an essential gradient of our method and needs to be checked carefully as we did in refs. [7,8]. Within this setting, we devised in ref. [7] a coarse-graining scheme, where we determine self-consistently the building blocks x, M, and $\delta S/\delta x$ form the stationary solution to Eqn. (1) for a series of given flow fields. The friction matrix M is evaluated with the help of molecular dynamics simulations from the above Green-Kubo formula. Since the dynamical equations are integrated only for a rather short time τ_{s}, we need neither a thermostat nor flow-adapted boundary conditions. Since we are working in a nonequilibrium ensemble corresponding to the chosen flow situation, we use Monte-Carlo simulations in a generalized canonical ensemble in order to prepare the appropriate initial conditions. The details of this method can be found in ref. [7].

Results and Discussion

Thermodynamically Guided Simulations for Flowing Polymers

We consider planar shear flow and different elongational flows for various flow rates. For each flow condition, we find the stationary solution of Eqn. (1) self-consistently by balancing the convective terms (the details of the flow conditions enter *via* the velocity gradients in the upper-convected derivative) with the dissipative, relaxation contribution. Our numerical results for structural and rheological properties are in good quantitative agreement with reference results obtained *via* standard nonequilibrium molecular dynamics simulations.[7,8] Fig. 2 shows the zero-shear rate viscosity $\eta_0 = \sigma_{12}/\gamma$ and first normal stress coefficient $\Psi_1 = (\sigma_{11} - \sigma_{22})/\gamma^2$ (for vanishingly small shear rates γ) as a function of chain length N. The theoretically expected scalings $\eta_0 \sim N$ and $\Psi_1 \sim N^3$ are obeyed to very good accuracy. A word of caution seems in order here: for longer

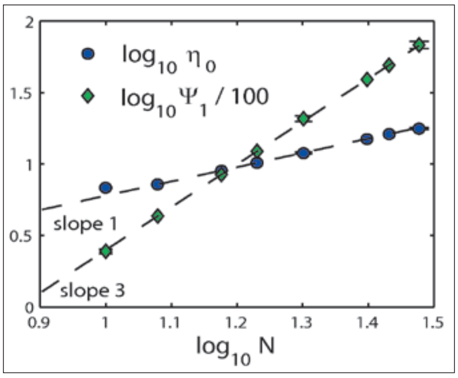

Fig. 2. Zero-shear rate viscosity η_0 and scaled first normal stress coefficient Ψ_1 as a function of chain length on a double-logarithmic scale. Symbols denote simulation results, while dashed lines are the theoretical predictions. Adapted from ref. [7].

chain lengths *N*, a crossover to a different *N*-dependence is observed due to entanglement effects.[6,15] This regime, however, requires a different coarse-grained description and is therefore outside the scope of conformation tensor models.

Also the nonlinear rheological behavior is correctly recovered with our method up to a critical flow rate. At this rate, the flow is strong enough to cause a breakdown of the time scale separation needed in our approach. Fig. 3 shows the shear viscosity η in planar shear flow as a function of shear rate γ. For low shear rates, a Newtonian plateau is observed with a rate-independent viscosity η_0. For shear rates larger than a characteristic rate γ_c, the viscosity starts to decrease considerably. This shear-thinning behavior is typical for the nonlinear rheology of polymer melts. For increasing lengths of polymer chains, the characteristic rate γ_c shifts to smaller values, *i.e.* the characteristic relaxation times become longer. These and similar findings for elongational flows are not only in qualitative agreement with reference results from nonequilibrium molecular dynamics simulations, also the numerical values are in very good agreement.[7]

Nonequilibrium Entropy and Friction Matrix

With the accurate results of the thermodynamically guided simulations at hand, we now proceed to reconstruct the constitutive equations. Thereby we benefit from the analytically known form of the reversible part of the equations in terms of the upper-convected derivative, see Eqn. (1) and ref. [16]. Due to the thermodynamic framework we are working in, the remaining task is divided in two parts: obtaining functional expressions for (i) the nonequilibrium entropy and (ii) the friction matrix.

Let us start with issue (i). From our numerical results for the entropy gradients $\delta S/\delta x$ in Eqn. (1), we obtain the nonequilibrium entropy $S(x)$ *via* thermodynamic integration. Due to frame invariance, the entropy $S(x)$ cannot depend on individual components of the tensor x but only on the three tensorial invariants of x, which can be chosen as $I_1 = \mathrm{tr}(x)$, $I_2 = 1/2[\mathrm{tr}(x.x) - \mathrm{tr}(x)^2]$, $I_3 = \det(x)$. Since polymer chains in the melt show almost ideal behavior, we use the entropy function of ideal chains $S_0(x)$ as a first approximations.[9,15] We find that the effective spring force for the gyration tensor is actually anharmonic, as expected for real, finite-length chains.[18] Therefore, we seek for corrections ΔS to the ideal entropy of the form $S(x) = S_0(x) + \Delta S(I_1)$. Fig. 4 shows that a quadratic ansatz for $\Delta S(I_1)$, $I_1 = R_G^2$, *i.e.* a quartic potential in the gyration radius, describes our numerical data quite well. Note, that the data shown are obtained for very different flow conditions and that ΔS in general depends also on the second and third tensorial invariant of x. Nevertheless, our simple ansatz is found to be quite adequate as the dependence of ΔS on the other two invariants is rather weak. It is interesting to note that the effective spring potential resulting from our nonequilibrium entropy was predicted analytically in ref. [18] from a perturbation analysis around ideal chain behavior for finite-length chains. Therefore, the deeper reason for the validity of the simple entropy form is probably the dominant leading-order correction to ideal chain behavior due to finite chain length.

We now turn to the remaining issue (ii) and attempt to find a functional form for the friction matrix M that reproduces our numerical values for the different components of this fourth-rank tensor. The simplest form for the matrix M that is in agreement with the symmetries of this quantity is given by $M = \nu x_0^2(11)_{\mathrm{sym}}$ with the relaxation frequency ν and $x_0 = R_G^2$ the equilibrium value of the gyration radius. The three-dimensional unit matrix is indicated by 1 and $(A)_{\mathrm{sym}}$ denotes proper symmetrization of the matrix A. This form, however, is found to describe our numerical data well only very close to equilibrium. In order to get an idea about necessary generalizations of M, let us model the fast bead fluctuations of $\Delta\Pi$ in the Green-Kubo formula by Gaussian noise. Then, one finds that M is of the form $M = \nu x_0(x1)_{\mathrm{sym}} + \mu(xx)_{sym}$, where the additional relaxation frequency μ is related to anisotropic bead diffusion under flow. Such a term has recently been incorporated in the friction matrix within a phenomenological constitutive model[19]

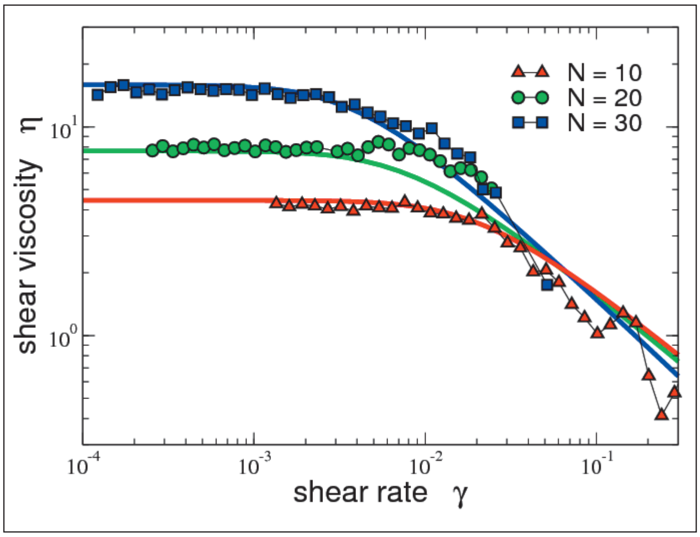

Fig. 3. Shear viscosity η as a function of shear rate for chain lengths of N = 10, 20, and 30 on a double-logarithmic scale. Symbols denote results of thermodynamically guided simulations, while lines are the results of the constitutive model, Eqns. (2) and (3).

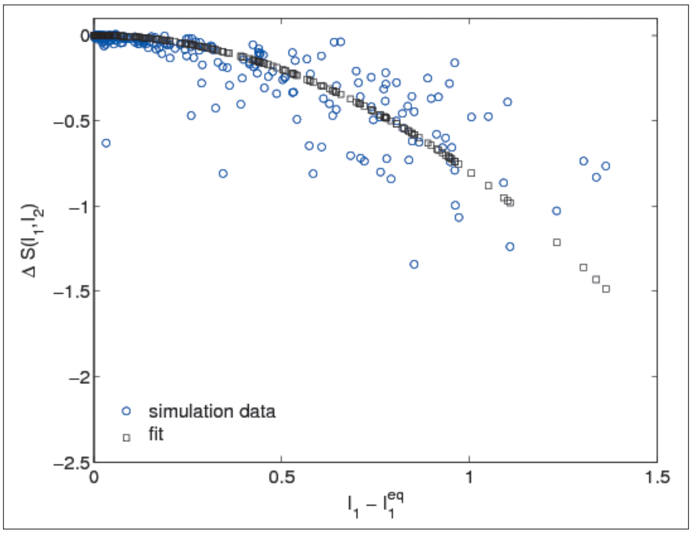

Fig. 4. Deviation of the nonequilibrium entropy from the entropy of ideal chains as a function of relative chain stretching.

and earlier already for semi-dilute polymer solutions.[20,21] Very recently, anisotropic diffusion has been observed in nonequilibrium molecular dynamics simulations of the present model system when subjected to planar shear or elongational flow.[22] We find that this extended form of *M* captures our numerical results for all components rather well. From a least-square fit, we obtain numerical values for the two relaxation frequencies ν and μ.[10]

Reconstructed Constitutive Equations

With the nonequilibrium entropy and the friction matrix at hand, we are now in a position to write down the closed form constitutive equation. Inserting the expressions for $S(x)$ and $M(x)$ into the general evolution equation (1) we obtain

$$x_{(1)} = (4\nu x_0 I + 2\mu x)\cdot(\Theta_3 I + \Theta_1 x), \qquad (2)$$

where the coefficients of the entropy gradient are given by $\Theta_1 = \delta S/\delta I_1$ and $\Theta_3 = I_3 \delta S/\delta I_3$. All coefficients of the time evolution equation (2) have been previously determined. Eqn. (2) for the conformation tensor is supplemented by the expression for the polymer contribution to the stress tensor $\sigma(x)$ given above, which now becomes

$$\sigma = -2nkT(\Theta_1 x - \Theta_{10} x_0), \qquad (3)$$

Θ_{10} being the value of Θ_1 in equilibrium. The predictions of the constitutive equations for the stationary state in simple shear flow are shown as lines in Fig. 3. Good agreement with the numerical results from our thermodynamically guided simulations is observed as long as the shear rate is not too large. Fig. 5 shows the prediction of the constitutive model (2, 3) for various stress components in start-up of steady shear flow. Also shown is the ratio of the first and second normal stress coefficient $\Psi_1 = (\sigma_{11}-\sigma_{22})/\gamma^2$, $\Psi_2 = (\sigma_{22}-\sigma_{33})/\gamma^2$. All these quantities show a smooth stress increase for low shear rates and the development of stress overshoots for higher rates. Besides a huge gain in efficiency, a great advantage of constitutive models like the one proposed here, Eqns. (2) and (3), is that it can be applied to arbitrary flow fields. This is in sharp contrast to standard nonequilibrium molecular dynamics simulations, that lack appropriate boundary conditions for all but the simplest flows. In order to illustrate this point, Fig. 6 shows the viscometric functions shear viscosity, η, and scaled elongational viscosities, H_1, and H_2 for various types of flows. The elongational viscosities are defined by $H_1 = \eta_1/[2(2+p)]$, $H_2 = \eta_2/[2(1+p)]$, where the two viscosity coefficients are given by $\eta_1 = (\sigma_{11}-\sigma_{33})/\varepsilon$ and $\eta_2 = (\sigma_{22}-\sigma_{33})/\varepsilon$. The different elongational flows correspond to uniaxial ($p = -0.5$), planar ($p = 0$), elliptical ($p = 0.5$), and equibiaxial elongation ($p = 1$). The notation is taken from ref. [23]. The viscosities are scaled in such a way that they should all approach the same value η_0 for vanishing flow rates. This behavior is expected theoretically from the retarded motion expansion[15] and has been confirmed experimentally[23] and by molecular dynamics simulations[5] for some selected flows. Convergence of the scaled viscosities towards a common value for low rates is also found from our thermodynamically guided simulations[8] and it is also present in the constitutive model proposed here, see Fig. 6. We have shown that this result is not fortuitous but that our constitutive equation can be interpreted as a generalization of the well-known Gieskus model[6,21] and reduces to the latter in weak flows.[10]

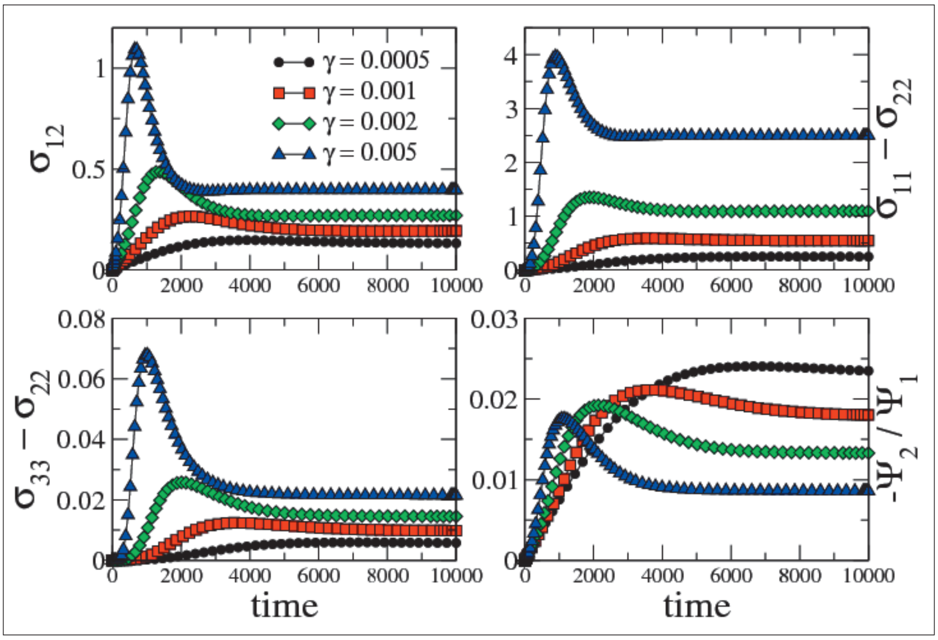

Fig. 5. Transient stress components in start-up of steady shear flow as a function of time as predicted by the constitutive Eqns. (2) and (3). As the shear rate increases, characteristic stress overshoots are observed.

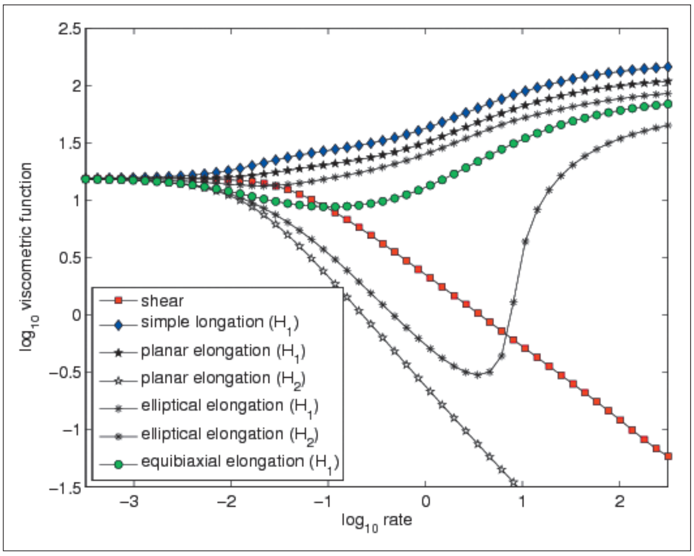

Fig. 6. The viscometric functions, *i.e.* the scaled viscosities η, H_1, H_2 defined in the text for shear (■) and different elongational flows are shown as a function of dimensionless flow rate. The elongational flows are simple elongation (◆), planar elongation (★,☆), elliptical elongation (✲,✱), and equibiaxial elongation (●). Strong shear thinning behavior is observed, whereas the polymer melt strain hardens in most elongational flows, except in planar elongation. Data are shown on a double-logarithmic scale.

Conclusions

Starting out with a systematic coarse-graining strategy applied to a low-molecular weight model polymer melt,[7] we have reconstructed the explicit form of the equation of change of the conformation tensor and provide an expression for the stress tensor in terms of polymer conformation. While the reversible part of the time evolution equations follows from the definition of the conformation tensor in terms of particle coordinates, the irreversible part had been evaluated directly from short molecular dynamics runs, short compared to the system's longest relaxation time. Initial configurations of the molecular dynamics runs have been prepared *via* Monte Carlo simulations in a generalized canonical ensemble, which is self-consistently determined by the systematic coarse-graining strategy. Upon employing an invariant formulation, where entropy is considered as a function of the three tensorial invariants of the conformation tensor, and inspired by analytical expressions for entropy and friction matrix from simple models, we reconstruct the form of the constitutive equations, Eqns. (2) und (3). These are a closed time evolution equations for the conformation tensor as well as a conformation-dependent expression for the stress tensor.

Values for numerical parameters ν, μ (characterizing the friction matrix), and Θ_1, Θ_3 (characterizing the entropy and its gradient) appearing in these expressions have been obtained for the FENE model polymer melts through coarse-graining. The proposed constitutive model has a number of attractive features. In the limit of weak flows, the classical Giesekus model is recovered, whereas generalizations of the latter appear for stronger flows. This analogy provides an effective relaxation time, which tends to decrease with increasing flow rate.[10] We have demonstrated how to obtain the few parameters of constitutive equation from a microscopic model – this bridges the huge gap between microscopic and macroscopic time scales. Once determined, we have hereby offered a molecular interpretation of the material parameters. Some of these parameters have previously been proposed on phenomenological grounds and treated as fit parameters.[19] With the presented work, the proposed, thermodynamically admissible, coarse-graining scheme has been applied successfully towards the development of closed, constitutive model, which could be of direct use in complex flow solvers.

Acknowledgements

I am grateful for valuable discussions with Martin Kröger and Hans Christian Öttinger. ETH Zurich is acknowledged for the financial support.

Received: January 24, 2011

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