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Quantitative predictions of the linear viscoelastic properties of entangled polyethylene and polybutadiene melts via modified versions of modern tube models on the basis of atomistic simulation data

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ABSTRACT

We present a hierarchical, three-step methodology for predicting the linear viscoelastic properties of entangled polymer melts. First, atomistic trajectories accumulated in the course of long molecular dynamics simulations with moderately entangled polymer melts are self-consistently mapped onto the tube model to compute the segment survival probability function $\psi(s, t)$ for primitive paths. Extracted directly from the atomistic simulations, the computed $\psi(s, t)$ accounts for all possible dynamic mechanisms affecting chain motion in entangled polymers such as reptation, contour length fluctuation, and constraint release. In a second step, the simulation predictions for $\psi(s, t)$ are compared with modern versions of the tube model, such as the dual constraint model of Pattamaprom et al. and the Leygue et al. model; the comparison reveals ways through which the two models can be improved and parameterized on the basis of the direct molecular simulation data. The key parameters turn out to be the entanglement chain length N_e and the entanglement time τ_e, both of which can be reliably extracted from the simulations. In a third step, the modified versions of the two models are invoked to predict the linear viscoelastic properties of the polymer under study over a broad range of molecular weights. The power of the new methodology is illustrated here for the case of linear polyethylene (PE) and cis- and trans-1,4 polybutadiene (PB) melts for which atomistic molecular dynamics data have already been obtained recently. We present results from the new approach for the zero-shear-rate viscosity η_0, and the storage G' and loss G'' moduli of the three polymers as a function of their molecular weight (MW), and a direct comparison with experimentally measured rheological data.

1. Introduction

Dynamics and rheology in entangled polymeric liquids is governed by topological constraints known as entanglements which dominate molecular forces and prevent chains from crossing one the other. Despite the complexity of the corresponding interactions, the pioneering works of Edwards, de Gennes and Doi [1–6] demonstrated that one can account for uncrossability constraints with a simple but powerful mean-field theory known as reptation. The reptation theory is built on the concept of the tube model defining a space around the chain within which this is allowed to execute motion. Over the years, the tube model coupled with mechanisms such as reptation, constraint release, contour length fluctuations and arm retraction in the case of branched molecules has developed to a quantitative theory for the description of the key rheological properties of polymers, especially in the linear viscoelastic regime [7]. Entangled melts of monodisperse and polydisperse linear polymer chains, of star and H-shaped polymers, and of long- and short-chain branched chains can all be described rather quantitatively in the framework of such a model.

Reptation involves a geometric reduction from the phase space of the detailed chain to that of its primitive path (PP). The PP is the shortest path that connects the two ends of the chain (which are considered as fixed in space) and follows the main chain contour without violating any topological constraints along the chain from one end to the other. The following two quantities are then introduced: the diameter d_t of the tube (effectively representing the strength of the topological constraints on chain dynamics) and the contour length L of the PP. From a mathematical point of view, the most fundamental quantity in the theory is the tube segment probability function $\psi(s, t)$ [1,2,5]. This is defined as the probability that a segment s along the PP contour will remain inside the initial tube after a time t; it can also be considered as the average probability that the corresponding PP segment has fully relaxed

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the stress initially imposed on it after a time t. If this function is known, all linear viscoelastic (LVE) properties of the system can be obtained in a rather straightforward manner [1].

For chain reptation in the space of fixed obstacles, $\psi(s, t)$ obeys a typical diffusion equation with appropriate initial and boundary conditions. For chain reptation in a polymer melt, one should further account for the fact that neighboring chains are not fixed obstacles but they move too, thereby continuously destroying and creating new entanglements. The chain itself also changes its conformation as it diffuses through the melt, and this causes fluctuations in its contour length. Thus, for the tube model to quantitatively describe the dynamics of real polymer melts, it has to account further for mechanisms such as contour length fluctuation (CLF) [8] due to the "breathing" motion of chain ends and constraint release (CR) related to the destruction of topological constraints due to the relaxation of chains surrounding the reference chain (or the tube itself) [9].

It is thus not surprising that, since the 1970s when the reptation picture and the tube concept were introduced, the tube model has undergone numerous modifications [7], most of them motivated either by the need to bring model predictions into a quantitative comparison with experimental data for model systems or by the need to describe more complicated chain architectures. Two such typical models are the dual constraint model of Pattamaprom et al. [10] and the Leygue et al. model [11]. These models can indeed offer quantitative predictions of directly measured rheological data for a variety of polymer architectures, but often this comes with the need to assume non-realistic values for some of the fundamental model parameters. We mention, for example, the value of the entanglement time τ_e (strictly defined as the time after which a polymer chain starts to feel the tube constraints) typically chosen to fit experimental data [10,12,13]. For polyethelene (PE) at 177 °C and polybutadiene (PB) at 140 °C, τ_e is computed from direct molecular dynamics (MD) simulations to be about 3 and 2–4 ns, respectively [12–16]. By making use of the temperature shift factor a_T reported by Raju et al. [17] for PE and Colby et al. [18] for PB, the corresponding values are 3.75 ns for PE at 190 °C and 44–65 ns for PB at 25 °C which differ appreciably from the values (7 ns for PE at 190 °C and 350 ns for PB at 28 °C) needed for modern tube models to fit experimental data [10].

A remarkable development recently has been the computation of the function $\psi(s, t)$ describing the survival probability of PP segments directly from atomistic molecular dynamics (MD) data [12–16]. The methodology (which accounts directly for CLF and CR mechanisms) first maps long atomistic MD trajectories onto time trajectories of primitive chains and then documents primitive chain motion in terms of a curvilinear diffusion in a tube-like region around the coarse-grained chain contour. In the calculations, the effective tube diameter is independently evaluated by observing the effect of tube constraints either on atomistic displacements or on the displacement of primitive chain segments orthogonal to the initial PP. The approach accounts both for chain reptation longitudinally inside the constraining tube as well as for local transverse fluctuations driven from constraint release and regeneration mechanisms, the latter causing parts of the chain to venture outside the average tube surface for certain periods of time. The new approach opened the way to bridging the outcome of direct MD simulations with tube models, since both can be compared on the basis of their prediction for the tube segment probability function $\psi(s, t)$ of the same system [12–16]. Furthermore, it allows one to utilize the results of the direct PP analysis in order to propose modifications to the models [16].

Our effort in this paper is to capitalize on this work and develop a systematic methodology that will enable the direct computation of the LVE properties of high-MW polymer melts by properly transferring information from lower-level (atomistic MD) simulations to closed-form tube models having the form of a reaction–diffusion-like partial differential equation.

Our paper has been structured as follows: In the following section we provide a concise summary of the modifications (see Ref. [16] for more details) made to the tube models (the dual constraint and the Leygue et al. ones) employed here to describe the rheological properties of long polymer melts. The corresponding original versions of these models have been presented in the Appendix of Ref. [12]. Here, we only note that, as far as the dual constraint model is concerned, wherever in that Appendix we had used $1 - cs$, here we replace it by s, because in the original model $s \in \left[-\frac{1}{c}, \frac{1}{c}\right]$ with $c = 2$ for a linear chain, whereas here and in Refs. [12–16] $s \in [0, 1]$. In Section 3 we provide some details of the numerical methodology used to solve the two models along with the values of the parameters employed in each one of them and of what experimental data we compared their predictions with. The paper proceeds with Section 4 where the major results are presented and concludes with Section 5 discussing the most important conclusions and future directions.

2. Brief account of the modified dual constraint and Leygue et al. models

2.1. The modified dual constraint model

In the modified dual constraint or Pattamaprom et al. model, the reaction–diffusion equation in solved in two stages. In the first stage, the equation incorporates only chain reptation and CLF effects but omits CR (i.e., it initially considers chain motion in a fixed tube):

$$\frac{\partial}{\partial t}\psi^*(s,t) = \frac{1}{\pi^2\tau_d}\frac{\partial^2}{\partial s^2}\psi^*(s,t) - \frac{1}{\tau^*(s)}\psi^*(s,t), \tag{1a}$$

where

$$\begin{aligned} &\tau_{\text{early}}(s) = \tau_e + \left(\tfrac{3\pi^{3/2}Z}{4c^2}s^2\right)^{\beta}\tau_R, \\ &\tau^*_{\text{late}}(s) = \tfrac{\tau_R}{c^2}\exp[U^*(s)], \\ &U^*(s) = \tfrac{3}{2}\tfrac{Z}{c}s^2, \end{aligned} \tag{1b}$$

with the value of the exponent $\beta = (2b)^{-1}$ taken from the scaling $\phi(t) \sim t^b$ when $\tau_e < t < \tau_R$, and $c = 2$ for a linear chain. The partial differential equation (PDE) Eq. (1a) is subject to the following initial and boundary conditions:

$$\begin{aligned} &\psi^*(s, t = 0) = 1 \\ &\psi^*(s = 0, t) = \psi^*(s = 1, t) = \exp(-t/\tau_e) \end{aligned}. \tag{1c}$$

The newly introduced boundary condition in the last equation is obtained, self-consistently, directly from (1a) by considering the case of times $t \ll \tau_d$ for which the reptation term in (1a) represented by the second derivative may be safely neglected [16]. Then, one obtains as a solution the function $\psi^*(s, t) = \exp[-t/\tau(s)]$. Since close to chain ends early fluctuations prevail, $\tau(s) = \tau_{\text{early}} \Rightarrow \tau(0) = \tau(1) = \tau_e$, thus $\psi^*(0, t) = \psi^*(1, t) = \exp(-t/\tau_e)$. Such a time dependence has indeed been observed in simulations [12–16]. The expressions for the early- and late-time CLF effects have been borrowed from the works of Doi [8] and Milner and McLeish, [19] respectively (see also the original papers of Pattamaprom et al. [10] for more details). $\tau^*(s)$, on the other hand, is given by

$$\tau^*(s) = \begin{cases} \tau_{\text{early}}(s) & \text{for } s < C_1^*, \\ \sqrt{\tau_{\text{early}}(s)\tau^*_{\text{late}}(s)} & \text{for } C_1^* < s < C_2^*, \\ \tau^*_{\text{late}}(s) & \text{for } s < C_2^*, \end{cases} \tag{1d}$$

where C_1^* denotes the segment position close to chain ends corresponding to the first crossover of τ_{early} to τ^*_{late} and C_2^* the segment position for the second crossover of τ_{early} to τ^*_{late} deeper inside the