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MAPPING OF ATOMISTIC SIMULATION DATA FOR THE DYNAMICS OF ENTANGLED POLYMERS ONTO THE TUBE MODEL: CALCULATION OF THE SEGMENTAL SURVIVAL PROBABILITY FUNCTION FOR MONO- AND BI- DISPERSE MELTS AND COMPARISON WITH MODERN TUBE MODELS

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Introduction

Topological constraints, arising from chain and chain uncrossability, are of primary importance for the high molecular weight polymeric liquids which are typically employed in practical polymer processing. However, it is tremendously difficult to consider these topological interactions in a rigorous fashion due to the huge number of degrees of freedom associated with polymer configurations. The problem was considerably simplified by the notion of a confining tube, introduced for the very first time by Edwards and de Gennes, [1] through which a chain can execute a reptation-like motion, as small-length scale fluctuations, irrelevant to the large-scale rheological properties of the polymer, may be neglected. A few years later, Doi and Edwards [2] (DE) developed a more elaborate version of the reptation theory which, since then, has attracted considerable attention and development.

Within the tube notion, the strength of the topological interactions is effectively represented by the effective diameter of the tube d_t. Therefore, our attention is focused on a coarse-grained picture of the real chain, the so-called primitive path (PP); the PP moves back and forth the tube in a snakelike fashion (thus, the term reptation) along its own contour with a curvilinear diffusion coefficient equal to the one of the Rouse chain along the tube. [2] The global rheological behavior of a melt of entangled polymers is essentially assumed to be equally well represented by the dynamics of the ensemble of their PPs (small scale fluctuations being omitted) whose motion is thought to be confined within the tube. The fundamental ingredient of the DE reptation theory is the function $\psi(s,t)$ which represents the probability that the original tube segment s remains within the tube the original tube (the tube at time t=0) after a time t. The overall tube survival probability function, $\Psi(t) \equiv \int_0^1 \psi(s,t)\,ds$, underlies all linear viscoelastic (LVE) properties of the polymer. [2]

Although the reptation theory has shown to be prominently successful, the predictions for the rheological properties of a polymer melt are diverging from known experimental results: the reptation theory predicts $\tau_d \sim N^3$ for the reptation (or disentanglement) time, $\eta_0 \sim N^3$ for the zero-shear viscosity, and $D_G \sim N^{-2}$ for the chain center-of-mass diffusion coefficient, where N denotes the chain length, diverges from the experimentally measured scalings, namely [3] $\tau_d \sim N^{3.4}$, $\eta_0 \sim N^{3.4}$ and $D_G \sim N^{-2.2}$. Thus, additional relaxational mechanisms for entangled chains besides reptation were introduced. Two such mechanisms are contour length fluctuations (CLF) and constraint release (CR). The former (CLFs) accounts for the thermal fluctuations of the PP contour and is considered as a single-chain phenomenon. The latter (CR) refers to the release of constraints confining the chain due to the relaxation of the surrounding chains and is perhaps the least understood of all relaxation mechanisms

because (in contrast to CLFs, for example) in order to describe it one needs to consider the collective motion of all chains. [4]

Despite the efforts to effectively introduce CLF and CR effects in the tube model, two key issues of the theory over the years remained open: (a) given the atomistic detail of a polymeric liquids, how to obtain the topological state in terms of PPs, and (b) how to extract the function $\psi(s,t)$, which lies at the heart of the tube theory. The paramount tool to address both of these questions is computer-guided experiments in which the full phase-space information (positions and velocities of all the atoms) in time is provided at any level of the description needed. An answer to question (a) has been given by Everaers et al., Tzoumanekas and Theodorou, and Kröger and co-workers (see Refs [5] and [6]).

We have recently provided [7] the first answer to question (b), namely the calculation of $\psi(s,t)$ by employing a methodology that reduces trajectories from atomistic molecular dynamics (MD) simulations to trajectories of primitive chains, followed by a geometric and dynamical mapping onto the tube model. The resulting zero-shear viscosity of moderately entangled polymer melts (linear polyethylene, linear cis-1,4-polybutadiene, and linear trans-1,4-polybutadiene) are in agreement with experimental data.[7] The methodology automatically accounts for CLF and CR phenomena, since the primitive path network at each instant is obtained by tracing first the microscopic dynamics of the system (by solving Newton's equations of motion in the course of long MD simulations) and then reducing each of the accumulated configurations to a representation in terms of shortest paths of the same topology as chains themselves relative to entanglements.

We have further conducted [8] a comparison of the obtained $\psi(s,t)$ against modern differential tube models that take into account both CLF and CR mechanisms. Certain quantitative (and sometimes even qualitative) discrepancies between the simulation results and theoretical models have been found, uggesting the need to revisit and refine modern tube models.

This paper is organized as follows: at first we present results from our approach for monodisperse (or polydisperse with a very small polydispersity index) polymer melt systems and a comparison with modern tube models. We also report results for the storage and loss moduli obtained from our dynamical mapping methodology and compare them with experimental data. Then, we present results for binary polymer mixtures (systems composed of long and short polymer chains) where results in favor of tube dilution are presented and suggest that the CR effect is strongly dependent on matrix chain length and concentration (or volume fraction ϕ_p of probe chains). [9] Finally, we present some of the conclusions of our study.

MONODISPRESE SYSTEMS

The methodology is reported in Ref [7] and will not be repeated here; the interest reader is referred to Ref [7] for methodological details and for the value of the tube diameter for each simulated system (see Table I in Ref [7]). In Refs [7] and [8] we have applied our methodology to three types of moderately entangled linear polymer melts [polyethylene (PE), *cis*-1,4-polybutadiene (PB), and *trans*-1,4- PB] of various molecular weights. Figure 1 displays a comparison of the functions $\psi(s,t)$ and $\Psi(t)$ between different polymer melts having the same number of monomers but a different number of entanglements per chain (Z=2.77, 3.36, and 5.26 for PB-*cis* 400, PB-*trans* 400, and PE 400, respectively) due to their different chemical structure. The $\psi(s,t)$ graphs, displayed in Fig. 1(a), show that for the very early times ($t=0.01\tau_d$), most of the middle segments of the primitive chains remain

inside the initial tube, whereas most of the outer segments (especially those closer to the two ends) have
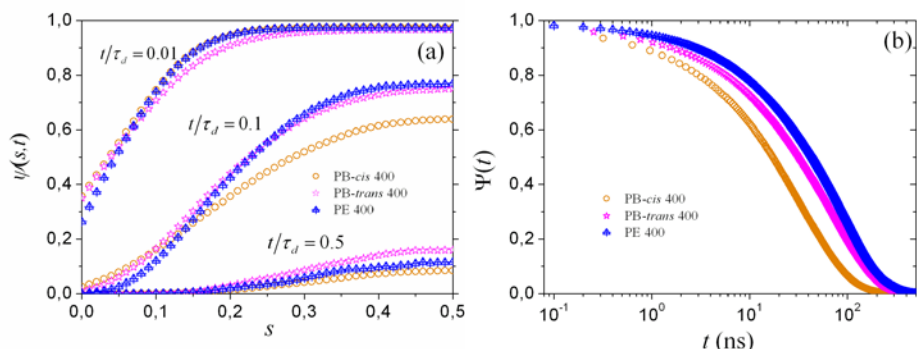

Figure 1. (a) Typical plots of the function $\psi(s,t)$ describing the probability that a primitive segment s remains in the initial tube after time t (scaled by the reptation time τ_d) , as computed from the new methodology for systems with the same number of monomers, but with different number of entanglements ($Z=2.77$, 3.36, and 5.26 for PB-*cis* 400, PB-trans 400, and PE 400, respectively). (b) Typical plots of the function $\Psi(t)$ representing the fraction of primitive chain that has remained in the initial tube after a time t for the same systems.
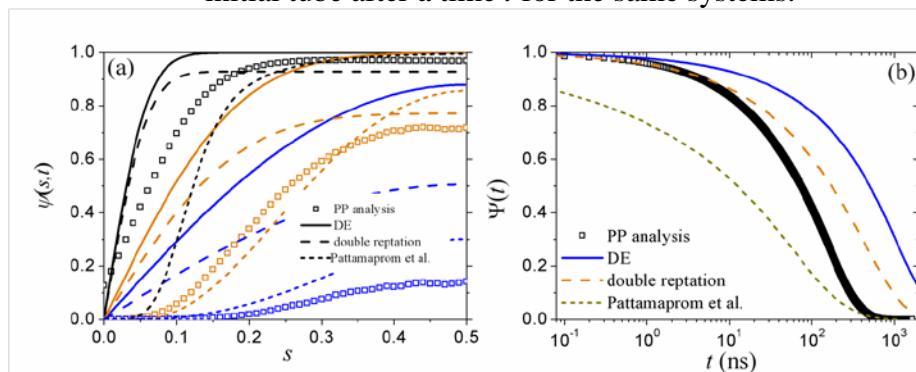

Figure 2. Comparison of the results of the PP analysis for PE 500 ($Z=6.67$ and $\tau_d{\approx}1042$ ns [7]) against the DE, double reptation [10] and Pattamaprom et al. [11] tube models at the level of: (a) the $\psi(s,t)$ function (black: $t=0.01\tau_d$, orange: $t=0.1\tau_d$ and blue: $t=0.35\tau_d$), and (b) the $\Psi(t)$ function.
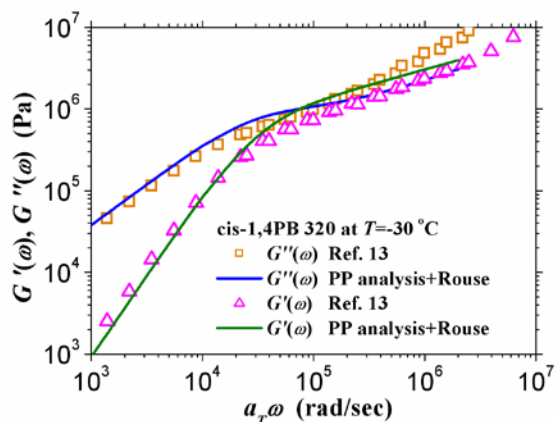

Figure 3. Computed spectra of storage and loss moduli as obtained from the present PP analysis for the PB-*cis*320 system (MW=4322 g/mol) and comparison with the experimental data of Ref [13] for a *cis-*

1,4-PB system with a similar molecular weight (MW=4400 g/mol). Rouse mode contributions have been accounted for according to Ref. [14] (see text).

escaped. As time elapses, the entire $\psi(s,t)$ curve is shown to reduce. Furthermore, after about half the reptation time chains are seen to have almost completely escaped the original tube, a feature attributed to CR effects. The corresponding results for the $\Psi(t)$ function for the same systems are shown in Figure 1(b), which are consistent with the estimated numbers for their average number of entanglements per chain, Z, reported above; i.e., in the system with the smaller Z value, the function $\Psi(t)$ relaxes faster with time.

The comparison with the DE,double reptation (DR) [10] and Pattamaprom et al. [11] tube models with the computed values for the $\psi(s,t)$ and $\Psi(t)$ for the PE 500 system (Z=6.67 [7]) are presented in Figure 2. For the Pattamaprom et al. model we used τ_R=125 ns. [12] The DE and DR models are observed to predict higher $\psi(s,t)$ values for all segments compared to the PP analysis at early times, especially for segments near chain ends, which is quite reasonable since they do not account for CLF effects. The disagreement between theoretical models and the our PP analysis is seen to get larger at later times. On the other hand, the Pattamaprom et al. model, that also accounts for CLF effects in addition to CR, predicts lower $\psi(s,t)$ values compared to the PP analysis at early times, especially for the segments closer to the chain ends. As times elapses, however, the relaxation of the PP analysis results is faster than that observed from the Pattamaprom et al. model.

Lastly, in Fig. 3 we compare our PP analysis predictions for the dynamic moduli for the PB-cis320 system with reported experimental data. [13] The plateau modulus has been calculated by making use of the following formula: [2]

$$G_N^0 = \frac{4}{5} \frac{\rho RT}{M} \frac{\langle L \rangle}{\langle a_s \rangle}. \tag{3}$$

Rouse mode contributions have been accounted for by employing Milner and McLeish expression: [14]

$$G_{Rouse}(t) = \frac{G_N^0}{Z} \left[\frac{1}{3} \sum_{i=1}^{Z} \exp\left(-\frac{2p^2 t}{\tau_R} \right) + \sum_{i=Z+1}^{N} \exp\left(-\frac{2p^2 t}{\tau_R} \right) \right]. \tag{4}$$

The agreement appears to be quite favorable, further supporting the validity of our computational PP analysis.

BIDISPRESE SYSTEMS

Bidisperse polymer melts (mixtures of two chemically identical and strictly monodisperse types of chain which differ only in their molecular weight) is a prototypical system for studying CR effects since one is able to control rather accurately the life times of entanglements on a few probe chains by varying the lengths of the two components or their volume fraction. Numerous experimental studies [15] have shown that the dynamics of these probe chain is greatly affected by their environment, namely the length of the matrix chains and the relative concentration of long and short chains. We have shown that the CLF effect is only negligibly affected by the matrix chain length and the volume fraction of the probe chain, ϕ_p. [9] We may then conclude that any differences observed in the dynamics of the probe chains in the various systems should be mainly attributed to CR. Thus, studying the dynamics of bidisperse systems provides the means for quantifying CR effects.

Our data support the hypothesis of *tube dilation* (i.e., the increase in d_t) in bidisperse melts: we got estimates of d_t around the probe C_{600} *cis*-1,4-PB chains from the corresponding atomistic segmental

mean square displacement (msd), and we found that, compared to ~30 Å for the corresponding pure component C_{600} cis-1,4-PB melt [7], its value was: (a) practically the same in all the matrices with
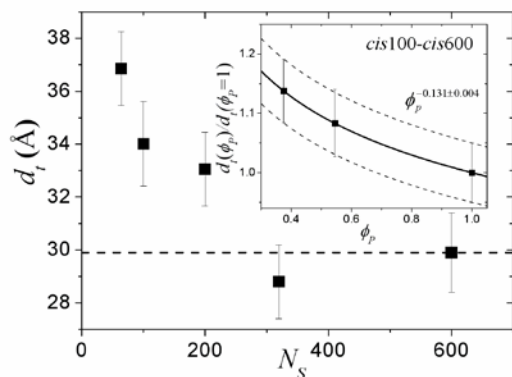

Figure 4. Variation of tube diameter d_t depending on the matrix chain length as determined from the atomistic segmental msd (cf. Fig. 1 in Ref. [7]). The inset shows its dependence on volume fraction ϕ_p of C_{600} cis-1,4-PB probe chains in the $cis100$-$cis600$ system.
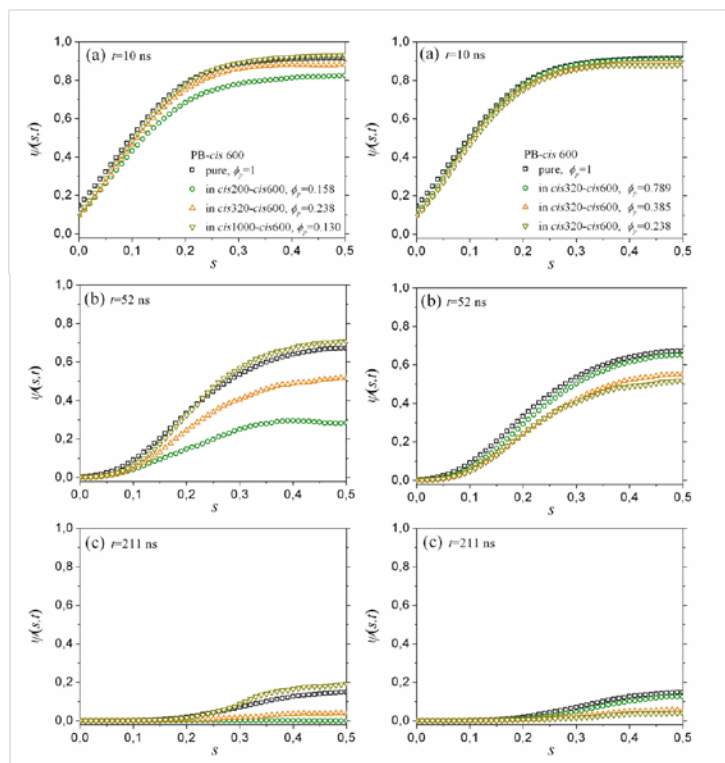

Figure 5. Computed $\psi(s,t)$ curves for the C_{600} cis-1,4-PB probe chains with respect to matrix chain length (left) and matrix composition (right). Simulation results for $\psi(s,t)$ are shown at three times: (a) early ($t = 10$ ns), (b) intermediate ($t = 52$ ns), and (c) late ($t = 211$ ns).

molecular weight well above M_e, and (b) larger in all the matrices with molecular weight below M_e (corresponding to C_{144} cis-1,4-PB chain) [see Fig. 4]. These results agree remarkably well with the theoretical ideas of Viovy et al. [16], although the extent $d_t(\phi_p)/d_t(\phi_p = 1)$ of tube dilation appears to

be quite slower [e.g., $\sim \phi_p^{-0.13}$ for the *cis*100-*cis*600 systems (inset of Fig. 4)] than the theoretical prediction ($\sim \phi_p^{-0.5}$); this seems to indicate a gradual transition of the presence of topological interactions by chains of molecular weight around M_e instead of an abrupt behavior (i.e., the Heaviside unit step function) assumed in the theory.

In Fig. 5 we plot the computed profiles for the C_{600} *cis*-PB probe chains in different matrices with respect to matrix chain length (left side) and matrix composition (right side) at three time instances: (a) an early (t=10 ns) corresponding approximately to $4\tau_e$, (b) an intermediate (t=52 ns) corresponding approximately to τ_d/10 ($\approx 23\tau_e$), and (c) a late (t=211 ns) corresponding approximately to τ_d/2 ($\approx 92\tau_e$). Here τ_e and τ_d denote the characteristic chain entanglement and disentanglement times, respectively, in the pure component PB-*cis*600 melt. Based on simulation data for the msd of the atomistic units their numerical values are τ_e=2.3±0.8 ns and τ_d=500±70 ns [7], at T=413 K and P=1 atm. Our results reveal that at short times the $\psi(s,t)$ curves for the *cis*320-*cis*600 and cis1000-cis600 systems are practically identical to those for the pure component melt, indicating that probe chains do not distinguish (dynamically) between matrices of different chain length, as long as these matrices are composed of chains longer than C_{320} *cis*-PB; this is equivalent to saying that probe chains feel the same topological network at these early times corroborating the absence of any CR effects associated with the relaxation of the C_{320} matrix chains; this is further evident from the independence of $\psi(s,t)$ on volume fraction ϕ_p in the *cis*320-*cis*600 system at t=10 ns . In contrast, CR is important in the *cis*200-*cis*600 system for the corresponding $\psi(s,t)$ curve comes out to be well below that in the pure component system. It is related to the fast relaxation of the shorter C_{200} *cis*-PB matrix chains, especially for segments away from the two chain ends (i.e., for 0.1<s<0.9); close to chain ends, CLF effects dominate. This piece of information from our simulations indicates the need to consider different rates of relaxation for different segments along the primitive chain in theoretical tube models for a better comparison with computed or experimentally measured data.

The $\psi(s,t)$ results for the probe chains at the intermediate time (t=52 ns) are displayed in Fig. 5(b). The $\psi(s,t)$ curves in the *cis*320-*cis*600 and *cis*200-*cis*600 melts are below that in the pure component melt, a direct consequence of the faster relaxation of the matrix chains themselves (C_{200} *cis*-PB chains relax faster than C_{320} *cis*-PB, as also confirmed by the values of the corresponding longest relaxation times at T=413 K and P=1 atm: $\tau_d \approx 55$ ns for the PB-*cis*200 melt and $\tau_d \approx 140$ ns for the PB-*cis*320 melt). Figure 2(b) (left side) also shows that the $\psi(s,t)$ curve for the probe C_{600} PB chains in the *cis*1000-*cis*600 system is only marginally above that in the pure component PB-*cis*600 melt. By comparison, at the intermediate time t=52 ns [Fig. 5(b) (right side)], the $\psi(s,t)$ curves in the binary systems with ϕ_p=0.238 and 0.385 display values considerably smaller compared to the pure component melt. For the system with the highest concentration in probe chains (ϕ_p=0.789), on the other hand, the computed $\psi(s,t)$ curves are close to those in the pure component melt.

Figure 5(c) shows the results for the relaxation of the C_{600} PB probe chains in the different polymer matrices at a later time ($\sim\tau_d$/2) where the $\psi(s,t)$ curves start approaching zero. By this time, the short matrix chains (C_{200} and C_{320}) have completely relaxed; C_{600} *cis*-PB chains themselves have also relaxed to a good degree. As a result, the corresponding $\psi(s,t)$ values in the *cis*200-*cis*600 and *cis*320-*cis*600 systems are almost zero for all segments. The corresponding results for the effect of matrix composition are shown in Fig. 2(c) (right side): in the systems with ϕ_p=0.238 and 0.385, we notice that $\psi(s,t) \approx 0, \forall s$ implying that all C_{320} matrix chains have fully relaxed. [In the system with ϕ_p=0.789, on the other hand, probe chains behave similarly to those in the pure component melt (they relax only slightly faster)]. The graphs of Fig. 5(c) confirm once more that differences in the values of the $\psi(s,t)$

curves referring to the various binary mixtures and to the pure component melt (i.e., CR effects) are less significant for small values of *s*.

CONCLUTIONS

We have reported computational results for the most fundamental quantity of the reptation theory, namely the segment survival probability function $\psi(s,t)$ and its average $\Psi(t)$, from simulations with model monodisperse and bidisperse *cis*-1,4-PB systems. We have also compared our results with the predictions of modern tube models in order to test their capability to correctly account for CLF and CR effects. The computed dynamic moduli of the PB-cis320 system are seen to be in good agreement with experimental findings. Computed results for the functions $\psi(s,t)$ and $\Psi(t)$ for C600 *cis*-PB probe chains in different binary mixtures have revealed the significant role of the CR mechanism in the rheological behavior of entangled polymer systems; the role of CR is weak only for segments closer to chains ends due to the dominant effect of CLFs there. Furthermore, we observed that the CLF effect is almost independent of the matrix environment. [9] Future tasks involve the extension to polymeric systems under flow to help understand the role of the so called convective constraint release (CCR) mechanism to melt dynamics.

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