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Hierarchical Modeling of Entangled Polymers

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Summary: We demonstrate that it is possible to link multi-chain molecular dynamics simulations with the tube model using a single chain slip-links model as a bridge. This hierarchical approach allows significant speed up of simulations, permitting us to span the time scales relevant for a comparison with the tube theory. Fitting the mean-square displacement of individual monomers in molecular dynamics simulations with the slip-spring model, we show that it is possible to predict the stress relaxation. Then, we analyze the stress relaxation from slip-spring simulations in the framework of the tube theory. In the absence of constraint release, we establish that the relaxation modulus can be decomposed as the sum of contributions from fast and longitudinal Rouse modes, and tube survival. Finally, we discuss some open questions regarding possible future directions that could be profitable in rendering the tube model quantitative, even for mildly entangled polymers.

Keywords: entanglements; polymer rheology; simulations; tube theory

Introduction

The ultimate goal of computer simulations in material science is to predict material properties at human timescales (seconds to hours) from the knowledge of the atomic structure.[1] To predict the dynamic properties of polymeric materials starting from atomistic details, the time step of the simulation has to be of the order of $2\,fs$.[2,3] Usual multi-chain simulations consist of 10^7–10^8 steps, thus the maximum time reached is of the order of hundreds of nanoseconds. The natural way to speed up the calculations is to coarsegrain several atoms inside a repeat unit into one or several repeat units along the chain into one blob[4] and derive the interaction potential between these coarsegrained units.[3] Coarsegraining m beads into one along the chain typically speeds up the simulations by at least a factor of m^3 (m because there are less particles to simulate and m^2 because one can use a bigger time step). The additional speed-up is usually achieved because the potentials become significantly softer, allowing even larger timesteps. However, very soon along this path the coarsegrained potential becomes too soft and does not prevent chains from passing through each other, thus losing all the effects due to entanglements. So far, the maximum reported speed up comparing coarsegrained to all atom simulations was 1600^2.

Fig. 1 shows the time range and maximum number of entanglements Z simulated so far for 4 different polymers. Maximum time reached is of order of hundred τ_e, and the maximum number of entanglements is 5 for polyethylene and 20 for polycarbonate. Note that the longest relaxation time scales as $Z^3\tau_e$ for linear chains and as $\tau_e \exp(\nu Z)$ for branched chains ($\nu \approx 0.6$), where Z is the number of entanglements. One can easily see that simulations reaching even $1000\tau_e$ will not be sufficient to predict the rheology of well entangled linear or branched polymers.

The usual way forward with entangled polymers is to use the tube theory for long time modeling, obtaining the parameters for the tube theory from molecular dynamics (MD) simulations.[8] However, the tube theory is not valid (at least quantitatively)

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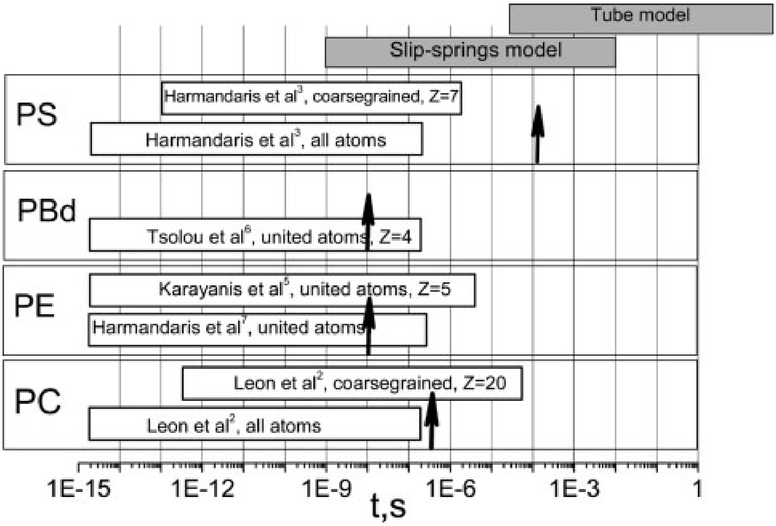

Figure 1.
The timescale of state-of-the-art MD simulations of four different polymers: polycarbonate, polyethylene, polybutadiene and polystyrene. Characteristic entanglement time τ_e is indicated approximately by the arrows. Areas of applicability of slip-spring and tube models are also shown approximately for the first three polymers.

for mildly entangled polymers,[9] and fitting the different simulation quantities leads to different tube parameters.[10,11] The reason for this is twofold. First, the tube theory assumes one-dimensional dynamics for the chain inside the tube, which might be true only for times much longer than τ_e (i.e. hundreds of τ_e) and for very entangled chains ($Z \sim 100$ or more). Second, the tube theory does not specify an explicit construction of the tube field, leaving open the possibility of multiple interpretations when applied to different experiments.

An alternative approach to coarsegraining was developed in ref.[4], but it involves rather complicated algorithms and the origin of the microscopic stress expression and its separation into intra- and interchain components are not very clear.

In this paper, we show that the slip-spring model[12] can serve as an intermediate between multi-chain MD simulations and the tube theory. Conceptually, this model is similar to the tube picture, including reptation, contour-length fluctuations and constraint release. However, it has two significant advantages: it contains an explicit expression for the entanglement field and it provides detailed information about all observables, which can be compared with MD simulations and the tube theory. Compared to the most coarsegrained MD, it enables a much needed speed-up by at least a factor of 1000, allowing simulations of long enough chains for an accurate comparison with the tube theory. In the next section, we briefly describe the slip-spring model. Then, we demonstrate that using mean-square displacements (MSD) of each monomer from MD we can obtain all the parameters for the slip-spring model, achieving simultaneous fits of MSD and stress relaxation. Then, we compare the stress relaxation from the slip-spring model with the tube theory, decomposing the stress contribution from different processes and extracting tube theory parameters, appropriate for our MD system.

Slip-Spring Model

Recently, a single chain model for entangled polymers, inspired by previous models

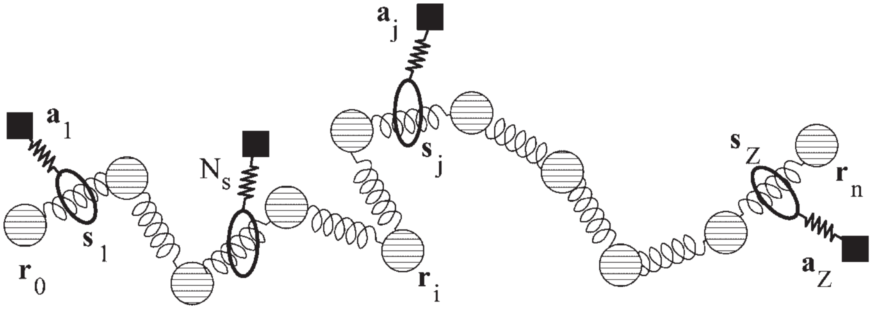

Figure 2.
Slip-spring model of entangled polymers: a standard Rouse chain of $N+1$ beads is constrained by a set of Z discrete virtual springs.

for networks[13] (see Fig. 2), was introduced by one of us.[12] The basic building block of the model is a Rouse chain of $N+1$ beads. The topological confinement field acting on the chain is introduced in a discrete manner as a set of virtual springs of N_s monomers each. These springs have one end attached to anchoring points $\mathbf{a}_j$ fixed in space, and the other end connected to a position $\mathbf{s}_j$ on the Gaussian chain by means of slip-links, which allow reptation-like motion. On average, there is a slip-link every N_e beads. The model contains all the mechanisms present in the tube model (fast Rouse relaxation, longitudinal modes, reptation, and constraint release) and has 3 parameters: N_e, N_s (the combination of which determine the plateau modulus), and ζ_s, the friction of the slip-links on their motion along the chain contour. For further details see reference.[12]

Using the potential energy of the chain/virtual spring system, the stochastic equations of motion for both the beads and the slip-links, as well as the expression for the stress tensor, can be derived. Disentanglement and re-entanglement are accomplished by the destruction and the creation of slip-links at the chain ends. During constraint release, entanglements are approximated as binary events and their number is held constant during the simulations (reasonable for a large number of chains at equilibrium). Some of the mechanisms, like reptation, constraint release and the sliding movement of the slip-links, can be deactivated to isolate their contribution to the relaxation of the chains. The slip-spring equations of motion do not yet have an analytical solution, but can be solved numerically to the desired accuracy with no uncontrolled approximations by means of Brownian dynamics simulations.

Comparison with Molecular Dynamics Simulations

Motivation

In an earlier paper, the slip-spring model was compared to experimental data from five different polymers.[12] This comparison suggested that the model could account for the major dynamical features that are generic to entangled "flexible" synthetic polymers in the linear regime. Also, the model could describe the transition from the unentangled to the entangled regime, which the tube theory cannot at present do. Further, the more ambitious task of simultaneously describing the results from several experiments using the *same* set of parameters was attempted. This was successful for some polymers but not for others[12] and several possible reasons were discussed. In order to understand the slip-spring model better and identify the reasons for both its successes and its failures, we decided to perform a systematic comparison with MD data. MD has the advantage that, unlike experiments, detailed information about the microscopic dynamics is easily accessible and this can be directly compared to the monomer motion in the slip-spring model. Like the tube model, the slip-spring model lacks a microscopic foundation. This becomes apparent if one attempts to extend the slip-spring model to the non-linear regime in a consistent manner. Therefore, in this work, we present initial comparison of the slip-spring model with MD data in the linear regime. Similar in spirit to ref.[12], here we attempt to choose appropriate parameters to match the monomer motions from the slip-spring model to those from MD and using the *same* set of parameters, attempt to describe $G(t)$. Our goals in performing such a comparison are three fold: 1) to determine whether the slip-spring model captures the qualitative features of the dynamics of melts as seen in MD and if so, at what time scales, 2) to obtain parameters (N_e and N_s) that can reproduce the dynamics in this range of time and 3) ultimately, to microscopically verify the assumptions used in the construction of the slip-spring model and if needed use input from MD to improve the existing model.

Molecular Dynamics Potential

In this work, we aim to establish the comparison procedure with a relatively simple many-chain system, and then apply it to more realistic systems shown in Fig. 1. To this end, we use the simplest generic bead-spring MD system suitable for polymer melts.[14] Monomeric units are represented as soft spheres of diameter σ and mass m. All of the monomeric units interact via a pairwise purely repulsive truncated and shifted Lennard-Jones potential,

$$U_{\mathrm{LJ}}(r) = \begin{cases} 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \frac{1}{4}\right] & \text{for} \quad r < r_c \\ 0 & \text{for} \quad r \geq r_c \end{cases} \tag{1}$$

where ε is the energy scale of the potential, r is the distance between two interacting monomers and $r_c = 2^{1/6}\sigma$.

The polymers are formed by connecting the monomers with an additional non-linear spring potential given by,

$$U_{\mathrm{FENE}}(r) = -\frac{kR_0^2}{2}\ln\left(1 - \frac{r^2}{R_0^2}\right), \tag{2}$$

where k is the spring constant and R_0 is the maximum extension of the bond between monomers.

The equations of motion are integrated using a velocity-Verlet algorithm in which all monomers are weakly coupled to a Langevin heat bath with coupling $\gamma = 0.5\tau^{-1}$, where $\tau = \sigma(m/\varepsilon)^{1/2}$ and at a temperature $T = \varepsilon/k_B$ (see ref.[14]). The time step for the integration is 0.012τ. For the FENE potential, we use $k = 30\varepsilon/\sigma^2$ and $R_0 = 1.5\sigma$. The parameter choice yields an average bond length of 0.97σ and guarantees sufficiently high linear monomer density along the chain to prevent chains from cutting through each other.

Comparison with MD Data

As mentioned earlier, we would like to compare the multi-chain MD data with that from the slip-spring model. For a successful comparison, two sets of parameters need to be determined for the slip-spring model. Firstly, the observables have to be expressed in a suitable system of units. The first set therefore constitutes the parameters required to map the length and time units of the slip-spring model to that of MD. If we consider chains with the same number of monomers for both the single chain and the multi-chain models, then a natural choice for the length scale mapping is the mean-square end-to-end distance of the chains. This leads to the unit length to be used in the slip-spring model, $b_{sl}^2 \equiv \langle R^2 \rangle_{\mathrm{MD}}/N$. For the mildly entangled melt studied here ($N+1 = 200$), $b_{\mathrm{sl}} = 1.32$. There is no such clear choice for the unit of the time, τ_{sl}. Hence, we leave it as a parameter to be determined by the fits to MD data. The second set of parameters are N_e and N_s. We will determine these two parameters, along with the unit time by fitting the slip-spring model to the MD data.

We have set ourselves the task of simultaneously describing two qualitatively different observables using the same set of parameters. First, we choose an observable that characterizes the dynamics of the system. We will use this data to determine the parameters for the slip-spring model. We will then use the same set of parameters to determine how well the stress relaxation modulus can be determined. For the variable that describes the dynamics, we choose the time dependence of the mean-square monomer displacements, $g_1(i,t)$. This quantity is easily accessible in simulations and there are theoretical predictions in the limit of infinite chains by Doi and Edwards using their tube model (ref.[15], Eqn. (6).112, page 213 for the scaling relationships). Traditionally, simulators have focused on the mean-square displacements averaged either over all the monomers or, if a careful comparison with Doi-Edwards' prediction is desired, only over a few monomers in the middle of the chain.

Usually, the values of N that can be studied by MD are limited to a few times N_e, *i.e.* the chains are only mildly entangled. Further, we know that the motion of the monomers at the ends of the chain is significantly different from those in the middle. These two facts together indicate that $g_1(i,t)$ averaged over all the monomers is unlikely to behave according to theoretical predictions. The average over a few monomers in the middle of the chain indeed agrees better with theory at the scaling level, but this essentially amounts to discarding significant amounts of data that could potentially be useful. With these in mind, we have chosen to compare the mean-square displacements of all the monomers obtained from MD to the slip-spring model. This however leads to distressingly large quantities of data to be plotted. So to reduce it to a manageable level, we have averaged the data over groups of 5 monomers starting from each end. As the two ends of the chain are equivalent, each curve in Fig. 3(a) corresponds to an average over 10 monomers. In order to prevent the plot spanning several decades along the y-axis, we divide $g_1(i,t)$ by the Rouse power law $t^{0.5}$. The MD data for chain length 200 are shown in Fig. 3(a). From the figure we can see that this plot is rich in maxima and minima (as opposed to the boring monotonicity of $g_1(t)$ either averaged over all the monomers or even over only the central monomers). Also, the variation along the y-axis is small enough that the data can be presented in linear scale. These two features in combination present a substantial challenge for any single-chain model. The best fits to the slip-spring model are shown in Fig. 3(a). It is clear that the slip-spring model can actually capture all the features and fit the data to within a few percent. From these fits we obtain $\tau_{\mathrm{sl}} = 33$, $N_e = 35$, $N_s = 7.5$. We then use these parameters to determine $G(t)$[16] and the corresponding plot is shown in Fig. 3(b). The agreement is excellent. Therefore, if we determine the fit parameters that can describe the dynamics of the monomers in a melt, it appears that the relaxation modulus, a macroscopic property, can be reproduced.

We claimed earlier that the slip-spring model can describe the transition from the entangled to the unentangled regime. To see if that is actually the case, we use the same set of parameters determined earlier to calculate the corresponding quantities for an (almost) unentangled melt of $N+1=50$. Fig. 3(c) and 3(d) indicates that although the agreement is slightly poorer for $g_1(i,t)$, it is still within 10% and $G(t)$ is indeed reproduced satisfactorily.

One of the advantages of the slip-spring model mentioned earlier is the speed up compared to multi-chain MD simulations. Naturally, this makes us wonder if further speed up can be achieved by further coarsegraining the slip-spring model. To this end, we consider a chain where m monomers have been grouped into one so that the chain now has $(N+1)/m = N_c$ monomers (rounded to the nearest integer). We correspondingly reduce both N_e and N_s by a factor m. As, by construction, the chain is Gaussian at all length scales, we rescale the unit length by $m^{0.5}$ and the unit

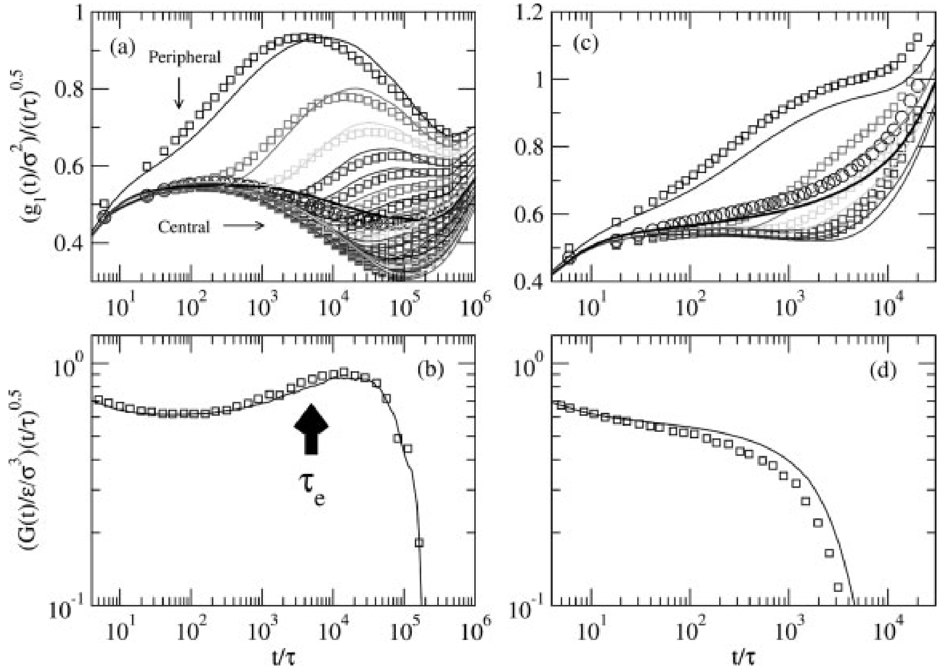

Figure 3.
Mean-square monomer displacements and relaxation modulus for chain lengths 200 and 50 using 1:1 mapping. The $g_1(i,t)$, (see (a) and (c)) obtained from MD is shown as squares and the average over all the monomers is shown in circles. Fits using the slip-spring model are shown as lines and the average is shown as a thick line. Parameters obtained by fitting are used to calculate $G(t)$ (shown as lines) and compared with that obtained from MD (symbols) (see (b) and (d)).

time by m^2. Comparison between the MD and the slip-spring model with this new set of parameters for the case of $m = 5$ is shown in Fig. 4(c) and 4(d). As expected, the coarsegrained model fails miserably at early times, but for $t/\tau > 1000$, the agreement is rather good. We have also verified that the model behaves as expected for both $m = 2.5$ and $m = 10$, so in principle even faster simulations should be possible. However, as the slip-links move in a straight line between monomers using values of $N_e < 1$ is problematic. This presents a natural upper limit to the extent of coarsegraining that can be achieved with the *current* slip-spring model.

Comparison with the Tube Theory

Stress Decomposition

The slip-spring model predicts a complex relaxation modulus that is in very good agreement with experimental measurements of linear unentangled and entangled monodisperse polymers and is consistent with the tube theory predictions[18] for highly entangled systems[12,16] (see Fig. 5).

According to the tube theory,[18] the stress relaxation of a linear monodisperse polymer with N monomers and Z entanglements can be expressed as

$$G(t) = G_e\left(\frac{4}{5}\mu(t)R(t) + \frac{1}{5Z}\sum_{p=1}^{Z-1}\exp\left(-\frac{p^2t}{\tau_R}\right) + \frac{1}{Z}\sum_{p=Z}^{N}\exp\left(-\frac{2p^2t}{\tau_R}\right)\right), \qquad (3)$$

where, G_e is the entanglement modulus and τ_R is the Rouse time of the chain. The first

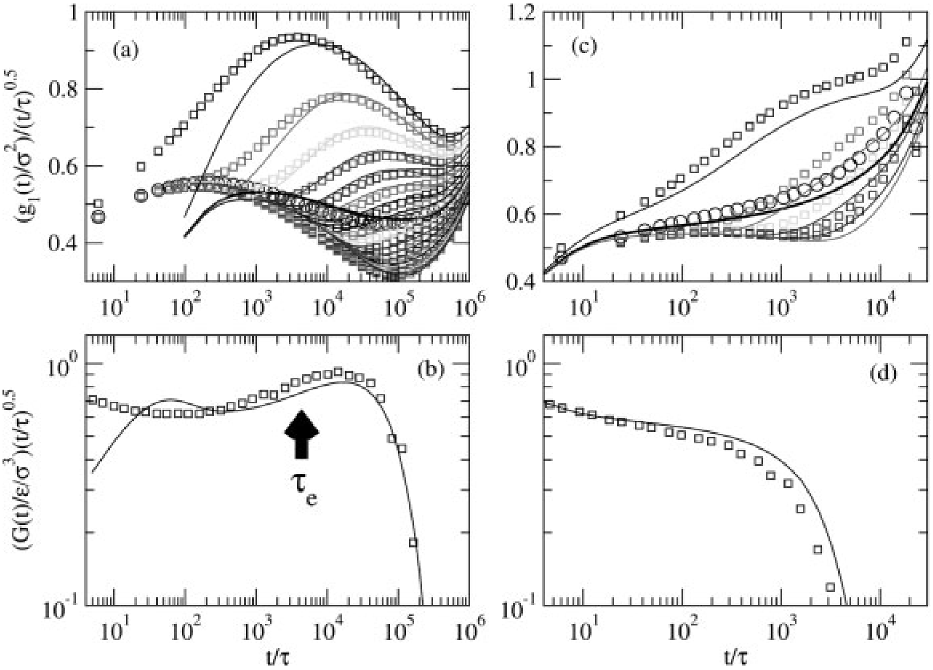

Figure 4.

Mean-square monomer displacements and relaxation modulus for chain lengths 200 and 50 using 1:5 mapping. The $g_1(i,t)$, (see (a) and (c)) obtained from MD is shown as squares and the average over all the monomers is shown in circles. Fits using the slip-spring model are shown as lines and the average is shown as a thick line. Parameters obtained by fitting are used to calculate $G(t)$ (shown as lines) and compared with that obtained from MD (symbols) (see (b) and (d)).

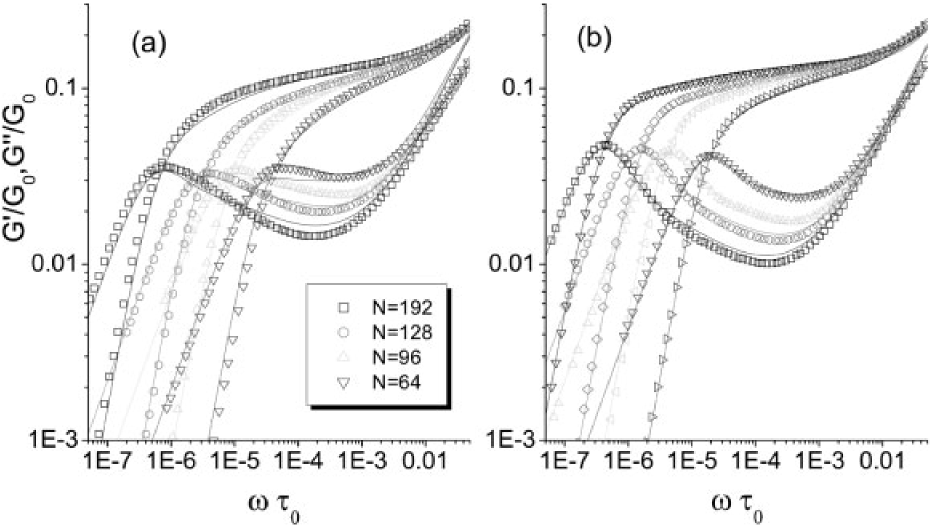

Figure 5.

Complex relaxation modulus from the slip-spring model (symbols, $N_e = 4$, $N_s = 0.5$, $\zeta_s = 0.1$) and best simultaneous fits to the tube theory (lines). (a): with constraint release, the tube theory parameters are $\tau_e/\tau_0 = 51.7$, $G_e/G_0 = 0.18$, $M_e/M_0 = 6.7$, using $c_\nu = 0.1$. (b): without constraint release, $\tau_e/\tau_0 = 44.5$, $G_e/G_0 = 0.17$, $M_e/M_0 = 5.7$, using $c_\nu = 0$.

term in the expression contains information about the chain escaping from the tube. Here, $\mu(t)$ is the fraction of the tube length which was not visited by the chain ends[15] (survived) during time t. $R(t)$ is the tube Rouse relaxation[19,18] quantifying constraint release. The second term describes the contribution to the relaxation modulus from the redistribution of the monomers along the tube after deformation, the so called longitudinal modes, modeled as a 1D Rouse process. Finally, the last term accounts for the relaxation due to the fast Rouse motion of the chain segments inside the tube.

In Eq. (3), the prefactor 4/5 comes from fact that 1/5 of the stress stored in the tube is relaxed after time τ_R by longitudinal modes.[15,18] Two assumptions are needed to obtain this result: 1) the dynamics of the redistribution of the monomers along the tube occurs as a 1D Rouse process and 2) the monomer friction during this 1D motion is equal to the friction experienced by the monomers in a Rouse chain undergoing 3D motion. The slip-spring model rests on none of these assumptions, so we can ask ourselves the question: what are the exact prefactors in the slip-spring model? Can this information be used to correct the tube expression for the stress?

In order to identify the contributions from the dynamic processes in the slip-spring model, and to compare them to the corresponding ones in the tube model, it is useful to decompose the relaxation modulus $G(t)$ from the slip-spring model as a sum similar to Eq. (3). To this end, we propose the following expression for the relaxation modulus of the slip-spring chains,

$$G(t) = G_e\left((1-\phi)\mu(t)R(t) + \frac{\phi}{Z}\sum_{p=1}^{Z-1}\exp\left(-\frac{t}{\lambda\tau_p}\right) + \frac{1}{Z}\sum_{p=Z}^{N}\exp\left(-\frac{2t}{\tau_p}\right)\right), \tag{4}$$

which contains 4 fitting parameters: G_e, ϕ, the amount of stress relaxed by longitudinal modes, M_e, the number of beads in an entanglement segment, related to the number of entanglements by $Z = N/M_e$, and λ, which allows for a different friction of the monomers undergoing 1D motion compared to 3D Rouse motion. τ_p is the relaxation time associated with the exact Rouse mode p.

To make the aforementioned comparison simpler, we switch off constraint release (so that $R(t) = 1$ in Eq. (4)). Then, we need to define the fraction of the original tube associated with the chains that survives at time t, $\mu(t)$. It is germane to note that in order for $G(t)$ to display a plateau, a chain needs to be constrained by at least two slip-links attached to the corresponding anchoring points (one slip-link can only constrain the motion of the center of mass of the chain, but $G(t)$ will not exhibit a rubbery plateau). Further, without constraint release, an appropriately defined $\mu(t)$ must be proportional to $G(t)$ in the terminal region with the prefactor $(1\text{-}\phi)G_e$. A $\mu(t)$ satisfying these criteria can be obtained as follows: define the length of the surviving tube of chain i at an elapsed time t, $L_i(t)$, as the minimum path joining the slip-links that have been constraining chain i for at least t. This yields

$$L_i(t) = \sum_{\substack{\text{slip-liks j living}\\ \text{longer than time t}}} dist(s_j, s_{j+1}). \tag{5}$$

Then, the tube survival fraction for chain i is

$$\mu_i(t) = \frac{L_i(t)}{\langle L(0)\rangle} \tag{6}$$

where the average in the denominator is over all the chains in the system.

In Fig. 6, the complex modulus obtained from the slip-spring model for N = 96 is decomposed as indicated in Eq. (4). The agreement between the $G^*(\omega)$ calculated from the simulations and the sum of the three contributions built from the definition of $\mu(t)$ is almost perfect. This demonstrates that (ignoring constraint release for the

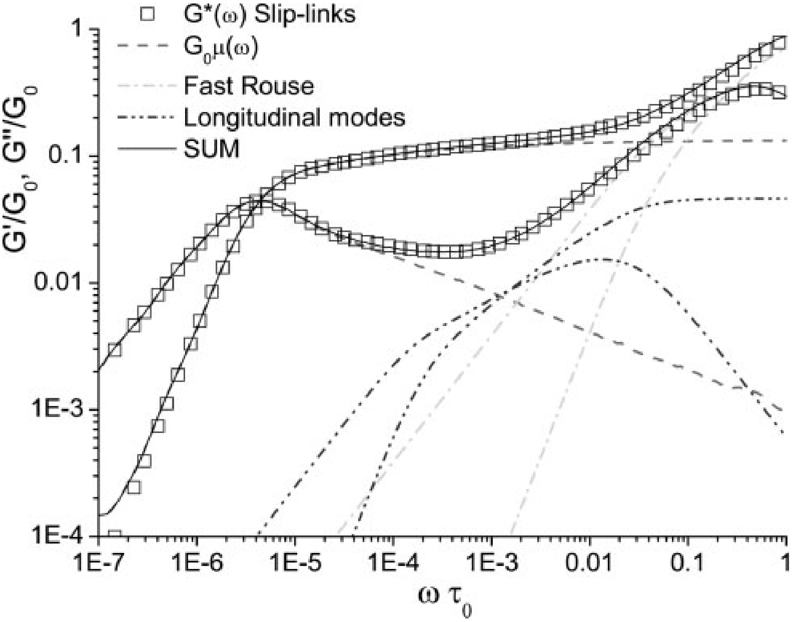

Figure 6.
Decomposition of the complex relaxation modulus from the slip-spring model without constraint release (symbols, $N_e = 4$, $N_s = 0.5$, $\zeta_s = 0.1$), $N = 96$, decomposed into the tube (dashed line), longitudinal (dash-dot-dot) and fast Rouse (dash-dot) contributions. The sum of these three is shown as a solid line and completely agrees with the $G^*(\omega)$ calculated from $G(t)$.

present), although the tube and the slip-spring models are built using different assumptions, they include identical dynamical processes.

We applied the same decomposition to chains with lengths ranging from $N = 8$ to 192, and found that it gives satisfactory results only for sufficiently entangled chains (i.e. for $N > 40$ in this case). The best simultaneous fit for N from 64 to 192 gives $G_e = 0.19$, $M_e = 5.7$ (in excellent agreement with the parameters shown in Fig. 5(b)), $\phi = 0.3$ (in contrast to 1/5 from the tube theory), and $\lambda = 0.7$. The last two parameters suggest that the longitudinal relaxation is more important and occurs faster than the tube theory prediction.

In order to verify these results, the logical next step would be to actually observe the 1D Rouse dynamics during the simulations. This can be accomplished by projecting the coordinates of the beads onto a well defined primitive path or mean path of the chain. Slip-spring's predictions obtained using this definition can then be directly compared to the identical quantity calculated from multi-chain MD simulations. These studies are currently in progress.

Contribution from Constraint Release

Assuming that the longitudinal, fast Rouse modes and the tube escape function $\mu(t)$ are not affected by constraint release, we can approximately calculate the tube Rouse relaxation function $R(t)$ by dividing the relaxation modulus with constraint release, $G^{\mathrm{CR}}(t)$, by the relaxation modulus without constraint release, $G^{\mathrm{No\ CR}}(t)$,

$$R(t) = \frac{G^{CR}(t)}{G^{NoCR}(t)} \tag{7}$$

This relationship is clearly approximate but should hold in the terminal region,

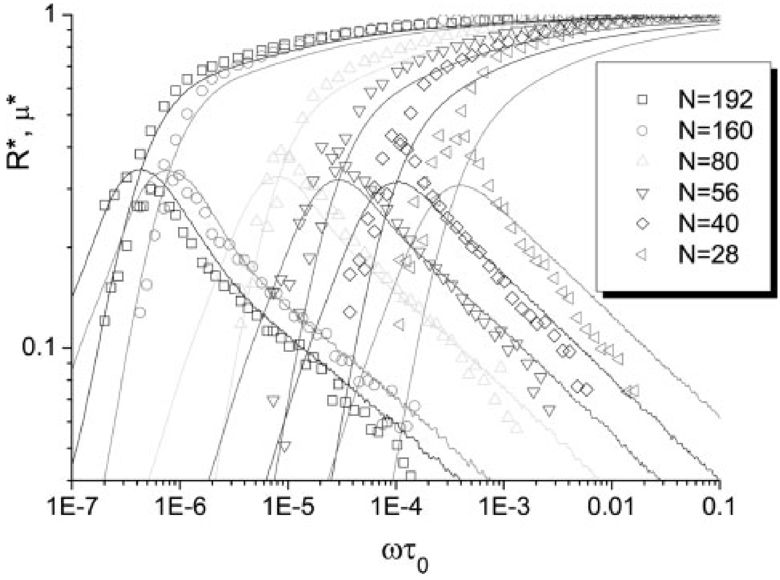

Figure 7.
Fourier transform of *R*(*t*) (Eq. (7)) using the slip-spring model (symbols, $N_e = 4$, $N_s = 0.5$, $\zeta_s = 0.1$). The Fourier transform for the corresponding $\mu(t)$ (lines) without constraint release is also shown.

where contributions from both the longitudinal and fast Rouse processes are negligible. In Fig. 7, the Fourier transform of $R(t)$, as well as $\mu(t)$ from simulations without constraint release are shown. For long chains, the agreement between these functions is striking. This could be interpreted as a validation of the double reptation assumption,[20,21] (which postulates that $G(t) \sim \mu(t)^2$), but it is likely that this is a straightforward consequence of the entanglements being modeled as binary events in the slip-spring model. In addition, for the chain lengths we consider here, theoretical predictions[18] yield similar $R(t)$ and $\mu(t)$. In principle, a better comparison between $R(t)$ and $\mu(t)$ would be possible if more data for $R(t)$ were available beyond the terminal region. It is extremely difficult to obtain this data since $G^{\mathrm{CR}}(t)$ decays much faster than $R(t)$ and consequently the signal from the simulations becomes too noisy. More stringent tests of constraint release models is understanding the stress relaxation of binary blends or of branched polymers. These studies will be performed in the near future.

Conclusions

We have demonstrated that the slip-spring model can serve as a bridge between coarse-grained MD simulations and the tube theory. On the one hand, careful fitting of the mean-square monomer displacement for each monomer yields all the slip-spring parameters. The predicted relaxation modulus is comparable to MD without the need for any further adjustment. On the other hand, slip-spring allow a speed-up of at least a factor of 1000, making it possible to run simulations of chains with 50 entanglements up to $10^6\tau_e$, which is long enough for comparison with the tube theory. In addition, this detailed analysis should lead to improvements and corrections to the tube theories and render them useful even for mildly entangled systems.

Despite this achievement, many open questions still remain for future investigation:

1. What is the best set of observables to choose for a comparison between MD and the slip-spring model in order to ensure that the latter is a reasonable

representation of the multi-chain MD system? In particular, should one look at fluctuations from mean quantities?
2. We intend to repeat our fitting procedure for atomistic MD simulations of real polymers and invite collaborations in this area. Apart from the obvious benefit of having slip-spring parameters for particular chemistry, the interesting question is whether the values of N_e and N_s are proportional to each other for different chemistries and if their ratio is universal (as implicitly assumed in the tube theory).
3. Constraint release is the ad hoc part of the slip-spring model, as the entanglements are *assumed* to be binary. This point needs to be verified using future MD simulations.
4. The slip-spring model has contributions to the stress-stress autocorrelation function from cross-correlations between real springs (the probe chain) and virtual springs (the confining potential due to other chains).[17] In MD, cross-correlations between different chains are also very important[22], but the interrelation between them is not well understood.
5. Once the slip-spring model is verified using MD simulations, its comparison with the tube model should lead to modifications of the latter. This work is currently in progress.

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