

Modeling Entangled Dynamics: Comparison between Stochastic Single-Chain and Multichain Models

Sathish K. Sukumaran^{*,†} and Alexei E. Likhtman[‡]

[†]*Department of Applied Mathematics, University of Leeds, Leeds LS2 9JT, U.K., and* [‡]*Department of Mathematics, University of Reading, Whiteknights, Reading RG6 6AX, U.K.*

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ABSTRACT: To test the effectiveness of stochastic single-chain models in describing the dynamics of entangled polymers, we systematically compare one such model—the *slip-spring* model—to a multichain model solved using stochastic molecular dynamics (MD) simulations (the Kremer–Grest model). The comparison involves investigating if the single-chain model can adequately describe both a microscopic dynamical and a macroscopic rheological quantity for a range of chain lengths. Choosing a particular chain length in the slip-spring model, the parameter values that best reproduce the mean-square displacement of a group of monomers is determined by fitting to MD data. Using the *same* set of parameters we then test if the predictions of the mean-square displacements for other chain lengths agree with the MD calculations. We followed this by a comparison of the time dependent stress relaxation moduli obtained from the two models for a range of chain lengths. After identifying a limitation of the original slip-spring model in describing the static structure of the polymer chain as seen in MD, we remedy this by introducing a pairwise repulsive potential between the monomers in the chains. Poor agreement of the mean-square monomer displacements at short times can be rectified by the use of generalized Langevin equations for the dynamics and resulted in significantly improved agreement.

Introduction

Entangled polymer liquids exhibit diverse rheological properties.¹ At least partly due to their commercial importance, past decades have witnessed considerable activity toward an understanding of these rheological phenomena in terms of the dynamics of the polymer chains. The currently most successful quantitative theory^{2,3} for the dynamics in the linear regime is an improvement on the original tube model of Doi and Edwards.⁴ The original model is based on a specific mechanism, called reptation, for the motion of a polymer in an entangled system and was introduced by de Gennes.⁵ Reptation is the one-dimensional diffusive motion of the chain along the axis of an imaginary tube. It is assumed that the tube strongly confines any chain motion perpendicular to this axis. This tube is thought to represent the topological confinement due to the other chains in the melt and the tube model actually replaces the many chain polymer melt problem by a single-chain enclosed in the tube. Further, on a large length-scale, the conformation of this tube is assumed to be Gaussian. The step length of this object a is also referred to as the tube diameter in the literature. The molecular weight of that portion of the chain whose mean-square end-to-end distance is a^2 is called the entanglement molecular weight, M_e . This can be related to the number of entanglements per chain, defined using $Z \equiv M/M_e$, where M is the molecular weight of the polymer. The tube theory has only one free parameter and given the relationship between these quantities, any one of them can be used for that purpose.

In spite of several successes, the tube model has some serious limitations.^{6–9} As mentioned earlier, the tube model only specifies the large scale structure of the tube. In particular, it assumes that the end-to-end distance of the tube is identical to that of the

chain within it. The finer details of the structure of the tube, especially near a , are left unspecified. For flexible polymers, a is larger than the Kuhn length of the polymer chain and small angle neutron scattering measurements¹⁰ clearly indicate that the structure of a polymer chain in a melt can be well approximated by the Debye function at all length scales larger than the Kuhn length of the chain. These lead to the conclusion that any theory aspiring to describe the dynamics occurring at size scales of the order of the tube step length (for instance, currently available neutron spin-echo observations⁹) while properly accounting for the static structure of the chain at this size scale must include detail at length scales smaller than that specified by the tube model. In other words, the tube model is too coarse grained. Another limitation of the tube model, probably related to the previous one, is that it does not quantitatively describe mildly entangled polymer melts.^{7,11} Also, the dimensions of the tube obtained by fitting the tube theory to different physical quantities lead to different and often inconsistent results^{8,9} (however, in this context see ref 12).

An alternative approach to studying the dynamics of polymers in the melt state is by using MD simulations. These simulations directly deal with the multichain problem; thereby obviating the need for the approximations inherent in the tube model. However, simulations that include atomistic detail^{13–16} and hence enabling direct identification with a particular chemical species require significant computational resources. As the different dynamical processes in well entangled melts span several orders of magnitude in time,^{3,4} it is currently and even for the foreseeable future impossible to perform these simulations up to rheologically relevant time scales. A natural way to speed-up the multichain simulation is to use a coarse grained description for the polymer chain in the melt. The interaction potentials for this description can be obtained by considering either several atoms within a chemical repeat unit^{13,14}—or even several repeat

*Corresponding author. E-mail: sa.k.sukumaran@gmail.com.

units along the chain^{15,16}—as one unit. The coarse grained potentials are softer than the corresponding original potentials. With progressive coarse graining, eventually the interactions between the units are not sufficient to prevent chain crossings and the melt fails to exhibit any signs of entanglements. Therefore, if we are interested in studying the effects of entanglements on the properties of polymer melts using *only* the coarse grained potentials (i.e., without explicitly tracking and preventing chain crossings¹⁷), the aforementioned fact limits the level of coarse graining at which the system can be studied.

If we forego a priori identification with any specific polymer (e.g., polystyrene¹⁶ or polyethylene¹⁴) we could instead use models that focus on the features generic to polymer liquids. Besides the local liquid-like monomer packing, such models should also include polymeric features such as the connectivity between the monomers and chain flexibility, and in addition, to study entanglement effects, the chains must not be able to cut through each other. One such model was extensively studied by Kremer and Grest.¹⁸ Simulations using these models are indeed faster than atomistic simulations and recently linear rheology has been calculated for a mildly entangled polymer (about seven entanglement segments per chain).¹² However, even for this model, direct comparisons with the tube theory² requires simulations of significantly longer chains, and these are not currently feasible.

The above considerations suggest that it would be useful to have a single-chain model that can serve as an intermediate between the multichain MD simulations and the tube theory. This model should include a finer level of detail than the tube model, correctly account for the chain statistics especially around the size scale of the step length of the tube and provide the required speed-up compared to the multichain simulations. A plausible candidate is the recently introduced slip-spring model.⁶ This model includes the same dynamical processes as the tube model, i.e., reptation, contour-length fluctuations and constraint release. However, unlike the tube model, it provides detailed information about all the observables related to the polymer chain and these can be directly compared with both the MD simulations and the tube theory. Also, the slip-spring model is faster by at least 2 orders of magnitude compared to the coarse grained MD. This fact enables simulations of sufficiently long chains for an accurate comparison with the tube theory.¹⁹

In the original publication,⁶ the slip-spring model was compared to the available experimental data (from neutron spin-echo, linear rheology, and diffusion measurements) for five different synthetic polymers. This comparison demonstrated that the model could indeed capture the salient features of the linear dynamics of entangled “flexible” polymers observed in the experimental data. Also, the comparison hinted that the model could qualitatively and potentially quantitatively describe the behavioral transition from the unentangled to the mildly entangled and finally to the well entangled regime. As already mentioned, fitting the tube theory to data from different experiments yield different values for the tube parameters.^{8,9} Therefore, the more ambitious task of using the same set of parameters to simultaneously describe the results from several experiments was attempted. This was partly successful, i.e., such a description was possible for polystyrene, polybutadiene and polyisoprene but not for polyethylene and polyethylene-propylene. A couple of possible reasons for the discrepancy were proposed.⁶ Hence, in order to better understand the slip-spring model and identify the reasons for both its successes and failures, we decided to perform a systematic comparison with MD data. MD has the advantage that detailed information about the dynamics of the monomers and the chains are readily accessible and these can be directly compared to the appropriate quantities in the slip-spring model. Further, linear rheology data of sufficiently good quality

calculated directly from MD simulations under equilibrium are now available.¹²

Like the tube model, the slip-spring model currently lacks a microscopic foundation. This leads to several problems when one attempts to extend the slip-spring model to the nonlinear regime in a consistent manner.²⁰ Therefore, in this work, we present a detailed comparison of the slip-spring model with MD data obtained under equilibrium. Our goals in performing such a comparison are 4-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 for the slip-spring model that can adequately reproduce the dynamics in this range of time, (3) to verify if the slip-spring model can adequately describe data from both unentangled and mildly entangled systems and from different experiments using the same set of parameters, and (4) ultimately, to microscopically verify the assumptions used in the construction of the slip-spring model and, if necessary, use input from MD to improve the existing model.

The rest of the paper is arranged as follows. In the next section, we will introduce both the multichain and the single-chain models that we use. We will follow this with a comparison between the MD data and the slip-spring model. We will then discuss the motivation for and the effect of introducing a pairwise potential between the monomers in the slip-spring model. Finally, we will conclude with a summary and a brief outlook.

Models

Molecular Dynamics. In the present report, we mainly study dense liquids of bead-spring polymers¹⁸ with no intrinsic stiffness. In this model, the chain monomeric units are represented as spheres of diameter σ and mass m . All monomeric units interact via a purely repulsive Lennard-Jones (LJ) potential (excluded volume (EV) interaction)

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

where ϵ is the energy scale of the potential, r is the distance between two interacting monomers and $r_c = 2^{1/6}\sigma$ is the cutoff distance for this potential. The polymers are formed by connecting the monomers with an additional finitely extensible nonlinear elastic (FENE) potential given by,

$$U_{FENE} = -(kR_0^2/2) \log(1 - r^2/R_0^2) \quad (2)$$

where k is the spring constant and R_0 is the maximum allowed extension of the bond between two beads. The equations of motion are integrated using the Verlet algorithm in which all monomers are weakly coupled to a Langevin heat bath with coupling $\Gamma = 0.5\tau^{-1}$, where $\tau = \sigma(m/\epsilon)^{1/2}$ and at a temperature, $T = \epsilon/k_B$.¹⁸ The time step for the integration is $\Delta t = 0.012\tau$. For the FENE potential, we use $k = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$.²¹ The parameter choice yields an average bond length $b \approx 0.97\sigma$ and guarantees sufficiently close contact between connected monomers to prevent chain crossings.

Monodisperse polymer melts of 50–100 chains of length $50 \leq N \leq 350$ at a bead density of $\rho = 0.85\sigma^{-3}$ are studied.¹² Even in the absence of any intrinsic stiffness, these polymer chains are non-Gaussian at short length scales and the mean square internal distances are proportional to $N - 1$ only for $N > 100$. For such chain lengths, the $c_\infty b^2 = \langle R^2 \rangle / (N - 1) = 1.75\sigma^2$.²¹ Here, c_∞ is the Flory characteristic ratio, b is the average bond length, $\langle R^2 \rangle$ is the mean-square end-to-end distance of the chain and N is the number of

monomers in the chain. As described in reference¹² we calculated the mean-square displacement of the monomer i , $g_1(i, t)$, and the time dependent stress relaxation modulus, $G(t)$, for all the systems mentioned above. These data were used for comparisons with the slip-spring model as discussed below.

Slip-Spring Model. Inspired by a previous model for network elasticity,²² a single-chain model to describe the dynamics of entangled polymers was introduced recently.⁶ The basic building block of the model is a Rouse chain of N beads. The confinement due to entanglements is introduced in a discrete manner (unlike in the tube model) using a set of virtual springs of N_s monomers each. One end of each of these springs is fixed in space and the other end is connected to the Rouse chain by a slip-link. On average, there is a slip-link every N_e monomers. The chain can only slide through these slip-links and this ensures that the long time dynamics is dominated by reptation. This model contains all the mechanisms included in the tube model. There are three adjustable parameters: N_e , N_s , and ξ_s , the friction of the slip-links when sliding along the chain contour. Here, only N_e and N_s are varied while fitting the slip-spring model to MD data. For reasons mentioned in ref 6, the ξ_s is fixed at $0.1\xi_0$, where ξ_0 is the bead friction of the Rouse chain.

The stochastic equations of motion for both the beads and the slip-links can be derived from the Hamiltonian of the system. Disentanglement of the chain from a slip-link and re-entanglement with a slip-link are accomplished by the destruction and the creation of slip-links at the chain ends. Constraint release is included by approximating the entanglements as binary events. The total number of entanglements is held constant during the simulations. This is reasonable for a large number of chains at equilibrium; in practice, the large number translates to running the simulations with at least 10 chains that affect each other's dynamics only through constraint release. Some of the mechanisms, like reptation, constraint release and the sliding movement of the slip-links, can be individually 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 and with no uncontrolled approximations by means of Brownian dynamics simulations. For further details about the model and for an important correction to the original publication, see respectively references.^{6,23}

By construction, the polymer chain in the slip-spring model is Gaussian at all length scales. This avoids the problem of incorrect chain statistics around the scale of the tube step length in the tube model. However, as noted above, the polymer chains in the MD simulations are not Gaussian at short length scales. Comparisons with the simplest slip-spring model in the next section are performed cognizant of this fact. In the following section, a pairwise potential between all monomers is introduced to approximate the chain structure observed in MD at all length scales. The effect of such potential on the dynamics will be discussed there.

Original Slip-Spring Model (with No EV Interactions)

Comparison with MD, 1:1 Mapping. In this subsection, we will present a comparison between the multichain MD data and the slip-spring model. For this purpose, we first perform simulations with chains of equal N in both MD and the slip-spring model. For any comparison with MD, two sets of parameters for the slip-spring model need to be

determined. First, the observables from both the models 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. As only the global static structure of the chains are comparable between the two models, a natural choice for the length scale mapping is equating the mean-square end-to-end distance of the chains in the two cases. This leads to the scale factor for the unit length of the slip-spring model, $b_{sl}^2 = \langle R^2 \rangle_{MD} / (N - 1)b^2$. As we are interested in studying the efficacy of the slip-spring model in describing mildly entangled melts, we first consider $N = 200$ (corresponding to $Z \sim 4$, see ref 12). In this case, $b_{sl} = c_\infty^{1/2} = 1.32$. There is no such obvious choice for the scale factor of the unit time, t_{sl} . Hence, we leave it as a fit parameter to be determined from the MD data. The second set of parameters are N_e and N_s . These two parameters, along with the unit time will be determined by fitting the slip-spring model to the MD data.

Similar in spirit to ref 6, we will attempt to simultaneously describe two qualitatively different physical variables using the same set of parameters. First, we choose an observable that characterizes the dynamics of the system to determine the parameters for the slip-spring model appropriate for the MD system under consideration. This parameter set will then be used to calculate $G(t)$ and compared with that obtained from MD. An appropriate variable that at least partially characterizes the dynamics of the monomers in the chain and that can be thought of as the dynamic analogue of the static mean-square internal distances^{12,21} is the time dependent mean-square monomer displacement of monomer i , $g_1(i, t)$. This quantity is readily accessible in simulations and there are theoretical predictions in the limit of infinite chains by Doi and Edwards using their tube model (see ref 4, eq 6.112, p 213 for the scaling relationships). Traditionally, simulations 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. We will argue below that, especially for mildly entangled chains, there is a better option than either of the two mentioned above.

We first calculate the $g_1(i, t)$ of every monomer i in the chain averaged over all the chains in the MD simulation. Unsurprisingly, the amount of data to be analyzed and plotted increases with increasing chain length. We have averaged the data over groups of 5 monomers starting from each end. After this averaging, the index i refers to the numbering of the particular group, see Figure 1. As the

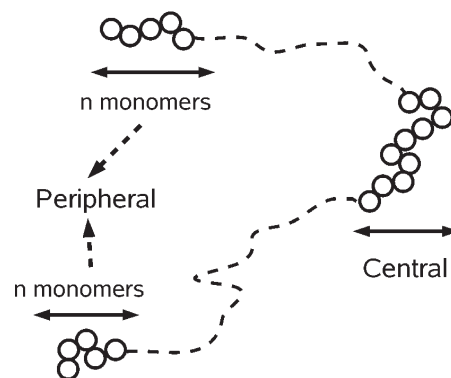


Figure 1. Cartoon representing the monomer grouping procedure used for the shown $g_1(t)$ curves. Data from n monomers are averaged to yield one curve. The curves are numbered starting from the ends until the middle is reached (from 1 to $N/2n$); see, for instance, Figure 2.

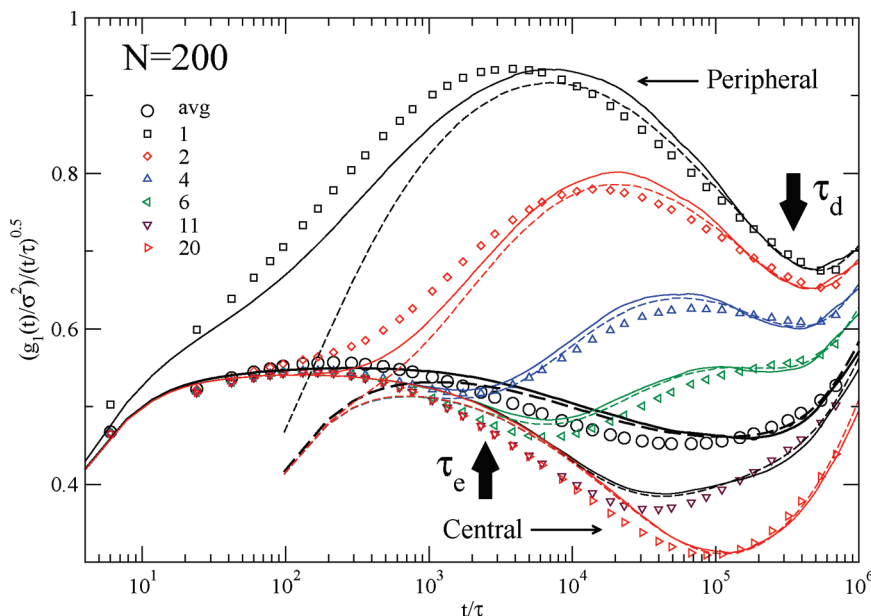


Figure 2. Mean-square monomer displacements and relaxation modulus for $N = 200$ using 1:1 and 1:5 mappings. For selected i , the $g_1(i, t)$ obtained from MD is shown as squares and the average over all the monomers is shown as circles. Fits using the slip-spring model are shown as lines and the average is shown as a thick line. $g_1(i, t)$ for the 1:5 mapping is shown as dashed lines. For an explanation of the numbering, see the caption corresponding to Figure 1.

two ends of the chain are equivalent, each curve in Figure 2 corresponds to an average over 10 monomers. To render the details in the plot clearly visible, besides the group of 10 monomers right at the center of the chain (the symbols labeled “20” for $N = 200$), we have shown only a few other groups of monomers. The symbols labeled “1” correspond to the monomers at the two ends of the chain. In order to accentuate the fine details along the y -axis, we divide this averaged $g_1(i, t)$ by the Rouse power law $t^{0.5}$. Horizontal lines on this plot would correspond to the Rouse prediction for infinitely long chains. The MD data for $N = 200$ are shown in Figure 2 as symbols. From the figure, we can see that the dynamics of the different parts of the chain are sufficiently distinct and exhibit different qualitative features. The data corresponding to the central monomers exhibit one maximum and one minimum (as opposed to the monotonic increase of $g_1(i, t)$). The behavior of some monomers between the ends and the middle is even richer; these display two sets of maxima and minima (for a further discussion of these features, see ref 12). The monomers at the end of the chain are hardly expected to be directly constrained by the entanglements, but they are nonetheless slowed down compared to the Rouse case (as indicated by the minimum) because they are connected to monomers that do experience these constraints. Also, the variation along the y -axis is small enough that the data can be presented in linear scale. Using recently developed software correlators^{12,24} allowed us to obtain data of excellent precision as evidenced by the absence of any discernible noise even in linear scale.

We are now in a position to appreciate why a simultaneous fit to the $g_1(i, t)$ from the different parts of the chain is potentially both a more useful and a more stringent test of the validity of the model than the traditional approaches.^{18,25} Averaging over five monomers from each half of the chain reduces the volume of data to be handled to a more manageable level while preserving the distinctive features of the dynamics of the different parts of the chain. For values of N corresponding to only a few entanglements per chain, the dynamics of a significant portion of the chain is sufficiently different from that of the central monomers. Focusing only

on the average over monomers in the middle of the chain—which does agree well with the scaling predictions of the tube theory^{18,25}—amounts to discarding considerable quantities of data. Discarding this data would be particularly egregious in the case of mildly entangled polymers where the fraction of monomers that exhibit multiple extrema is significant. Quite independent of any reference to the tube theory, this feature could perhaps be used to at least qualitatively distinguish between unentangled, mildly entangled and well entangled systems.

The best fits to the slip-spring model are shown in Figure 2 as solid lines. It is clear that the slip-spring model can quantitatively capture the distinct shape of $g_1(i, t)/t^{1/2}$ from the different parts of the chain to within a few percent. From these fits we obtain $t_{sl} = 1.32$, $N_e = 35$ and $N_s = 7.5$. We then use these parameters to calculate $G(t)$ and the corresponding plot is shown in Figure 6. 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. Next we check if data from different N can be described using the same set of parameters. To this end we use the parameters obtained by fitting $N = 200$, to check if the dynamics and the relaxation modulus of both a less entangled ($N = 100$, $Z \sim 2$) and a more entangled system ($N = 350$, $Z \sim 7$) can be adequately described. The data for the dynamics are shown respectively in Figure 3 and Figure 4 and the $G(t)$ in Figure 6. The excellent agreement of the slip-spring model predictions for both these quantities with the MD data further improves our confidence in the slip-spring model. Finally, we had stated earlier that the slip-spring model could potentially describe the transition from the entangled to the unentangled regime. To verify if this is actually the case, we use the same set of parameters to calculate the corresponding quantities for an (almost) unentangled melt of $N = 50$ ($Z \sim 1$, see ref 12). Figure 5 and Figure 6 indicate that although the agreement is slightly poorer for $g_1(i, t)$, it is still within 10% and $G(t)$ is indeed reproduced satisfactorily.

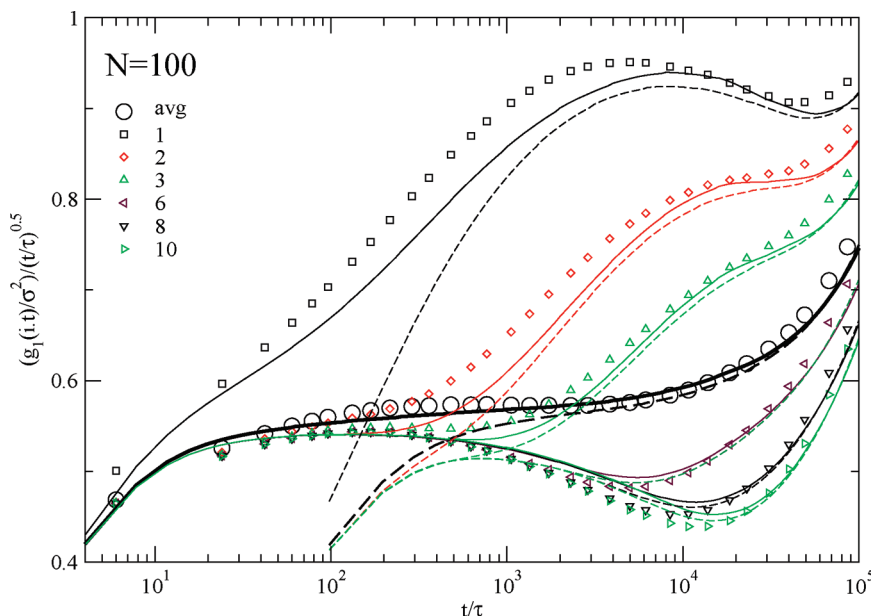


Figure 3. Mean-square monomer displacements and relaxation modulus for $N = 100$ using 1:1 and 1:5 mappings. For selected i , the $g_1(i,t)$ obtained from MD is shown as squares and the average over all the monomers is shown as circles. Fits using the slip-spring model are shown as lines and the average is shown as a thick line. $g_1(i,t)$ for the 1:5 mapping is shown as dashed lines.

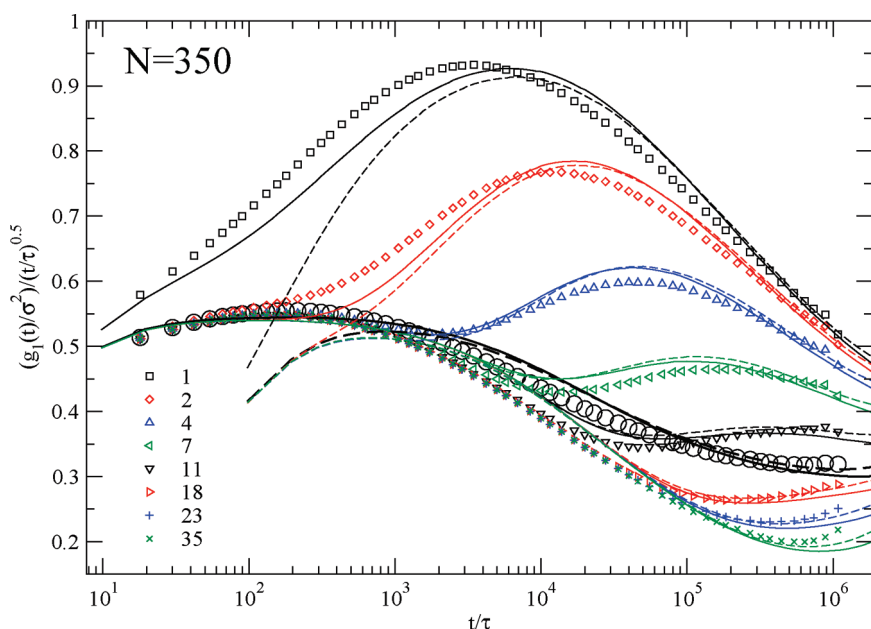


Figure 4. Mean-square monomer displacements and relaxation modulus for $N = 350$ using 1:1 and 1:5 mappings. For selected i , the $g_1(i,t)$ obtained from MD is shown as squares and the average over all the monomers is shown as circles. Fits using the slip-spring model are shown as lines and the average is shown as a thick line. $g_1(i,t)$ for the 1:5 mapping is shown as dashed lines.

A few remarks about the speed-up achieved using the slip-spring model in comparison with MD is in order. We will perform this comparison for the 1:1 mapping hitherto discussed. As we have already mapped the length and the time scales involved in the two models, we will calculate the time (in seconds) required for both to run for a simulation time of 1τ . For the comparison we choose a typical case, $N = 200$. To run for 1τ , the MD simulation¹² takes about 1.84 s whereas the slip-spring model takes about 9.2×10^{-3} s to run on a 2.2 MHz AMD-Athlon X64 processor. For this particular case, this indicates that the slip-spring model is about 200 times faster than the MD.²⁶ This speed-up is due to three factors. First, we perform the MD simulations using 70 chains but the slip-spring simulations using only 10 chains.²⁷ Second, in the slip-spring model, we can use

a time step that is about 16 times larger than that used in MD. The remaining speed-up is due to the fact that the original slip-spring model includes only bonded interactions obviating the need to loop over the nonbonded monomers while calculating the force acting on a particular monomer.

Coarse Graining the Original Slip-Spring Model. As discussed above, one of the advantages of the slip-spring model is the speed-up compared to multichain MD simulations. Naturally, this begets the question if further speed-up (over and above the one obtained by using a single-chain model when compared to multichain MD) can be achieved by coarse graining the slip-spring model. To this end, we consider a slip-spring chain whose every m monomers have been grouped into one. The chain now has only $N/m = N_c$

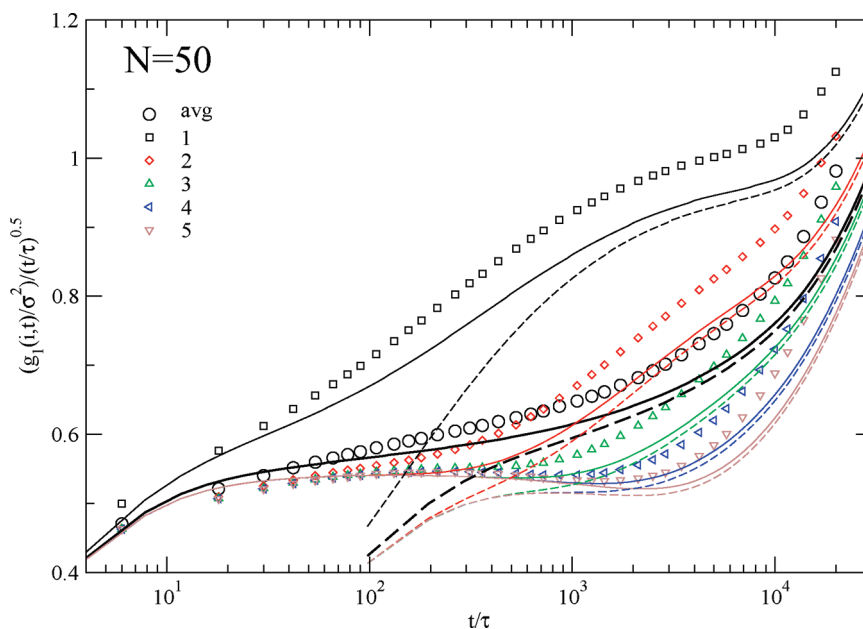


Figure 5. Mean-square monomer displacements and relaxation modulus for $N = 50$ using 1:1 and 1:5 mappings. For selected i , the $g_1(i,t)$ obtained from MD is shown as squares and the average over all the monomers is shown as circles. Fits using the slip-spring model are shown as lines and the average is shown as a thick line. $g_1(i,t)$ for the 1:5 mapping is shown as dashed lines.

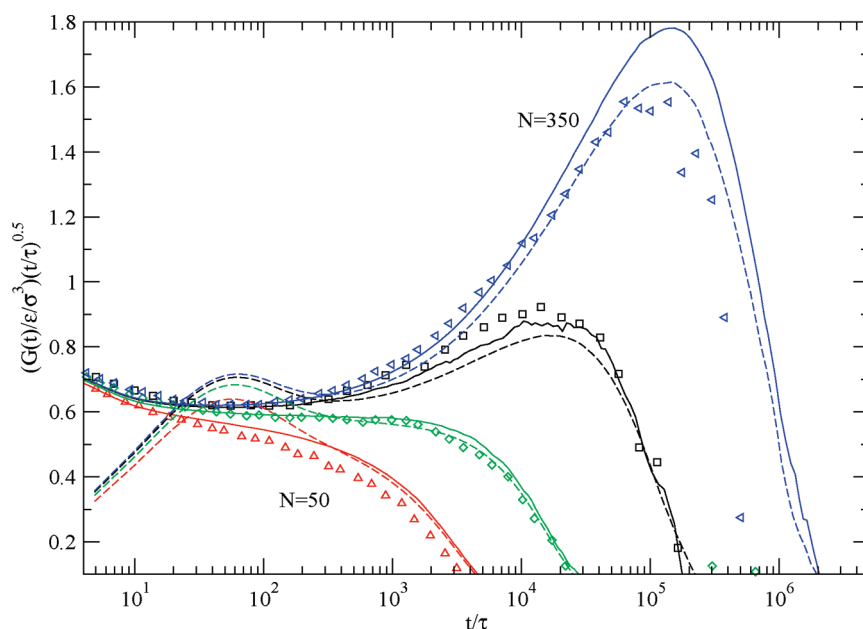


Figure 6. Parameters obtained by fitting $g_1(i,t)$ are used to calculate $G(t)$. $G(t)$ for the 1:1 mapping are shown as continuous lines, for the 1:5 mapping as dashed lines and from the MD as symbols.

“monomers” (rounded to the nearest integer). Coarse graining of the monomers increases the fundamental time scale of the model and leads to the speed increasing by a factor of m^2 while having to simulate only N/m “monomers” boosts the speed by a factor m leading to a total speed-up of at least m^3 .²³ We then correspondingly reduce both N_e and N_s by the factor $m = 5$, so that the coarse grained values $N_{e,c} = N_e/m = 7$ and $N_{s,c} = N_s/m = 1.5$. As the polymer chain in the slip-spring model is Gaussian at all length scales, we rescale the unit length by $m^{1/2}$ and the unit time by m^2 . For $m = 5$, these relations yield $b_{sl,c} = 1.32 \times 5^{1/2} = 2.95$ and $t_{sl,c} = 1.32 \times 5^2 = 33$. Comparison between the MD and the slip-spring model $g_1(i,t)$ with this new set of parameters is shown as dashed lines in Figure 2–Figure 5 for $N = 200, 100, 350$,

and 50 respectively. The corresponding $G(t)$ is shown in Figure 6. As expected, the coarse grained model fails to capture the dynamical features at early times, but for later times the agreement is acceptable. 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. In the current version of the model, the motion of the slip-links along the chain when in between the monomers is assumed to be in a straight line formed by the instantaneous positions of the two monomers.⁶ Values of $N_e < 1$, therefore, might render the dynamics of the monomers strongly dependent on the actual details of the slip-link motion. Since we seek to avoid such a situation, this presents a natural upper limit to the extent of coarse graining that can be achieved with the current slip-spring model.

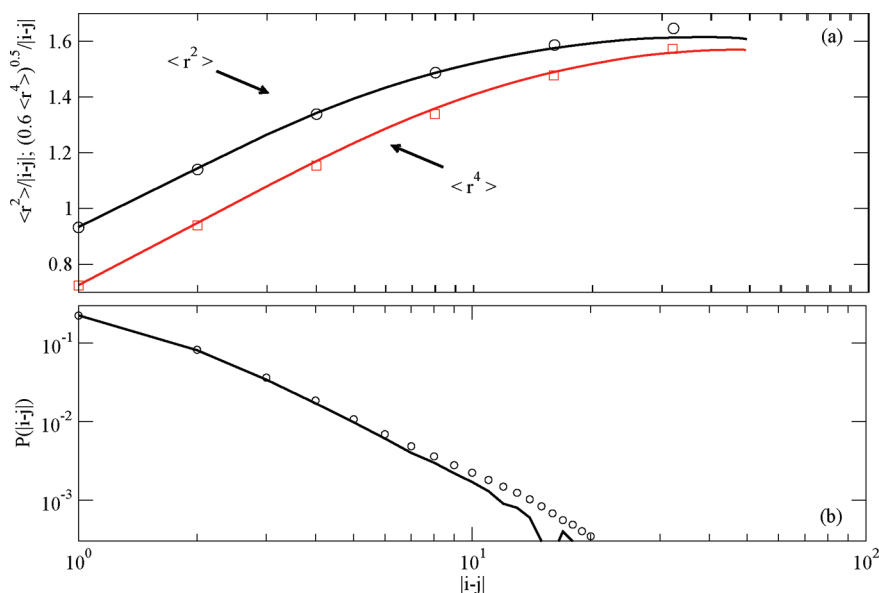


Figure 7. (a) Mean-square internal distances, mean fourth power of the internal distances and (b) bond vector correlations as a function of $|i-j|$ from MD and the slip-spring model with interactions for $N = 50$. In all the subplots, the symbols indicate MD results, the solid line corresponds to using the cutoff function given by eq 4 in eq 3.

Static Structure of the Polymer. As mentioned earlier, the slip-spring model is Gaussian at all length scales as opposed to the chains in the MD simulations. However, the slip-spring model does match the dynamics as seen in MD rather satisfactorily. The success of the slip-spring model in reproducing the dynamics as seen in MD when the static structure is clearly wrong is either mere coincidence or due to some specific reason that at present is a mystery to us. In any case, further study is warranted and in the next section we will probe the effect of introducing EV intrachain interactions.

Modified Slip-Spring Model (with Adapted EV Interactions)

All the monomers of the polymer melt in the MD simulations interact strongly with each other due to EV interactions (see eq 1). In spite of this, the mean square end-to-end distance of the chains is (approximately) proportional to the chain length for sufficiently long chains due to (partial) screening of the interactions.^{4,28} Good measures of chain statistics are second and fourth moments of intermonomer distances $\langle (r_i - r_j)^2 \rangle$ and $\langle (r_i - r_j)^4 \rangle$, and the normalized tangent-tangent correlation function along the chain $P(s) = \langle (\mathbf{r}_i - \mathbf{r}_{i-1}) \cdot (\mathbf{r}_{i+s} - \mathbf{r}_{i+s-1}) \rangle / \langle b_i^2 \rangle$, where $\langle b_i^2 \rangle$ is the mean squared bond length. These are plotted in Figure 7 (symbols), where the curves in part a are normalized by the values expected for a Gaussian chain with unit Kuhn segment length. $P(s)$ is expected to be an exponential for Gaussian chains. The fact that all three curves deviate from expected behavior suggests that the excluded volume screening is incomplete, with some residual repulsion between the monomers of the same chain. In order to reproduce the static properties of the chain within the slip-spring model, we have to introduce some repulsion between the monomers. We propose to do it in the form

$$U(r_i, r_j) = U_{nb}(|r_i - r_j|)f_{cut}(|i-j|) \quad (3)$$

where $U_{nb}(r)$ is the same repulsive potential as in the MD simulations, and $f_{cut}(|i-j|)$ is a decaying function appropriately chosen to reproduce the static properties of the chain. For convenience we approximate the FENE potential by a harmonic one $U_H(r) = 25.4r^2$ and the Lennard-Jones potential by a shifted truncated Gaussian $U_{nb}(r) = (3.8 \times 10^4 \exp(-10.5r^2) + 0.81r^2)$

for $r < 2^{1/6}$. We then run the slip-spring model with these potentials and adjust $f_{cut}(|i-j|)$. A function which works reasonably well for all the molecular weights under consideration is

$$f_{cut} = \begin{cases} 1 & \text{for } |i-j| = 1 \\ \frac{1}{15000} \frac{1}{|i-j|^{1/2}} \frac{1}{1 + 25/(|i-j| - 2)^3} & \text{for } |i-j| = 2 \\ \frac{1}{15000} \frac{1}{|i-j|^{1/2}} \frac{1}{1 + 25/(|i-j| - 2)^3} & \text{for } |i-j| > 2 \end{cases} \quad (4)$$

We observed that in order to reproduce the asymptotic behavior of $P(s) \sim s^{-3/2}$ we needed $f_{cut}(s) \sim s^{-1/2}$, when $s \gg 1$. However, we have not found an argument supporting this conclusion.

Now that an adequate potential is available, let us compare the dynamic quantity, $g_1(i, t)$ for $N = 50$. The lowest chain length studied is chosen so that the effect of the additional potential on the dynamics is readily apparent with only minimal effect due to entanglements, see Figure 8. It appears that the functional form of $g_1(i, t)$ is now sufficiently different. If we choose t_{sl} to match the long time MD results, the agreement is significantly poorer at short and intermediate times.

The data in Figure 8 suggests that agreement can be improved by increasing the time-correlation between the monomer positions for times less than τ_e . A sensible method for achieving this is to modify the equations of motion by substituting time-correlated noise for the Gaussian noise used in ref 6. This demands the use of the generalized Langevin equation instead of the Markovian version used thus far. In the generalized equation the fluctuating force does not decorrelate instantaneously but has a finite relaxation time.^{29,30} For our purposes, we make two additional assumptions: (1) All the monomers have identical first and the second moments of the fluctuating force. (2) The friction is isotropic. Given these two assumptions, the general equation can be simplified to

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i + \int_0^t M(t-s) \mathbf{v}_i(s) ds + \mathbf{g}_i(t) \quad (5)$$

Here, m_i , \mathbf{r}_i , and \mathbf{v}_i are respectively the mass, position and velocity of particle i . The force on particle i due to the interparticle interactions is \mathbf{f}_i . In lieu of the two assumptions

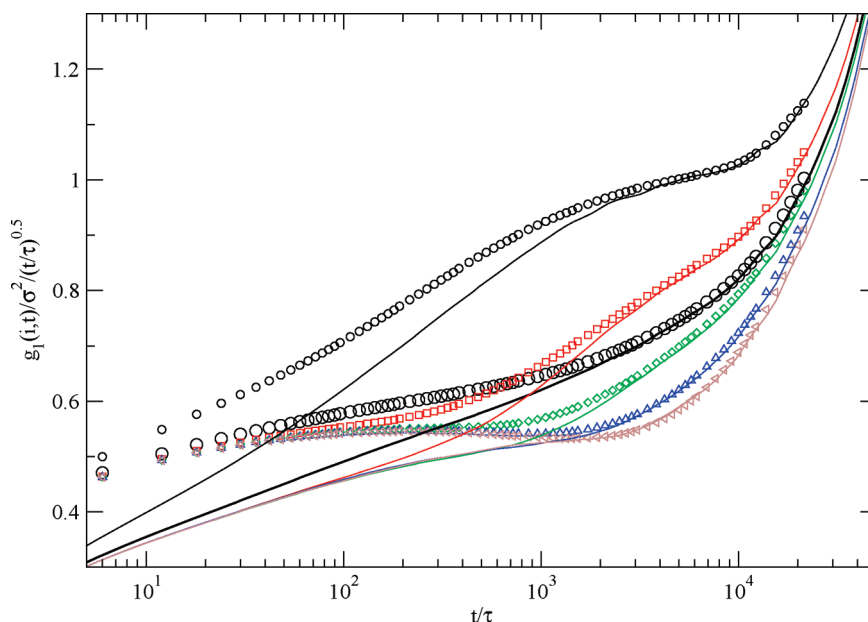


Figure 8. $g_1(i,t)$ for $N = 50$ using the two different adapted EV potentials discussed in the text. The symbols indicate MD results and the solid lines corresponds to using the adapted EV potential in the slip-spring model.

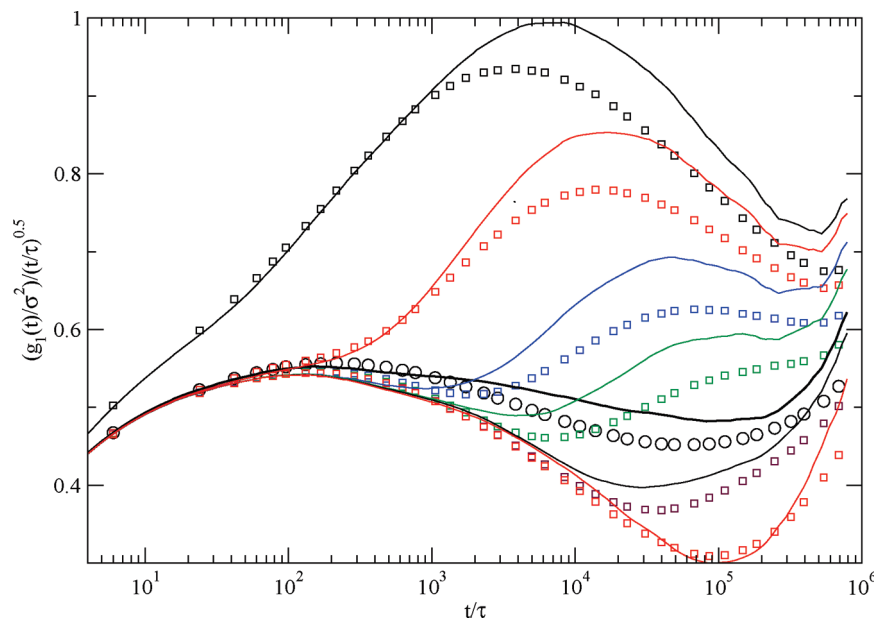


Figure 9. $g_1(i,t)$ for $N = 200$. The symbols indicate MD results, and the solid lines correspond to using the adapted EV potential and three memory modes. The large circles and the thick line indicates $g_1(t)$, i.e., averaged over all the monomers in the chain.

mentioned earlier, the fluctuating forces, \mathbf{g}_i , satisfy $\langle g_i \rangle = 0$ for all i and $\langle g_{\alpha,i}(t_1)g_{\beta,i}(t_2) \rangle \equiv g_{\alpha}(t_1)g_{\beta}(t_2) = \delta_{\alpha\beta}k_B T M(t_1 - t_2)$, where α and β represent spatial components and $k_B T$ is the thermal energy.

The numerical technique for simulating such equations when the kernel can be represented as a sum of exponentials $M(t) = \sum_k \lambda_k e^{-t/\tau_k}$ was recently proposed by Cotter and Reich.³¹ We implemented their version of the discretized dynamics without momentum conservation, and discovered that it is possible to reproduce early time mean-square monomer displacement using three modes in $M(t)$. However using trial and error for choosing the correct amplitudes and time constants for the modes is time-consuming and rather tedious.

Of the six additional parameters related to the three memory modes we introduced, only five are independent. This is because the $\sum_k \lambda_k \tau_k$ should equal the total friction acting on each particle and is determined by the long time behavior of the monomers.

Also, the time shift factor $t_{sl} \equiv 1.0$ since no further adjustment of the time scale is allowed. This leaves the aforementioned 5 parameters along with N_e and N_s for a total of 7 fitting parameters. The fitting parameters were determined by matching the $g_1(i,t)$ of the central monomers for $N = 200$ in the slip-spring model to MD results. This yielded for the 3 modes $k = 1, 2, 3$, (τ_k, λ_k) values (0.05, 195), (15, 0.22), and (200, 0.025) respectively. Note that the relaxation time of the longest memory mode $\tau_3 = 200\tau$ is still shorter than $\tau_e \approx 1.2 \times 10^3 \tau$. The slip-link parameters were $N_e = 35$ and $N_s = 4.0$ and the fits are shown in Figure 9. The fit is about 10% off for the peripheral monomers. This could indicate that the memory kernel associated with these monomers is actually different from that of the central monomers. The quality of the fits can almost surely be further improved but each iteration requires a new, computationally expensive, simulation. In spite of this, what is worthy of note is that the agreement for early times (until about $t \approx 10^3 \tau < \tau_e$) is significantly better

compared to the interacting case but without time-correlated noise. Also, the $G(t)$ calculated using only the pairwise interactions in the system for the parameters given above (not shown) shows good agreement with the MD data at long times. The disagreement at early times could potentially be rectified by including the stress contribution from the correlated random noise g_i .

The results of this section show that it is possible to match both static and dynamic properties of the melt by a single chain model with one-to-one mapping at the expense of introducing additional interactions between nonbonded monomers and memory kernels for the random forces. However the model is not very practical since its CPU cost is comparable to the MD simulations and the fitting procedure is quite dreary. We discuss the implications of these results in the next section.

Conclusions

We have presented extensive comparisons between a multi-chain model for polymer melts solved using MD and a single-chain model, the slip-spring model. The immediate goal was to test the power and the limitations of the slip-spring model but with a longer term view to better understand the model and also to establish its microscopic foundations. We will now discuss our findings vis-a-vis the goals we had set ourselves in the introduction.

Before we proceed further a few comments regarding the comparison between the models might prove useful. Typically the time dependence of both $g_1(i,t)^{25}$ and $G(t)^{32}$ are presented as log-log plots as the data span several decades along both the axes. In these plots it is extremely difficult to discern disagreements of even several tens of percent. Also the data obtained from simulations is usually not of sufficient precision to draw meaningful conclusions from such disagreements. This might lead researchers to wonder why we bother drawing attention to deviations of 10 – 15%. First, using software correlators we obtain data of significantly better precision than that usually available in the literature. Equipped with such quality of data more careful comparisons are indeed worthwhile. Therefore, we have removed part of the time dependence – the Rouse prediction at intermediate times—for both $g_1(i,t)$ and $G(t)$ (by dividing and multiplying by $t^{1/2}$, respectively). This allows us to plot both the quantities in linear scale. It is only this combination of using software correlators and rescaled y-axis in the plots that even reveals differences of 10 – 15% between the slip-spring model and the MD results that we occasionally observe and allows for the exacting examination of the slip-spring model performed in this paper.

Even a quick perusal of the $g_1(i,t)$ calculated for different chain lengths from the slip-spring model with no nonbonded interactions convinces us that the qualitative behavior is in accord with that expected from MD. Fitting the $g_1(i,t)$ from the slip-springs for $N = 200$ to MD yielded $N_e = 35$ and $N_s = 7.5$ and these two parameters determine the extent of the dynamical confinement experienced by the monomers. We did not discuss the uniqueness of these parameter values in this work and hope to investigate this issue at greater depth in the future. Typically, tube diameter calculated from different experimental quantities yields different values⁸ (however, see ref 12 for two different estimations of the tube diameter from MD that actually agree). So, for a stringent test of the model, we compared the linear relaxation modulus $G(t)$ calculated using the *same* parameters with MD and the agreement is indeed excellent. Having accomplished this we proceeded to test the appropriateness of this parameter set for the description of the same two physical quantities but for systems that were both more and less entangled. Once again, the slip-spring model performed creditably. Straightforward coarse graining of the

monomers yielded significant speed-up of the simulations with the dynamical and stress relaxation behavior in accordance with expectations.

In spite of the aforementioned successes of the model, “something is rotten in the state of Denmark” (see Shakespeare, *W. Hamlet*, Act 1, Scene 4). A quick comparison between the static structure of the chains obtained from the single-chain and the multichain model confirms this observation. Chains in the slip-spring model are Gaussian at all length scales whereas in our MD simulations they are Gaussian only asymptotically (for $N > 100$). The slip-spring model appears to successfully describe the dynamics without the correct static structure. The reasons for this success are unknown at present. To correct the static structure, we introduced a suitably chosen pairwise repulsive potential between the monomers. The improvement in the static structure was however seriously offset by the failure of the model with the adapted EV interactions to describe the dynamics. This resulted because the pairwise potential altered the qualitative behavior of $g_1(i,t)$ and if we matched the long time dynamics, severe disagreement at short times resulted.

We had solved the original slip-spring model using Brownian dynamics simulations. We then replaced these update equations with those based on generalized Langevin equations with exponentially decaying memory kernels.³¹ We found that when we introduced a minimum of three modes for the memory function the short time dynamics could be succinctly described. Adjusting the various parameters—such that the slip-spring $g_1(i,t)$ fits the MD data—is an extremely tiresome procedure and hence a direct calculation of the memory function from MD is highly desirable. If this can be accomplished, that will leave just two fitting parameters, N_e and N_s . What we have endeavored to demonstrate here that this particular route appears rather promising and work along these lines is currently in progress. After this, the natural next step would be to understand how the coarse graining of these systems can be accomplished leading to a unified hierarchical understanding of multichain and single-chain models. These however are for the future.

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- (11) A clarification regarding terminology is relevant at this point. In this work we distinguish between mildly entangled and well entangled melts. The number of entanglements per chain, Z , is of order 1 for mildly entangled melts and of order significantly greater than 10 for well entangled melts. Admittedly, this distinction is not a precise one, but nonetheless it is useful in practice as the tube model quantitatively describes data from certain experiments (for, e.g., stress relaxation) but only for well entangled melts.³³

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- (26) The frequency of adding data to the correlator affects the speed at which the program can run. In the MD, data is added every time step to calculate $G(t)$ and every 500 steps for g_1 . The comparison with the slip-spring model presented is for $G(t)$ calculated using data at every time step and g_1 calculated using data every 50 steps. If instead we add data to the g_1 correlator every 20 steps, the slip-spring model is around 128 times faster. In contrast to the MD,¹² it is not necessary to add data to the $G(t)$ correlator at every time step in the slip-spring model. This would result in a further speed-up of the slip-spring model than that quoted in the main text.
- (27) One might wonder why the MD simulations were not performed with 10 chains or the slip-spring simulations with 70 chains for easier comparison. This is due to two reasons. The size of the box used in the MD simulation of a polymer melt must be sufficiently large to ensure that parts of the chain that should not interact with each other actually do *not* do so; i.e., one should beware of the periodic image in a neighboring box. As the box size is related to the number of chains in the MD box through the density of the system, the number of chains cannot be arbitrarily reduced. We can indeed perform the slip-spring simulations with 70 chains but this is unnecessary to obtain good statistics and therefore a waste of computing resources. Data of excellent quality can be obtained using just 10 chains and hence the comparison used provides a fairer measure of the actual speed-up obtained.
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