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Joseph D. Dietz and Robert S. Hoy

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Joseph D. Dietz and Robert S. Hoy

AFFILIATIONS
Department of Physics, University of South Florida, Tampa, Florida 33620, USA

*Author to whom correspondence should be addressed: rshoy@usf.edu

ABSTRACT

The widely used double-bridging hybrid (DBH) method for equilibrating simulated entangled polymer melts [Auhl et al., J. Chem. Phys. 119, 12718–12728 (2003)] loses its effectiveness as chain stiffness increases into the semiflexible regime because the energy barriers associated with double-bridging Monte Carlo moves become prohibitively high. Here we overcome this issue by combining DBH with the use of core-softened pair potentials. This reduces the energy barriers substantially, allowing us to equilibrate melts with $N \gg 40 N_e$ and chain stiffnesses all the way up to the isotropic–nematic transition using simulations of no more than $100 \times 10^6$ time steps. For semiflexible chains, our method is several times faster than the standard DBH; we exploit this speedup to develop improved expressions for Kremer–Grest melts’ chain-stiffness-dependent Kuhn length $\ell_K$ and entanglement length $N_e$.

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I. INTRODUCTION

Equilibration of simulated entangled polymer melts is a long-standing challenge. The longest relaxation time for a single $N$-mer chain, i.e., the disentanglement time $\tau_d$ after which the chain has escaped from its original tube, is $\tau_d = \tau_e (N/N_e)^{3/4}$, where $N_e$ is the melt’s entanglement length and $\tau_e$ is a microscopic time scale. Since chains’ mean radius of gyration $R_g$ and end–end distance $R_{ee}$ scale as $N^{1/2}$ and interactions of chains with their own periodic images produce spurious results, the minimum simulation cell side length $L_{\text{min}}$ also scales as $N^{1/2}$, and thus the minimum simulation volume $V_{\text{min}}$ scales as $N^{3/2}$. For a melt of fixed monomer number density $\rho$, this means that the minimum number of monomers $N_{\text{min}} \sim N_e^{3/2}$. Thus, the total computational effort required to equilibrate a polymer melt is

$$E \sim V_{\text{min}} \tau_d \sim N^{3/2} \left( \frac{N}{N_e} \right)^{3/4} \tau_e \sim N^{4/3} \tau_e,$$

provided the polymer chains follow physically realistic dynamics (i.e., reptation). This nearly-$N^3$ scaling limited early molecular dynamics (MD) and Monte Carlo (MC) simulations of polymer melts to at-most-weakly entangled chains with $N$ no more than a few $N_e^{3/4}$ and still limits simulations of well-entangled chains to durations of no more than a few $\tau_d$ even on modern supercomputers.

Many problems of current interest can be addressed through simulations of duration much shorter than $\tau_d$. However, this still leaves the problem of equilibration; simulations must begin with a reasonable-guess initial configuration and then run for a time sufficient to ensure it reaches equilibrium before the “production” run can begin. If the chains follow physically realistic dynamics, this requires an equilibration run of duration $\gtrsim \tau_d$. Fortunately, these runs need not follow physically realistic dynamics, and several modern equilibration algorithms exploit this fact. The simpler algorithms fall into two basic categories: core-softening and topology-changing. Both approaches greatly speed up diffusive equilibration by eliminating the constraints on chains’ transverse motion (and hence their slow reptation dynamics), but both have inherent limitations.

Core-softening speeds up diffusive equilibration by allowing chains to cross. However, it also produces a local melt structure that can differ substantially from the equilibrium structure for the final interactions. For example, the cluster-level structure of hard-sphere liquids is more ordered than that of WCA liquids at the same temperature and density because the latter have more free volume. The degree to which comparable many-body effects occur in polymer melts has not been explored, but it is reasonable to assume that the intermediate-scale melt structure couples rather strongly to the monomer-scale structure via chains’ connectivity and semiflexibility. Any resulting structural differences must be annealed out via diffusion after the potentials are restored to their final form, and
the minimum required annealing time is often \textit{a priori} unclear, particularly for the higher-order structural correlations that determine \( N_e^{\text{max}} \). The standard KG model is employed in its standard temperature range \((k_B T \lesssim \epsilon)\), the forward moves become prohibitively unlikely for \( \kappa \gtrsim 2.5\epsilon \).

The required equilibration times are several times shorter than for the widely used KG bead–spring polymer model. We demonstrate our method using the semiflexible version of the KG melt, which is computationally expensive as chain stiffness increases. For the standard temperature \((T = \epsilon/k_B)\), double-bridging algorithms \cite{DBH} are effective only up to \( \kappa \approx 2.5\epsilon \) because for larger \( \kappa \), the larger energy barriers for angle-swapping makes their MC acceptance rates prohibitively low; see Fig. 1. To reduce these energy barriers, we initially employ a core-softened pair potential that allows thermally activated chain crossing but preserves the large-scale chain structure, and then gradually harden it until the final potential employed in the production runs [i.e., the standard Lennard-Jones potential \( U_{\text{LJ}}(r) \)] is operative.

A natural choice for a core-softened pair potential is the generalized Lennard-Jones (Mie) potential \cite{Mie}:

\[
U_{\text{Mie}}^{n-m}(r) = \frac{\epsilon}{n-m} \left[ 2^{n/6} m \left( \frac{\sigma}{r} \right)^n - 2^{m/6} n \left( \frac{\sigma}{r} \right)^m \right],
\]

which is symmetric with respect to an exchange of \( n \) and \( m \). The standard LJ potential is recovered for \( n = 2m = 12 \). The factors of \( 2^{n/6} \) and \( 2^{m/6} \) place the minimum of \( U_{\text{Mie}}^{n-m}(r) \) at \( r = 2^{1/6} \sigma \) (the standard Lennard-Jones value) for any \( n \) and \( m \). However, \( U_{\text{Mie}}^{n-m}(r) \) is not optimal to use during equilibration of polymers with attractive pair interactions \((r_c > 2^{1/6} \sigma)\) because there is no advantage to be gained by modifying the attractive \((r > 2^{1/6} \sigma)\) portion of the pair potential. Therefore, we proposed \cite{gekhtman2022} the modified generalized-LJ potential

\[
U_{\text{Mie}}^{n}(r) = \begin{cases} 
U_{\text{Mie}}^{n-m}(r), & r \leq 2^{1/6} \sigma, \\
U_{\text{LJ}}^{n}(r), & r > 2^{1/6} \sigma.
\end{cases}
\]

II. EQUILIBRATION METHOD

A. Interaction potentials

We demonstrate our method using the semiflexible version of the widely used Kremer–Grest (KG) bead–spring polymer model. \cite{kremer1990} The standard nonbonded-pair, covalent-bond, and bond-angular interactions for this model are, respectively, the truncated and shifted Lennard-Jones potential:

\[
U_{\text{LJ}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + \frac{1}{4} \left( \frac{\sigma}{r} \right)^6 \right].
\]

where \( \epsilon \) and \( \sigma \) are characteristic energy and length scales, \( r \) is the internuclear distance, and \( r_c = 2^{1/6} \sigma \) is the cutoff radius, the FENE potential:

\[
U_{\text{FENE}}(r) = \frac{k R_0^2}{2} \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right],
\]

where \( k = 30\epsilon \sigma^{-2} \) and \( R_0 = 1.5\sigma \), and

\[
U_{\text{ang}}(\theta) = k [1 - \cos(\theta)],
\]

where \( \theta = \cos^{-1}(\hat{b}_i \cdot \hat{b}_{i+1}) \) is the angle between consecutive bond vectors \( \hat{b}_i \) and \( \hat{b}_{i+1} \). This model was recently shown by Svaneborg, Everaers, and colleagues to accurately capture the dynamics of a wide variety of commodity polymer melts when \( \epsilon, \sigma, \) and \( \kappa \) are taken as adjustable parameters and mapped to SI units. 

Equilibration of entangled KG melts becomes increasingly computationally expensive as chain stiffness increases. For the standard temperature \((T = \epsilon/k_B)\), double-bridging algorithms \cite{DBH} are effective only up to \( \kappa \approx 2.5\epsilon \) because for larger \( \kappa \), the larger energy barriers for angle-swapping makes their MC acceptance rates prohibitively low; see Fig. 1. To reduce these energy barriers, we initially employ a core-softened pair potential that allows thermally activated chain crossing but preserves the large-scale chain structure, and then gradually harden it until the final potential employed in the production runs [i.e., the standard Lennard-Jones potential \( U_{\text{LJ}}(r) \)] is operative.

A natural choice for a core-softened pair potential is the generalized Lennard-Jones (Mie) potential \cite{Mie}:

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\[
U_{\text{Mie}}^{n}(r) = \begin{cases} 
U_{\text{Mie}}^{n-m}(r), & r \leq 2^{1/6} \sigma, \\
U_{\text{LJ}}^{n}(r), & r > 2^{1/6} \sigma.
\end{cases}
\]
Our method works by beginning with soft repulsive pair inter-actions \((n \ll 12)\), adjusting \(k\) to keep the mechanical-equilibrium bond length \(\ell_0\) at its standard value,\(^{25}\) and then performing double-bridging moves while gradually increasing \(n\). In the standard KG model, \(k = 30e/\sigma^2\) is the solution to

\[
\frac{\partial}{\partial r} U_{\text{FENE}}(r) \bigg|_{r=\ell_0} = 0, \tag{7}
\]

where \(\ell_0 \equiv 0.960897\sigma\). When the pair potential is \(U_{\text{MLJ}}^n\), the FENE spring constant producing an mechanical-equilibrium bond length equal to \(\ell_0\) is instead given by the solution to

\[
\frac{\partial}{\partial r} \left( U_{\text{MLJ}}^n(r) - \frac{k_n R_0^2}{2} \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right] \right) \bigg|_{r=\ell_0} = 0, \tag{8}
\]

i.e.,

\[
k_n = \frac{6n(\ell_0^2 - R_0^2)}{(n-6)R_0^2\ell_0^6} \alpha. \tag{9}
\]

Then, the overall interaction potential between covalently bonded monomers is

\[
U_{\text{bond}}^n(r) = U_{\text{MLJ}}^n(r) - \frac{k_n R_0^2}{2} \ln \left[ 1 - \left( \frac{r}{R_0} \right)^2 \right]. \tag{10}
\]

As shown in Fig. 2, \(U_{\text{MLJ}}^n\) and \(U_{\text{bond}}^n\) both soften when \(n\) is decreased with \(m\) held fixed. Below, we will show that beginning runs with \(n = 2\) and gradually incrementing \(n\) through the set

\[
\Xi = \{2, 3, 4, 5, 5.75, 6.5, 7, 8, 9, 10, 11, 12\} \tag{11}
\]

produces orders-of-magnitude increases in the average DBH swap success rate, which, in turn, leads to much faster equilibration. Note that this protocol does \emph{not} reduce the angular component of the energy barrier \(\langle \Delta U_{\text{ang}} \rangle\) for a given double-bridging move (Fig. 1). Instead, the softer bond interactions [Eqs. (9) and (10) substantially reduce \(\langle \Delta U_{\text{bond}} \rangle\), while the softer pair interactions [Eqs. (5) and (6)] allow chain crossing (for \(n \leq 8\)) as well as deeper interpenetration of swap-candidate pairs that in turn reduces \(\langle \Delta U_{\text{ang}} \rangle\).

\[\text{B. Detailed protocol}\]

Any polymer–melt-equilibration protocol begins by generating an initial state; better initial states allow for shorter equilibration runs. Svaneborg et al. recently showed\(^{27}\) that the equilibrium Kuhn length of \(0 < \kappa \lesssim 2.5\) e KG chains at the standard melt temperature \(T = e/k_B\) is well-approximated by\(^{36}\)

\[
\ell_K = \frac{2\kappa e + \exp(-2\kappa e) - 1}{1 - \exp(-2\kappa e)}(2\kappa e + 1) + 0.77[\tanh(-0.03\kappa^2 e^2 - 0.41\kappa e + 0.16)] + 1. \tag{12}
\]

The first term in Eq. (12) is the standard Flory term,\(^{27}\) and the second term is an empirical correction term associated with the long-range bond-orientational correlations found in dense polymer melts.\(^{38}\)

For any given \(\kappa\), we generate initial states by placing \(N_{\text{ch}}\) freely rotating (FR) \(N\)-mer chains with the bond angle

\[
\theta = \theta^\ast (\kappa) = \cos^{-1} \left( \frac{\ell_K(n)/\ell_0 + 1}{\ell_K(n)/\ell_0 - 1} \right) \tag{13}
\]

in a cubic cell of volume \(V = N_{\text{ch}}N/\rho\), where \(\ell_K(n)\) is given by Eq. (12). FR chains with \(\theta = \theta^\ast (\kappa)\) are guaranteed to have the correct \(\langle \ell_K(n) \rangle\) in the large-\(N_{\text{ch}}\), large-\(N\) limit. To minimize finite-sampling errors, we fit the average chain statistics \(\langle R^2(n) \rangle\) to the WLC formula

\[
\langle R^2(n) \rangle = \ell_K \left[ 1 - \frac{\ell_K}{2n\ell_0} \left[ 1 - \exp \left( -\frac{2n\ell_0}{\ell_K} \right) \right] \right] \tag{14}
\]

at intermediate \(n\) (e.g., \(N/4 \leq n \leq N/2\)) and reject the state if the fit \(\ell_K\) deviates from the prediction of Eq. (12) by more than 2%. All results presented in Secs. II B and III are for \(N_{\text{ch}} = 1000\) and \(N = 400\).

Once we have generated a satisfactory initial state, we set \(n = 2\) in Eqs. (6) and (10) and begin the MD simulation. All monomers have mass \(m\), and all MD simulations are performed using LAMMPS.\(^{39}\) Because \(n = 2\) FENE bonds are much weaker than their \(n = 12\) counterparts (Fig. 2), a very small initial time step \(\Delta t_{\text{init}}\) is required to avoid overstretched-bond crashes arising from initial monomer overlap. We choose \(\Delta t_{\text{init}} \sim 0.001\tau_{\text{LJ}}\), where \(\tau_{\text{LJ}} = \sqrt{\beta\sigma^2/e}\) is the standard Lennard-Jones time unit. After ramping the MD time step up to its final value \((\Delta t = \tau/125)\) over a few hundred \(\tau_{\text{LJ}}\), we activate the MC double-bridging moves.

In our simulations, one double-bridging move (Fig. 1) is attempted per every \(10^4\) monomers per \(\tau_{\text{LJ}}\), i.e., moves are attempted
at a rate $R_{MC} = 10^{-5}N_{eq}N/t_{LJ}$. Moves are attempted only for pairs of chains that (i) allow for a bond-swap that preserves the length of both chains (i.e., keeps the melt monodisperse) and (ii) do not involve creation of a new covalent bond with length $\ell > 1.3\sigma$.

Before describing our protocol any further, it is worthwhile to examine how the MC double-bridging success rate varies with $\kappa$ and $n$. Figure 3 shows success rates for $2 \leq n \leq 12$ and $0 \leq \kappa \leq 5.5\epsilon$. We find that the success rates for $\kappa \geq \epsilon$ and $n \leq 9$ are approximately fit by

$$S(\kappa, n) = a \exp \left[-b \frac{\kappa}{\epsilon} - d n - e n^2 \right],$$

where $a \approx 1.6 \pm 0.037$, $b \approx 0.77 \pm 0.015$, and $d \approx 0.35 \pm 0.01$. The large value of $b$ indicates why the standard [$n = 12$-only] DBH equilibration becomes impractical for $\kappa > 2.5\epsilon$. On the other hand, the large value of $d$ indicates that combining DBH with core-softening is an effective way of addressing this issue.

Auhl et al. suggested that a fixed number of successful MC swaps per monomer is necessary to equilibrate polymer melts. Because DBH keeps systems strictly monodisperse, the probability that a swap candidate lies in the vicinity of a given bond scales as $1/N$, which suggests that the minimum total duration of the equilibration run ($t_{eq}$) scales at least linearly with $N$ for $N \gg N_e$. Combined with the results shown in Fig. 3, this suggests that $t_{eq}$ should be at least

$$t_{eq}(\kappa) = \frac{fN}{S(\kappa, 0)} t_{LJ} \equiv \frac{fN}{a} \exp \left[-b \frac{\kappa}{\epsilon} \right] t_{LJ},$$

where $f$ is a numerical prefactor. Since we wish to develop an efficient equilibration algorithm, a reasonable criterion for $f$ is that it must allow well-entangled ($N \gg N_e$) systems to be equilibrated using runs of $N_t \leq N_{eq}^{\max} = 100$ million time steps. For $N = 400$, meeting this criterion for systems near the onset of local nematic order ($\kappa = 5.5\epsilon$) requires $f \leq f_0 = 46.3354$. We will show below that $f = f_0$ is indeed sufficient to equilibrate these $\kappa = 5.5\epsilon$ melts in $N_{eq}^{\max}$-time step runs, while smaller-$\kappa$ melts can be equilibrated much faster.

To ensure equilibration of the interchain structure on all length scales, $t_{eq}$ should also be at least $2t_e$, where $t_e = t_B(N_e)$ is the Rouse time of a typical entangled segment. At least half (i.e., $t_e$) of this time should employ the final ($n = 12$) pair interactions to ensure that the local interchain and intrachain structure of the melt reflects these interactions. Svaneborg and Everaers recently showed that

$$t_e(\kappa) = \frac{N_e^2}{N_{eq}} t_B(\kappa) = \frac{12\rho K}{\pi^2 \kappa^4} N_e^2 / \ell_K(\kappa),$$

where $N_K \equiv N_e/\ell_K$ is the number of Kuhn segments per entanglement, the Kuhn time $t_K$ is the time over which Kuhn segments diffuse a distance comparable to their own size, and $\eta_K$ is the local Kuhn-segment-scale melt viscosity. We ignored the $O(1)$ prefactor in the rightmost term of Eq. (17) and employed the approximation $t_e(\kappa) = N_K^2 / \ell_K(\kappa)/\ell_K t_{LJ}$, with values of $\ell_K(\kappa)$ calculated from Eq. (12) and an initial estimate $N_e(\kappa) = 77 \exp(-\kappa/1.1) + 9.4$. This allowed us to estimate $t_e(\kappa)$ and thus $t_{eq}(\kappa, N)$; a more accurate expression for $N_e(\kappa)$ is given in Sec. IV.

Combining the above arguments with an additional empirical criterion that equilibration runs’ duration should be at least $200N\tau$ suggests that a reasonable duration for the entire run is

$$t_{eq}(\kappa) = \max[2t_e(\kappa), t_{fix}(\kappa), 200N\tau],$$

Values of $t_{fix}$, $t_e$, and $t_{eq}$ obtained from Eqs. (16)–(18) are given in Fig. 4. For context, note that the estimated values of $t_{fix} = 3(N/N_e)$ for these systems (using the $N_e$ values given in Sec. IV) range from $\sim1.4 \cdot 10^6 \tau$ for $\kappa = 0$ to $\sim7.1 \cdot 10^6 \tau$ for $\kappa = 5.5\epsilon$.

The next question to answer is how should the run be divided among the various values of $n$ [Eq. (11)]. Clearly, spending more time at smaller $n$ allows more swaps to be executed, which improves equilibration. However, as discussed above, the $n = 12$ portion of the runs should last at least $t_e$. After some trial and error, we devised two $ad$ hoc division schemes that satisfy both criteria: one for $\kappa \leq 2.5\epsilon$ and another for $\kappa > 2.5\epsilon$.

For $\kappa < 2.5\epsilon$, the total run duration is $200N\tau$. We assign the last $2t_e$ of the run to $n = 12$ and the remaining $\tau^*(\kappa) = 200N\tau - 2t_e(\kappa)$ to $n = 12$ and the remaining $\tau^*(\kappa)$
The number of Kuhn segments \( L \) PP, \(\text{PPA}, \) Here, to \( N \) that are not random-walk-like between entanglements. In the simulation cell. 40 systems created by randomly placing and orienting chains within the cell.

Next, we check whether all systems have, in fact, reached equilibrium by the end of these runs. We performed long follow-up runs to produce greater decorrelation of systems’ structure. Figure 6 shows ensemble-averaged results for \( \ell_K \) and number of Kuhn segments per entanglement \( N_{ek} \) at the end of each \(\ell_K \) \( N_{ek} \).

most successful swaps and the most chain crossing of any stage [Figs. 2 and 3 and Eqs. (19) and (20)], produce very substantial dis-entanglement for most \( k \). As \( n \) continues to increase, \( N_{ek} \) values progress steadily toward their final values, at rates that decrease with increasing \( n \), for all systems. This trend suggests that our use of core-softened potentials does not significantly perturb systems away from their equilibrium structure and is consistent with previous studies that have employed core-softening to promote chain crossing.

To verify this hypothesis and as a further check for equilibration on all length scales, we calculated the structure factor \( S(q) \) at the end of each \( n\)-step and found that it evolves monotonically toward equilibrium as \( n \) increases for all \( q \) and all \( k \). Further details are given in Appendix A.

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Semiflexible \( (R) \) Values of \( \kappa \) all \( n \) entanglements per chain, but also show no systematic trends with time. For somewhat larger fluctuations because they have only \( \sim \) magnitudes below 0.5% for \( \kappa \) above) using the formula \[ R \text{ can be predicted from the details of the algorithm (as described } \] employ only the standard \( n \) and estimated speedups for our protocol relative to DBH runs that \( \text{pared to } \) \( \text{single-system, non-ensemble-averaged fluctuations in these quantities. We, therefore, conclude that all systems are (at least) asymptotically close to equilibrium at the end of their equilibration runs.} \]

The protocol described above is more complicated than standard DBH equilibration; supporting its use requires demonstrating that it produces a significant speedup. In Table I, we show that this is indeed the case. We list the number of successful bond-swaps per monomer over the course of the equilibration runs for each \( \kappa \), and estimated speedups for our protocol relative to DBH runs that employ only the standard \( n = 12 \) interactions. The speedup ratios \( R \) can be predicted from the details of the algorithm (as described above) using the formula

\[ R(\kappa) = \frac{\sum_{i=1}^{n} \tau_i S(\kappa, N_i)}{\tau_{\text{fix}}(\kappa) S(\kappa, 12)}. \]  

Values of \( R \) increase monotonically with \( \kappa \) and are above 20 for semiflexible \( (\kappa \geq 2\epsilon) \) chains.

Previous implementations of DBH\textsuperscript{10,17} have employed force-capped Lennard-Jones potentials that allow deeper chain interpretation and reduce the energy barrier for chain crossing. The original implementation\textsuperscript{10} also employed a ramping procedure for \( k \), stepping it from \( 10 \sigma^{-2} \) to \( 30 \sigma^{-2} \) over the course of equilibration runs. Both procedures reduce the estimated speeds \( R \) achieved by our method by an amount that depends on implementation details. Table I also presents the estimated speeds \( R^{*} \) over an implementation wherein Lennard-Jones forces are capped at their values for \( r = 0.8 \sigma \) and equal times are spent on the above-mentioned three \( k \) values. These estimates are smaller, typically \( \sim 3 \) for semiflexible chains. However, using lower \( k \) without also reducing \( n \) substantially increases \( \bar{\ell}_0 \), impeding equilibration on all length scales, e.g., by producing massive chain retraction when \( k \) is increased. Thus, we assert that these values of \( R^{*} \) are, in fact, loose lower bounds for the actual speeds achieved by our algorithm. Moreover, since well-entangled semiflexible chains require a substantial amount of time to equilibrate, even a speedup factor of 3 is valuable. For example, equilibrating our \( N_{\text{db}} = 1000 N = 400 \) melts for an additional \( 200 \times 10^6 \) time steps \( \text{i.e.}, N_{\text{db}}(R^{*} - 1) \) for \( k = 5.5 \sigma \) would require hundreds of hours and thousands of CPU-core hours on a typical cluster node.

Finally, note that a separate set of simulations that followed the same protocol but were half as long \( \text{i.e., have } f = 0.5 \) in Eq. (16) \textsuperscript{17} produced \( N_{\text{db}} \) values that were systematically lower than those reported above, but by only about 1 percent. From these data, we can conclude that the minimum number of swaps per monomer required to fully equilibrate well-entangled semiflexible bead–spring melts is about 2.5.

### IV. Equilibrium Structure of Semiflexible Kremer-Grest Melts

Figure 7 summarizes the structure and entanglement of our fully equilibrated \( N = 400 \) melts. All results are averaged over the

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**TABLE I.** Successful DBH swaps per monomer and estimated speedup ratios provided by our method. The speedup \( R \) is equal to \( N_{\text{db}}/N_{\kappa} \), where \( N_{\text{db}}^{12} \) is the estimated number of time steps an \( n = 12 \)-only DBH equilibration run would take to achieve the same number of swaps/monomer that our method achieves in \( N_{\kappa} \) time steps. \( R^{*} \) is the estimated speedup over the protocol discussed in Ref. \textsuperscript{10} wherein the Lennard-Jones interactions are force-capped and equal times are devoted to stages with \( \kappa^2/\epsilon = 10, 20, \) and 30.

| \( \kappa/\epsilon \) | Swaps/monomer | \( R \) | \( R^{*} \) |
|---------------------|--------------|------|-----|
| 0                   | 10.04        | 23.0 | 2.1 |
| 0.5                 | 11.54        | 28.2 | 2.6 |
| 1                   | 10.24        | 30.1 | 2.8 |
| 1.5                 | 7.84         | 31.0 | 3.0 |
| 2                   | 5.46         | 31.3 | 3.1 |
| 2.5                 | 3.62         | 31.5 | 3.2 |
| 3                   | 3.30         | 31.6 | 3.1 |
| 3.5                 | 3.16         | 31.8 | 3.2 |
| 4                   | 2.94         | 33.1 | 3.2 |
| 4.5                 | 2.84         | 34.8 | 3.2 |
| 5                   | 2.76         | 37.4 | 3.1 |
| 5.5                 | 2.72         | 40.1 | 3.0 |

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**FIG. 6.** Temporal fluctuations in \( \ell_{\kappa} \) and \( N_{\kappa} \) during the extended \( n = 12 \) runs.
includes a systematic $O(N^{-1})$ error arising from improper treatment of chain ends that causes it to predict $N_{el} = 0$ for unentangled chains with $L_{pp} \leq L$. To correct for this we performed equilibrated melts with $N = 100, 133, 200$ for all $\kappa$ by cutting the parent $N = 400$ chains into pieces$^{43}$ and then continuing $n = 12$ equilibration for an additional $2\tau_e$. We also prepared equilibrated $N = 533, 800$ melts for $\kappa \leq \epsilon$ using the same procedure described in Sec. II. Then, we performed extended $n = 12$ runs of duration $20\tau_e$ and analyzed the entanglement of $\tau_e$-separated snapshots as described above.

Figure 8 summarizes our findings. Panel (a) shows the $N_e$ values estimated from Eq. (21) as well as fits to

$$N_{est}^{\infty}(\kappa, N) = N_e^{\infty}(\kappa) - \frac{b(\kappa)}{N}$$

(25)

for selected $\kappa$. This empirical form accurately describes the data for all $\kappa$ and $N \geq 2N_{est}^{\infty}(\kappa)$ considered here and should remain accurate in the $N \to \infty$ limit.$^{43}$ Panel (b) shows results for $N_{est}^{\infty}(\kappa)$. We find

$21$ $\tau_e$-separated snapshots from the extended $n = 12$ runs for each of the ten independently prepared samples, i.e., over 210 statistically independent snapshots for each $\kappa$. Panel (a) shows how $\ell_K$ increases with $\kappa$. For the $N = 400$ chains considered here, Eq. (12) underpredicts $\ell_K$ by $\sim 3\%$ for $\kappa = 0$, is accurate to within $\sim \pm 1\%$ for $\epsilon < \kappa < 5\epsilon$, and underpredicts $\ell_K$ by $\sim 3\%$ for $\kappa \geq 5\epsilon$. We find that $\ell_K$ is better fit by the very similar expression

$$\frac{\ell_K}{\ell_0} = \frac{2\kappa/\epsilon + \exp(-2\kappa/\epsilon) - 1}{1 - \exp(-2\kappa/\epsilon)(2\kappa/\epsilon + 1)} + 0.364 \frac{1}{\tanh(0.241\kappa^2/\epsilon^2 - 1.73\kappa/\epsilon + 2.08) + 1}.$$  

(23)

This expression underpredicts $\ell_K$ by $\sim 3\%$ for $\kappa = 0$, but it is accurate to within $<1.5\%$ for all $\kappa > 0$.

Panel (b) shows results for $N_e(\kappa) = N_{est}(\kappa)\ell_K(\kappa)/\ell_0$. We find that $N_e(\kappa)$ is well fit by

$$N_e(\kappa) = 71.2 - 61.3 \tanh\left(\frac{\kappa}{1.631\epsilon}\right)$$.

(24)

This formula for $N_e(\kappa)$ has not been purged of the finite-$N$ errors that are present in many $N_e$-estimators.$^{43}$ Specifically, Eq. (21)
that $N_e^m(\kappa)$ is well fit by

$$N_e^m(\kappa) = 80.5 - 70.4 \tanh \left( \frac{\kappa}{1.579e} \right). \tag{26}$$

Note that other topological-analysis methods, such as $Z$, CreTA, and thin-chain PPA, will, in general, give different $L_{eq}(\kappa)$ and thus quantitatively different formulas for $N_e(\kappa)$. The plateau in $N_e^m$ for $4 \leq \kappa \leq 5.5e$ is consistent with both our earlier results for $p \approx 7\sigma^{-3}$ systems and Bobbili and Milner’s results for entangled Olympic-ring polymer melts. More generally, it is consistent with Milner’s suggestion that entanglement is maximal and has a plateau in the semiflexible-chain regime where entangled segments approximately correspond to Kuhn segments ($N_{BK} = 1$).

V. DISCUSSION AND CONCLUSIONS

Bead–spring polymer melts remain of substantial interest owing to both their utility for elucidating general features of polymer rheology that remain poorly understood and their ability to map quantitatively to common synthetic polymers. Semiflexible bead–spring melts have attracted renewed interest owing to their ability to probe the poorly understood crossover regime between flexible and stiff entanglement and to their potential applicability for modeling recently developed conjugated polymers which lie in this regime and are under intensive study for their potential use in flexible electronic circuits.

Here, we developed and described a method that is suitable for preparing equilibrated well-entangled ($N \approx 40N_e$) semiflexible bead–spring polymer melts for chain stiffnesses up to the isotropic–nematic transition. Our method combines two previously employed methods (core-softening and double bridging) in a novel controlled fashion. It provides a speedup by a factor of at least 3 over standard DBH and can be straightforwardly improved upon in several different ways. For example, the use of Monte Carlo prepackaging schemes that reduce local density fluctuations in the initial states would bring these states closer to equilibrium and reduce $\tau_{eq}$. Combining such schemes with a protocol that uses a more sophisticated criterion for optimizing the initial states’ chain statistics should prove fruitful. Furthermore, since we did not attempt to optimize our choices of $\Xi$ and $\tau(\kappa)$, further refinement might provide a significant additional speedup. Note that our method is suitable for generating coarse-grained configurations which can be used in conjunction with configurational-backmapping methods to generate equilibrated well-entangled semiflexible atomic or united-atom model polymer melts.

We conclude with a remark on the relation of the equilibration method described herein to methods that employ core-softening but not topology-changing. The latter are capable of equilibrating semiflexible polymer melts using the computational resources available to typical academic research groups. They are likely the best currently available method that is straightforwardly applicable to branched or ring polymer melts where DBH-like Monte Carlo moves are chain-architecture-specific and challenging to implement. They are also readily applicable to atomistic models with stiff bond-angular interactions. On the other hand, for linear bead–spring polymers, they produce substantially lower chain mobilities and correspondingly slower convergence of $N_e$ than achieved when topology-changing moves are added. Further details are given in Appendix B.

The code used in this work is being made available as part of LAMMPS’ EXTRA-PAIR and EXTRA-MOLECULE packages (https://lammps.sandia.gov/), and LAMMPS scripts for our method as well as the equilibrated melts described above are available on our website (http://labs.cas.usf.edu/softmattertheory/).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon request.

APPENDIX A: VERIFICATION OF MULTISCALE STRUCTURAL EQUILIBRATION

In this Appendix, we demonstrate that the $N = 400$ melts prepared using the procedure described above are well-equilibrated on all length scales. We show that the pair correlation functions and static structure factors of our most flexible and stiffest melts evolve monotonically with increasing $n$ and have converged by the end of the $n = 12$ stage of their equilibration runs. Although $g(r)$ and $S(q)$ are each other’s Fourier transforms and hence formally contain the same information, visual inspection of both is useful because each highlights aspects of the progress toward equilibrium that are not apparent from inspection of the other. All data are averaged over the ten independently prepared samples described in Sec. III.

Figure 9 illustrates the evolution of $g(r)$: colors indicate data from the end of each $n$-step. As $n$ increases and $U_{\text{MBJ}}(r)$ and $U_{\text{bond}}(r)$ approach their final functional forms, the peaks in $g(r)$ gradually sharpen. The broad initial peak for low $n$ splits in two: the larger-$n$ peaks at $r \approx \ell_k \approx 0.97\sigma$ and $r \approx 2\ell_k \sigma$, respectively, correspond to covalently bonded neighbors and nearest nonbonded neighbors. This splitting roughly corresponds to cessation of chain crossing; see Fig. 2. At larger $n$, higher-$K$ systems have sharper peaks at larger $r$ owing to their larger $\ell_k$. We emphasize that equilibration algorithms that employ only core-softening (i.e., do not employ topology-switching) would require substantially longer runtimes to achieve the same convergence to equilibrium over the range $9 \leq n \leq 100$.
Figure 10 illustrates the evolution of $S(q)$. $\lim_{q \to 0} S(q)$ decreases rapidly with increasing $n$ as long-wavelength density fluctuations anneal out; this decrease is a key indicator of equilibration.\footnote{7,\textsuperscript{10,14,16-18}} On the other hand, for $5.0 a^{-1} < q < 8.0 a^{-1}$, $S(q)$ increases with increasing $n$. This trend is aligned with the sharpening of the first peak in $g(r)$ at $r = \ell_0$. Finally, for $q > 8.0 a^{-1}$, $S(q)$ decreases with increasing $n$ as intermonomer distances substantially below $\ell_0$ become increasingly unlikely. Again, we emphasize that this progression toward the equilibrium structure (especially at low $q$) must necessarily be slower in the absence of topology-switching.

At the end of the equilibration runs, the primary peaks in $S(q)$ are, respectively, located at $q = 6.0 a^{-1}$ and $q = 7.4 a^{-1}$ for $\kappa = 0$ and $\kappa = 5.5 e$. Intriguingly, the $\kappa = 5.5 e$ distribution exhibits a prominent secondary peak at $q = 5.6 a^{-1}$ that is not present for flexible chains. Semiflexible-chain monomers are far more likely to be surrounded by interchain (as opposed to intrachain) neighbors than their flexible-chain counterparts; we believe that this secondary peak is a signature of the concomitant increased local interchain ordering.

APPENDIX B: COMPARISON TO A CORE-SOFTENING-ONLY APPROACH

As shown in Figs. 9 and 10, the core-softened interactions employed here lead to the two-body structure that differs from the equilibrium structure over a wide-range of length scales. Analogous simulations that employed only core-softening, i.e., simulations that followed the same $2 \leq n \leq 12$ progression described in Sec. II but did not employ any double-bridging moves, produce a very similar evolution of structure with increasing $n$. However, as we will show here, chain mobility in these simulations is much lower and the convergence of $N_e$ toward equilibrium is correspondingly slower.

Figure 11 illustrates how the absence of double-bridging moves can greatly slow equilibration even when chain crossing is allowed. Panel (a) compares the core-softening-only vs combined-approach monomeric mean-squared displacements in semiflexible melts with $2e \leq \kappa \leq 4e$. Here, the reference ($t = 0$) state is the beginning of the $n = 2$-step (Sec. II). For all chain stiffnesses, the mobilities are comparable until $\langle (\Delta r)^2 \rangle$ exceeds $\sim 10 a^2$. Subsequently, chains are far more mobile when double bridging is employed, and $\langle (\Delta r)^2 \rangle$ values in these runs are roughly an order magnitude larger than their core-softening-only counterparts by the end of the $n = 12$ stage. For intermediate $t$ and $n$, the effective power law $\dot{\gamma}(t) = d \ln[\langle (\Delta r)^2 \rangle] / d \ln(t)$ of the subdiffusion in the core-softening-only simulations is substantially lower. We emphasize that this lower mobility occurs even though chains are crossing (presumably at approximately the same rate since the barriers to crossing depend only on $n$; see Fig. 2) in both sets of simulations. It indicates that chains in the core-softening-only simulations remain at least somewhat confined to their tubes.

Panel (b) shows the ratio of $N_e$ at the each $n$-step to the equilibrium ($\langle N_e \rangle$). As in Fig. 5(b), $N_e/\langle N_e \rangle$ converges to unity (within
our statistical uncertainties of ∼0.5%) by the end of the combined-protocol runs. For the core-softening only runs, however, the final $N_e/(N_e^0)$ values range from 0.92 to 0.98. In general, parameters such as $N_e$ that depend on higher-order structural correlations on some length scale $s$ cannot be expected to have equilibrated until typical monomers have diffused by more than $\sqrt{s}$. For $N_e$, one expects $s \geq a$, where the tube diameter $a = \sqrt{N_e \sigma_0 / \kappa}$. Here, $7\sigma < a < 9\sigma$ for all $\kappa \geq \epsilon$; thus, the poorer convergence of $N_e$ in the core-soften-only runs is unsurprising. One might argue that this slower convergence is an artifact of our gradual stepping of the interactions from $\kappa = 2\kappa_0$ to $\kappa = 4\kappa_0$ values range from 0.92 to 0.98. In general, parameters such as $N_e$ that depend on higher-order structural correlations on some length scale $s$ cannot be expected to have equilibrated until typical monomers have diffused by more than $\sqrt{s}$. For $N_e$, one expects $s \geq a$, where the tube diameter $a = \sqrt{N_e \sigma_0 / \kappa}$. Here, $7\sigma < a < 9\sigma$ for all $\kappa \geq \epsilon$; thus, the poorer convergence of $N_e$ in the core-soften-only runs is unsurprising. One might argue that this slower convergence is an artifact of our gradual stepping of the interactions from $\kappa = 2\kappa_0$ to $\kappa = 4\kappa_0$.

Fig. 11. Mobility and convergence of $N_e$ to equilibrium for $N = 400$, with (solid curves) and without (dashed curves) double-bridging moves. Panel (a) shows monomeric mean-square displacements starting from the beginning of the $n = 2$ step. Vertical dotted lines indicate the beginning of the $n = 9$ step and roughly mark the cessation of chain crossing. Panel (b) shows $N_e/(N_e^0)$, where $(N_e^0)$ are the ensemble-averaged equilibrium values; the final values for the combined protocol differ slightly from unity because these results are not ensemble-averaged. Results for $\kappa < 2\kappa_0$ and $\kappa > 4\kappa_0$ are consistent with the trends shown here and are omitted for clarity.

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