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Plateau Modulus in the Lateral Motion Model for Melt Polymer Dynamics: A Computer Simulation

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ABSTRACT: A numerical simulation model is considered to study the relaxation of polymer melts within the context of the lateral motion model. This model assumes that the chain motion is primarily lateral motion along the backbones of neighboring chains. It is unclear whether a plateau would be observed in the relaxation modulus, if this is the mechanism of the chain dynamics. The simulation model considers the relaxation of a many-chain system. The beads of a given chain are paired with the beads of other chains. The two beads in a pair are constrained to move in unison. The chains are also allowed to slide along the backbones of the chains with which they have contacts through moves that interchange adjacent bead pairing. These moves mimic the types of motions present in the simplest form of the lateral motion model. The relaxing energy of this multichain system is found to display a pronounced plateau, demonstrating that models which are not based on a tube hypothesis can produce a plateau in the relaxation modulus.

I. Introduction

Linear chain polymer melts have a very characteristic form of the relaxation modulus.[1] The viscoelastic response of these systems to an applied strain displays a very rapid relaxation regime and slow relaxation regime, separated by the plateau region. The fast relaxation is independent of chain length, indicating that it involves local relaxations of the chains. The long time relaxations depend on chain length, displaying a dependence of roughly $N^{3.4}$ for the relaxation time.

The reptation model[2-4] describes the motion of the chains over short distances as three-dimensional Rouse motion. This model assumes that beyond some entanglement length, a, the interactions with neighboring chains suppress the lateral chain motion. The chain motion over distances greater than the entanglement length is modeled by the chain motion in a tube, the diameter of which is on the order of the entanglement length. In this model the rapid relaxations are associated with local three-dimensional chain motions over distances shorter than a, while the long time relaxation is associated with the diffusion of the chain out of the tube, which is defined by the environment at the time of the applied strain. The value of the relaxation modulus in the plateau region is used to empirically define the tube diameter, and the presence of the plateau region is taken as an experimental sign of the suppression of the lateral chain motion.

Recently, a number of new models[5-24] have been proposed to describe the dynamics of these systems. In particular, we have presented a model which assumes that the lateral chain motion is not suppressed.[17-24] Any pair of chains in the same region of a melt will be highly entangled. If the lateral chain motion is not suppressed, then the lateral motion of each chain must occur largely along the backbones of the neighboring chains, due to the highly entangled nature of each pair of chains. We have shown how models based on this concept can lead to very reasonable results for the chain dynamics[17,19,22,24] and for the viscoelastic relaxation[20,23] in the postplateau region. However, unlike the reptation model, this model provides no obvious simple reason why there should be a plateau in these systems.

In this paper we explore a stochastic computer simulation model for the local chain relaxation. In this model the configurations of a number of Gaussian chains are chosen randomly. The initial configurations are obtained by an affine stretching of chains chosen from a thermal distribution. The positions of the end beads of the chains are held fixed throughout most calculations, although calculations with mobile end beads are also discussed. To model the effects of interchain contacts on the chain relaxation, each internal bead of the chains (i.e., each bead which is not an end bead) is randomly paired with some other internal bead. The effect of the interchain contacts is accounted for by treating each bead in the pair as in contact with an image of the chain of the other bead. This image chain is translated so that this second bead of the pair has the same position as the first. The motivation for this procedure is to have the lateral motion and relaxation of each bead in every chain coupled to the lateral motion

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of some other "typical" chain in contact with it. The "typical" neighboring chain in the simulation procedure is a randomly chosen image of a chain somewhere else in the simulation. When this image chain moves, the chain that it is an image of is constrained to move with it, so that they remain translated images of each other. This pairing procedure has no effect on the configurations of the chains.

When one bead in the pair is moved during the simulation, the second bead is required to move with it. This couples the relaxation of the two chains involved in an interchain contact. The simulation model also includes moves which mimic the motion of one chain along the backbone of another chain at a contact point. This is included by allowing the interchange of adjacent bead pairings. Suppose bead a in chain α is paired with bead b in chain β, and the neighboring bead in chain α, bead $a + 1$, is paired with bead c in chain γ. The interchange of these pairings results in the $(a,b),(a+1,c)$ pairings being replaced by the pairings $(a,c),(a+1,b)$. This interchange corresponds to the chains β and γ moving along the backbone chain α.

This combination of local translations of pairs of beads comprising interchain contacts and the interchange of pairings mimics the types of motions considered in the lateral motion models.[17,19] Motions of these two types are stochastically attempted in a Monte Carlo simulation, and the relaxation of the coupled multichain system is examined as a function of the number of steps in the simulation.

II. The Model

In this section the computation model is described. A number of chains, each composed of n_b beads are chosen randomly. Consecutive beads in the chains are harmonically bound to each other with a force constant k. The initial displacements of the bonds in the z direction are independently chosen from a Gaussian distribution

$$\rho(\Delta z_j) = (2\pi\sigma_0^2)^{-1/2} \exp(-\Delta z_j^2/2\sigma_0^2) \qquad (1)$$

where Δz_j is the z component of the jth bond displacement. The mean squared width of the initial bond length distribution is given by

$$\sigma_0^2 = \gamma^2 K_B T/k \qquad (2)$$

where K_B is Boltzmann's constant and T is the temperature. If the γ is set to unity, this corresponds to a thermal distribution of bond lengths. The case $\gamma > 1$ corresponds to an instantaneous stretching of the many-chain systems along the z axis, and the set of Δz_j's chosen from (1) and (2) correspond to the system immediately after the stretching. We model only the relaxation of the z component and ignore the x and y components. This reduces the simulation time by a factor of 3 without sacrificing the essential physics of the problem. In the relaxation phase of most simulations, the end beads of the chains are held fixed at their initial positions.

After the initial chain configurations have been chosen, the beads are randomly paired (excluding the end beads for the chains). This is done by choosing one internal bead in a chain and randomly choosing another internal bead from any of the chains. This is continued until every internal bead is paired with another internal bead. Suppose z_a and z_b are the coordinates of two beads, a and b, that are paired. To model the constraints that chains pose to the lateral motion of other chains, we treat the beads a and b as being in contact. Bead a is in chain α and bead b is in chain β. To mimic the contact between these chains, we translate the beads in chain β by $\Delta z_{ab} = z_a - z_b$ for the purpose of this interchain contact. The translated coordinate of b is $z'_b = z_b + \Delta z_{ab} = z_a$. (Throughout this paper the convention is employed that z'_m denotes the coordinates of a translated image of bead m, the untranslated coordinate of which is z_m.) Thus, chain α and the translated chain β have the same coordinate at the interchain contact point. Of course, the description of the interchain contact is invariant to whether chain β or chain α is translated. In the simulation a list of bead coordinates z_a and a list of bead pairings (a,b) are maintained and updated after each move.

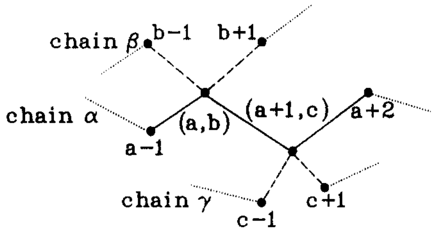

Figure 1. Interchain contacts involving beads a and $a + 1$ in chain α are modeled by pairing bead a with bead b in chain β and pairing bead $a + 1$ with bead c in chain γ. These pairings place bead a in contact with a translated image of chain β and bead $a + 1$ in contact with a translated image of chain γ. These image chains are translated so that the image of bead b has the same coordinate as bead a and the image of bead c has the same coordinate as bead $a + 1$.

To allow relaxation of the stretched multichain system, two types of moves are allowed. The first type retains the set of interchain pairings and allows for the motion of bead a and of the bead b with which bead a is paired. The displacements of the two beads are the same in the move, maintaining the constraint that the translated coordinate z'_b is the same as z_a. This move results in replacing z_a within its new value z_a^{new} and z_b with the new value $z_b^{\text{new}} = z_b + z_a^{\text{new}} - z_a$.

The second type of move allows lateral motions of the chain along the backbone of chains with which they have contacts. Suppose a and $a + 1$ are two consecutive beads in chain α. Bead a is paired with bead b in chain β, and bead $a + 1$ is paired with bead c in chain γ. In the move the pairings (a,b) and $(a+1,c)$ are switched, producing the new pairings (a,c) and $(a+1,b)$.

Having qualitatively described the types of moves in the model, we can now describe the relaxation procedure in detail. After the initial configuration of the chains and the pairings of the beads are selected, a large number of stochastic moves are made. Each move consists of randomly selecting a bead and a neighboring bead on the same chain. It is required that both of these beads, a and $a + 1$, are internal beads. The beads, which are paired with a and $a + 1$, are denoted as beads b and c, respectively. There are harmonic potentials between the (a,b) pair of the beads $a - 1$, $b - 1$, and $b + 1$. Likewise, there are harmonic bonds between the $(a+1,c)$ pair and the beads $a + 2$, $c - 1$, and $c + 1$, and there is a bond between a and $a + 1$. This is shown in Figure 1. The terms in the potential involving the (a,b) and $(a+1,c)$ pairs have the form

$$V_a = \frac{1}{2}k[(z_{a-1} - z_a)^2 + (z_{a+1} - z_a)^2 + (z_{a+2} - z_{a+1})^2 + (z'_{b+1} - z'_b)^2 + (z'_{b-1} - z'_b)^2 + (z'_{c+1} - z'_c)^2 + (z'_{c-1} - z'_c)^2] \qquad (3)$$

The primes indicate that the beads $b - 1$, b, and $b + 1$ have been displaced by $z_a - z_b$ so that $z'_b = z_a$ and that the beads $c - 1$, c, and $c + 1$ have been displaced by $z_{a+1} - z_c$ so that $z'_c = z_{a+1}$. The beads $a - 1$, $a + 2$, $b - 1$, $b + 1$, $c - 1$, and $c + 1$ are held fixed for the move of a and $a + 1$. V_a can be rewritten as the sum of its minimum value and harmonic terms accounting for the fluctuation of z_a and z_{a+1} from their values at the minimum. The values of $z'_b = z_a$ and $z'_c = z_{a+1}$ which minimize V_a are given by

$$z_{a,m} = [4(z_{a-1} + z'_{b-1} + z'_{b+1}) + z_{a+2} + z'_{c-1} + z'_{c+1}]/15 \qquad (4a)$$

$$z_{a+1,m} = [4(z_{a+2} + z'_{c-1} + z'_{c+1}) + z_{a-1} + z'_{b-1} + z'_{b+1}]/15 \qquad (4b)$$

The potential V_a can be rewritten as

$$V_a = V_m + 2k(z_a - z_{a,m})^2 + 2k(z_{a+1} - z_{a+1,m})^2 - k(z_a - z_{a,m})(z_{a+1} - z_{a+1,m}) \qquad (5)$$

where V_m is V_a evaluated at $z_a = z_{a,m}$ and $z_{a+1} = z_{a+1,m}$. The additional terms account for the deviations in z_a and z_{a+1} from their values at the minimum in V_a.

The move is accomplished in two submoves. In the first submove a trial move involving the interchange of the pairings from $(a,b),(a+1,c)$ to $(a,c),(a+1,b)$ is attempted. After the interchange the (a,c) pair is bound to $a - 1$, $c - 1$, and $c + 1$, as well as to $a + 1$, and the $(a+1,b)$ pair is bound to $a + 2$, $b - 1$, and $b + 1$. The coordinates z_{a-1}, z_{a+2}, z'_{c-1}, z'_{c+1}, z'_{b-1}, and z'_{b+1} are held fixed during the interchange. The local potential energy after the attempted move, $V_a^{\rm new}$, is still given by (3). However, after the interchange the contact conditions are $z'_c = z_a$ and $z'_b = z_{a+1}$. The values of these coordinates that mimimize $V_a^{\rm new}$ after the interchange are given by

$$z_{a,m}^{\rm new} = [4(z_{a-1} + z'_{c-1} + z'_{c+1}) + z_{a+2} + z'_{b-1} + z'_{b+1}]/15 \qquad (6a)$$

$$z_{a+1,m}^{\rm new} = [4(z_{a+2} + z'_{b-1} + z'_{b+1}) + z_{a-1} + z'_{c-1} + z'_{c+1}]/15 \qquad (6b)$$

The set of pairings $(a,b),(a+1,c)$ or $(a,c),(a+1b)$ defines the value of the potential minimum and the location of z_a and z_{a+1} at the potential minimum. The total potential is given by the value of the potential at the minimum plus quadratic terms in $\Delta z_a \equiv z_a - z_{a,m}$ and $\Delta z_{a+1} \equiv z_{a+1} - z_{a+1,m}$ (see eq 5). This form of the potential is the same before and after the trial interchange. We define the interchange submove to occur at fixed values of Δz_a and Δz_{a+1}. It only affects V_m. This attempted interchange move is accepted or rejected according to the standard Metropolis Monte Carlo algorithm,[25] comparing the Boltzmann factors for the energies V_a before and after the attempted move.

After the interchange move is accepted or rejected, a trial move of Δz_a and Δz_{a+1} is made by randomly selecting $\Delta z_a^{\rm new}$ and $\Delta z_{a+1}^{\rm new}$ according to

$$\Delta z_a^{\rm new} = \Delta z_a + 2\delta(\xi_1 - 1/2) \qquad (7a)$$

$$\Delta z_{a+1}^{\rm new} = \Delta z_{a+1} + 2\delta(\xi_2 - 1/2) \qquad (7b)$$

where ξ_1 and ξ_2 are random numbers distributed uniformly between 0 and 1. The maximum step size δ is set to $(K_{\rm BT}/k)^{1/2}$ in all calculations. This move of Δz_a and Δz_{a+1} affects only the last three terms in (5). V_m is unchanged. The potential is evaluated at the new values of Δz_a and Δz_{a+1}, and the move is accepted or rejected in the standard Metropolis Monte Carlo fashion.

The combination of the interchange submove and the submove of Δz_a and Δz_{a+1} is considered a single move of the a and $a + 1$. If either or both of the submoves is accepted, this results in a change in $z_a = z_{a,m} + \Delta z_a$ and $z_{a+1} = z_{a+1,m} + \Delta z_{a+1}$ and in z'_b and z'_c. If the interchange move is rejected, then $z'_b = z_a$ and $z'_c = z_{a+1}$ after the total move. If it is accepted, then $z'_c = z_a$ and $z'_b = z_{a+1}$ after the total move. The move results in a change in the translated value of the coordinate of b from $z'_b{}^{\rm before}$ to $z'_b{}^{\rm after}$. This is accompanied by an equal displacement of the untranslated value of this coordinate from z_b to $z_b + z'_b{}^{\rm after} - z'_b{}^{\rm before}$. Likewise, the coordinate for c changes from z_c to $z_c + z'_c{}^{\rm after} - z'_c{}^{\rm before}$.

In the simulation there are n_c chains, each containing n_b beads. The total number of internal beads in $n_c(n_b - 2)$. A time step in the simulation is defined as $n_c(n_b - 2)/6$ moves.

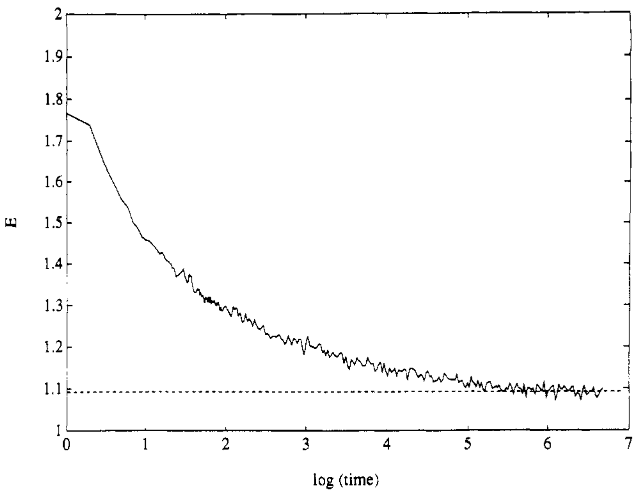

Figure 2. Average energy per bond plotted versus log t for $\gamma = 1.5$, $n_b = 101$, and $n_c = 198$. The horizontal dashed line is the average value obtained from the last 26 points in the figure.

III. Results

In Figure 2, the results are shown for a calculation with a force constant of $k = 2$ and $K_{\rm B}T/k = 1$. The number of beads per chain is $n_b = 101$, and the number of chains is $n_c = 198$. The initial stretching ratio γ is set to 1.5. The data presented are the average energy per bond. Notice that this is a plot of E versus log t. If the interchain contacts were not present, then each chain is a Rouse chain with fixed ends. Each chain has $n_b - 2$ internal modes, which can relax, and the end-to-end mode, which remains unrelaxed. The relaxed value of the energy per bond for a chain with fixed ends, without interchain contacts, is therefore $E_{\rm R} = [(n_b - 2)\,{}^1/_2K_{\rm B}T + {}^1/_2\gamma^2K_{\rm B}T]/(n_b - 1)$ since ${}^1/_2K_{\rm B}T$ is the average energy of a relaxed mode and ${}^1/_2\gamma^2K_{\rm B}T$ is the average energy of a stretched mode. For the case with $n_b = 101$, $\gamma = 1.5$, and $K_{\rm B}T/2 = 1$, the value of the totally relaxed chain energy per bond is $1.0 + (\gamma^2 - 1)/100 = 1.0125$. The data in Figure 2 strongly suggest that the system does not relax to this fully relaxed value when interchain contacts are included. Since end beads of the chains are not involved in pairings, a chain cannot slide past the end of another chain with which it has a contact. If it could, then the system would eventually relax completely. The incomplete relaxation, which is apparent in Figure 2, corresponds to the plateau in the relaxation modulus. For this reason, we refer to this incomplete relaxation as a plateau throughout the remainder of this paper.

A plot of $\log(E - E_{\rm R})$ versus log t is shown in Figure 3. The plateau is very pronounced. The horizontal line indicates the value obtained for E by averaging the last 26 points. The straight line with negative slope is added to help visualize the extent to which the data display a plateau. This line fits the lot$(E - E_{\rm R})$ vs log t data quite well between 5×10^1 and 5×10^4 time steps, while at times beyond 5×10^5 the data show no apparent decay. It should

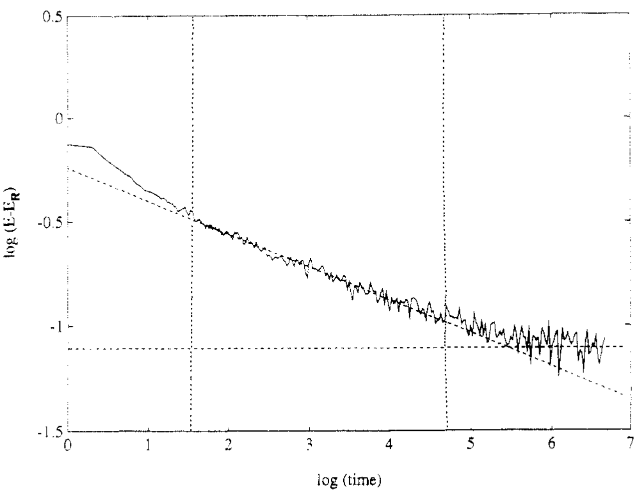

Figure 3. Plot of $\log(E - E_R)$ versus $\log t$ for $\gamma = 1.5$, $n_b = 101$, and $n_c = 198$. The horizontal dashed line provides the logarithm of the value obtained by averaging $E - E_R$ over the last 26 points.

Table I. Values of the Final Energy for $\gamma = 1.5$[a]

N	E_F	$E_F - E_R$
100	1.093 ± 0.002	0.080 ± 0.002
200	1.079 ± 0.002	0.072 ± 0.002
400	1.075 ± 0.003	0.072 ± 0.003

[a] $N = n_b - 1$, where n_b is the number of beads in each chain. The values of the final energies E_F are obtained by averaging over the last 26 points for which values were stored. In the last column $E_R = 1.0 + (\gamma^2 - 1)/N$ has been subtracted from the values for E_F.

be noted that, while the straight line fits the data well in the intermediate time regime, the data could also be quite well fit by a nonstraight curve, treating the intermediate regime as a crossover region from the early more rapid decay to the later plateau region. The important feature is the evident plateau in the relaxation curve.

In Table I, data are compared for chains of length $n_b = 101$, 201, and 401. The values for the final energy E_F are obtained by averaging the last 26 points for which data are stored. If the last 21 or 31 points are used to obtain the averages, the results differ from the values in the table by only ±0.001 to ±0.002 in each case. The estimates of the statistical errors given in the table are obtained assuming that the data points used in the average are statistically independent. From Figure 2, it would appear that this approximation is reasonably accurate. There is a slight change in going from $n_b = 101$ to $n_b = 201$, but no significant change between the $n_b = 201$ and $n_b = 401$ results. Thus, the results appear well converged with regard to chain length, indicating that end effects are not important. The $\log(E - E_R)$ versus $\log t$ plot is presented for the $n_b = 401$ case in Figure 4. Clearly, it is very similar to the $n_b = 101$ case in Figure 3. All the calculations presented have a total of 5×10^6 time steps. This corresponds to a total of approximately 1.65×10^{10} moves. Each of these calculations takes approximately 2 weeks of CPU time on an IBM RS6000/320H workstation.

In Table II, data are compared for $\gamma = 1.0$, 1.25, 1.50, and 1.75. In each case $n_b = 401$, and the calculations have 5×10^6 time steps. The values for the final energies are obtained by averaging over the last 31 points. Also given in the table are values calculated from the expression $E_0 + G_0(\gamma^2 - 1)$, where $E_0 = 1.01$ and $G_0 = 0.05$. As can be seen from the table, this expression fits the numerical data to within the statistical uncertainty of the calculations.

In the calculations reported above, the end beads in the chains are fixed. To study the effect of this feature of the procedure, some of the simulations have been repeated

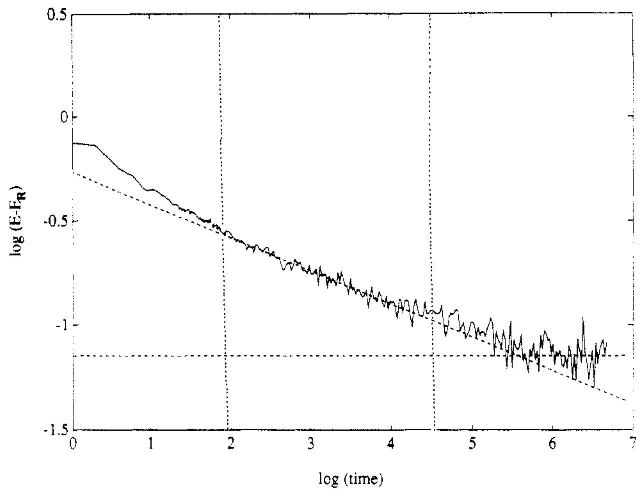

Figure 4. Same as Figure 3 for the case $\gamma = 1.5$, $n_b = 401$, and $n_c = 49$.

Table II. Values for the Final Energy as a Function of γ[a]

γ	E_F	$1.01 + 0.05(\gamma^2 - 1)$
100	1.01	1.01
1.25	1.04	1.04
1.50	1.07	1.07
1.75	1.12	1.11

[a] Values of E_F are given for calculations with $N = 400$, where $N = n_n - 1$. In column three, values which are calculated from $E = 1.01 + 0.05(\gamma^2 - 1)$ are given for comparison.

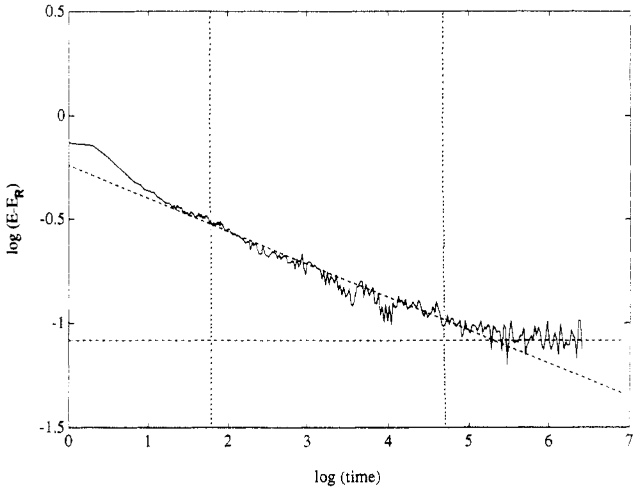

Figure 5. Same as Figure 3, except moves of end beads are included in the calculation.

with mobile end points. The end points in these simulations are not involved in pairings. The only modification in the simulation procedure is that additional moves, corresponding to displacements of the end beads, are attempted. One displacement move of each end bead is attempted each time step, and it is accepted or rejected in accord with the usual Metropolis Monte Carlo algorithm. The relaxation curve for the case with $\gamma = 1.5$ and $n_b = 101$ is shown in Figure 5. Clearly, it is very similar to the corresponding results with fixed end beads shown in Figure 3. The value of the plateau calculated from the last 26 points in Figure 5 is 1.095, which agrees with the result with fixed end beads to within statistical error.

At first it may seem surprising that the moves of the end beads have so little effect on the relaxation of the system. Because the random pairing algorithm is employed in the simulations, each chain has contacts with other (image) chains, which have their centers of mass distributed randomly (for the strained system) around its center of mass. As a result, each chain behaves as if it is in a strained bulk system and its relaxation is complete whether or not the ends are mobile.

IV. Discussion

In this work, a computational model has been examined which explores the relaxation of coupled multichain systems. This model mimics the features of lateral motion models for the dynamics of linear chain polymer melts. The focus of this work is the question of whether these models should exhibit a plateau region in the relaxation modulus. The calculations presented clearly display a plateau. This result is significant since a plateau is often taken to be the signature of the transition from short-range three-dimensional chain motion to longer distance reptative motion along the chain backbone. This work demonstrates that this transition is not necessary for the appearance of a plateau and that a plateau should be expected from models based on lateral chain motion.

The model considered in this work contains many features which are physically very similar to features of linear chain polymer melts. On the other hand, it is a simplified model and differs from real systems in a number of regards. Two chains are required to have the same position at the point of contact. This contact point moves along each of the chains involved in the contact through the interchange of pairing moves in the simulation. In real systems two chains are in contact as long as the elastic forces along the chains hold them in physical contact. As the chains move and relax, the local configuration of the chains may at some time result in forces which pull the pair of chains away from each other at the contact point. However, as long as the two chains are highly entangled, the two chains cannot readily separate over long distances. This picture of a contact sliding along the backbones of the chains is a model simplification, but it does incorporate this feature of highly entangled chains.

In the model, the contact points move along the chain backbone through the interchange of bead pairing moves. This type of motion along the backbone ignores the fact that as one chain moves along the backbone of another chain, the other chains pose barriers to this motion. The interchange move is equivalent to assuming that the chains can find paths past these barriers within relatively short times. Lateral motion models[17,19] that make assumptions of this sort provide results similar in many regards to the results of the reptation model. We have also recently explored ways of explicitly incorporating these barriers to lateral motion due to three chain and higher interactions.[21,24] These barriers to lateral motion should make the motion more hindered. In this regard, the model considered here makes the least constraining assumption. Since this model produces a plateau, it is reasonable to expect that more constrained lateral motion models should display a plateau as well.

Another simplification in the model is that the choice of pairings is totally random. In real polymer systems, if bead a in chain α is in contact with bead b of chain β, then there is a higher than random probability that nearby beads in chain α have contacts with beads from chain β. It is difficult to assess the effects that this local correlation in the bead pairings might have on the magnitude of the plateau. Furthermore, since each bead is paired with a randomly chosen bead in our simulation procedure, random long-range correlations in the motion of the chains are introduced into the calculations. This may also affect the magnitude of the plateau. We hope to explore the impact of these features of the simulations in future work.

The model considers only a limited set of stochastic local chain moves. The time dependence of the relaxation of the potential energy of the system in the model may differ from the time dependence of the preplateau relaxation in real polymer systems, due to the use of stochastic moves and because of the simplifications in the model just discussed. However, the appearance of the plateau in a model based on lateral chain motions is the important point, not the shape of the relaxation curve at early times.

The calculations demonstrate that the model displays a plateau. There remains the question of why the relaxation of the chains is incomplete. For a large system at temperature T, the average energy of the system is well approximated by the value of E satisfying[26]

$$\frac{\mathrm{d}S}{\mathrm{d}E} = \frac{1}{T} \tag{8}$$

where $S(E)$ is the entropy of the system at the energy E. Equation 8 is equivalent to minimizing the Helmholtz free energy as a function of E. Without the pairings of the beads, the system is a collection of N_I independent oscillators, where N_I is the total number of internal beads. The canonical entropy $S(T)$ should be the same as the microcanonical entropy $S(E)$ evaluated at the canonical energy $E(T)$, as long as this system is sufficiently large that the fluctuations in E are not significant. $S(T)$ can be evaluated for a system of N_I independent oscillators from

$$S(T) = -K_\mathrm{B} \int \mathrm{d}\boldsymbol{\xi}\, \rho(\boldsymbol{\xi}) \ln \rho(\boldsymbol{\xi}) + C \tag{9}$$

where $\boldsymbol{\xi} = (\xi_1, \xi_2, ..., \xi N_I)$ are the normal mode coordinates of the system, C is a constant, and the density $\rho(\boldsymbol{\xi})$ has the form

$$\rho(\boldsymbol{\xi}) = \prod_{j=1}^{N_I} (2\pi\sigma_j^{\,2})^{-1/2} \exp(-\xi^2/2\sigma_j^{\,2}) \tag{10}$$

The mean squared width of the jth mode is given by $\sigma_j^2 = K_\mathrm{B}\mathrm{T}/k_j$ and k_j is the force constant for the mode. Substitution of (10) into (9) yields

$$S_1(E) = \frac{N_I}{2} K_\mathrm{B} \ln(E/N_I) - \frac{K_\mathrm{B}}{2} \sum_{j=1}^{N_I} \ln k_j + C_1 \tag{11}$$

where $E = {}^1/_2 N_I K_\mathrm{B} T$ has been employed. (Since Monte Carlo simulations are being discussed, only the potential energy contributions are included.)

The form of $S(E)$ for the system when the beads have been paired is somewhat more complex. For a fixed set of bead pairing, there are $N_I/2$ independent coordinates, instead of N_I, because of the constraint that the two beads in a pair move together. Each of the $N_I/2$ bead pairs is harmonically bound to four other beads, accounting for the two bonds involving each of the beads. For a fixed set of bead pairings, there is a minimum energy configuration of these $N_I/2$ coordinates. The corresponding energy, E_min, and the mode force constants for the $N_I/2$ normal mode oscillators of the system depend on the particular set of bead pairings. The energy of the system at a given temperature has a contribution from the $N_I/2$ normal modes, plus a temperature-dependent average value of E_min

$$E(T) = \frac{N_I}{4} K_\mathrm{B} T + \bar{E}_\mathrm{min}(T) \tag{12}$$

The contribution to the entropy $S(E)$ from the normal modes has the same form as (11). There is another contribution from the number of different sets of bead pairing which give a $E_{\min}$ within some small energy shell of width ΔE about $\bar{E}_{\min}$. The function $S(E)$ for this system has the form

$$S_2(E) = K_B \ln[N(\bar{E}_{\min})] + \frac{N_I}{4} K_B \ln[(E_H)/(N_I/2)] - \left\langle \frac{1}{2} K_B \sum_{j=1}^{N_I/2} \ln K_j \right\rangle + C_2 \quad (13)$$

where $E_H = E - \bar{E}_{\min}$ is the energy of the harmonic modes. The constant C_2 depends on the width of the energy shell. This compensates for the dependence of $N(\bar{E}_{\min})$ on ΔE. The $\langle ... \rangle$ for the third term indicates that the term is averaged over all pairings which have a value of $E_{\min}$ that falls within the energy shell. All values of $E_{\min}$ (that is, all possible divisions of the energy E between $E_{\min}$ and E_H) should be accounted for in obtaining $S(E)$. However, for a large system, the fluctuations about the dominant value of $E_{\min}$ are small, and the entropy (13) obtained using this value of $E_{\min}$ should be accurate.

Without evaluating $E_{\min}$ and the normal mode force constants for every possible set of bead pairing, $S_2(E)$ and $E_{\min}$ cannot be determined in greater detail. However, it is clear that the entropy functions for the two systems, $S_1(E)$ and $S_2(E)$, should be expected to differ. According to (10), if $S_1(E)$ and $S_2(E)$ differ by more than an energy-independent constant, then the corresponding equilibrated energies of the systems are different as well. This results in the final energy of the system with bead pairings, E_F, being higher than the relaxed energy of the unpaired system of chains, E_R.

On a more qualitative level, as the bead paired system relaxes, each chain slides along the contours of the chains in contact with it. On the average this motion is in the direction which reduces the excess stretching in its bonds. This bias on the motion of the chains along each other results in less randomness in the set of bead pairings and a lowering of the corresponding terms in the entropy (terms one and three in eq 13). At some point the loss in entropy due to further relaxation offsets the decrease in energy and the system has equilibrated.

The data in Table II show that, even for the $\gamma = 1.0$ case, the value of E_F is not the value, $E_0 = 1.0$, that would be obtained for the chains without pairings. Rather a slightly higher value $E_F = 1.01$ is found. This reflects the fact that the system with pairings is different than the system without pairings, and the entropy function $S(E)$ is different for the two cases. The energy depends only on γ^2, since this is a harmonic system. E_F can be expanded in γ^2 about $\gamma^2 = 1$. The leading terms give $E_F = E_0 + G_0(\gamma^2 - 1)$. This form fits the numerical data to within statistical errors for the parameters $E_0 = 1.01$ and $G_0 = 0.05$. The value of E_0 indicates that the fully relaxed system with bead pairings should be slightly more stretched that the system without bead pairings. The $G_0(\gamma^2 - 1)$ term gives the energy per bond above the random thermal energy. The stress is given by the quantity $dE_F/d\gamma$ multiplied by N_B, the number of bonds that cross a section of the x-y plane with unit area. For small γ, the leading terms in N_B is independent of γ. The plateau modulus is obtained by dividing this stress by γ. This gives $2G_0N_B$ for the plateau modulus. The energy of the system before relaxation (at $t = 0$) is γ^2, and the contribution in excess of thermal energy is $\gamma^2 - 1$. The corresponding initial stress is $2N_B$. This gives an entanglement number of monomer units of $N_e = 20$ for this model, where this quantity is defined in terms of the plateau in the usual phenomenological manner.[2]

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