# Scaling Analysis of Multichain Cooperative Motions in the Lateral Motion Model for Polymer Melts

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ABSTRACT: A scaling analysis is presented for the evaluation of the time dependence of the lateral chain motion in monodisperse polymer melts. This analysis accounts for the correlations between the motions of neighboring chains, as well as for the correlations between the motions of beads in the same chain. These correlations result in a slowing of the Brownian chain dynamics. This analysis predicts that the bead mean squared displacement depends on time as $g \sim t^{2/7}$ for times less than the terminal time. The terminal time is found to scale as $N^{3.5}$. The center of mass diffusion constant has a component, which arises from the relative motions of neighboring chains, that scales as $N^{-2.5}$. There is also a component, which accounts for the correlated motion of all chains in a region of the melt, that scales as $N^{-2.1}$. This latter component should dominate for sufficiently long chains due to its milder scaling.

## I. Introduction

In this manuscript we present a scaling argument for the mean squared bead displacement due to lateral chain motion in a monodisperse melt of linear long chain polymers. This scaling argument accounts for the correlation between the motion of a given bead and the motion of other beads in the same chain and nearby chains. The extent of these correlations depends on the length scale for the bead motion. A diffusion constant for motion on each length scale is determined from the number of beads which have correlated motions on this length scale. This scaling argument yields a mean squared displacement which has the form $g \sim t^{2/7}$ for times less than the terminal time. This behavior of $g(t)$ leads to a terminal time which scales as $\tau \sim N^{3.5}$. The scaling of the diffusion constant for the relative motion of the centers of mass of two entangled chains is given by $D_{cm}^{rel} \sim R_G^2/\tau \sim N^{-2.5}$. However, there is also a contribution to the chain center of mass motion due to the correlated motion of all chains in a volume with spacial dimension $\xi$. The value of $\xi$ which provides the optimal center of mass diffusion yields a diffusion constant which scales as $D_{cm} \sim N^{-2.1}$. This latter scaling should dominate for sufficiently long chains.

This work demonstrates that consideration of the lateral chain motion reproduces the basic scaling relationships for polymer melt systems exceptionally well. In a separate paper[1] we compare the relaxation modulus predicted on the basis of the lateral chain motion with experimental results for monodisperse and bidisperse melts. The agreement is excellent.

A number of models for the dynamics of melt polymer systems have been proposed.[2-22] The reptation model[2-4] is the most widely employed of these models. The reptation model is based on the premise that the lateral chain motion is suppressed in the melt due to interchain interactions. As a result the motion of each chain is restricted to a snakelike slithering along its own backbone, except over short distances. The primary justification for the reptation model lies in its ability to reproduce polymer phenomenology. The current work demonstrates that alternative assumptions also reproduce those aspects of polymer phenomenology that we have considered.

The outline of the paper is as follows. The scaling argument is presented in section II. Section III summarizes the results of the model and provides a discussion of the simplifications in the model. An appendix is included, which discusses the concepts of cooperative modes and correlated motions in greater detail.

## II. Theory

We begin by considering a two chain picture.[17,19] Each chain in a melt is in contact with on the order of $M$ units on other nearby chains, where $M \sim N^{1/2}$ and $N$ is the number of monomer units per chain. This follows from the following scaling argument. The chain radius of gyration scales as $N^{1/2}$. Each chain is in contact with the chains in a region about its center of mass, which has a volume on the order of $R_G^3 \sim N^{3/2}$. This volume contains on the order of $N^{3/2}$ monomer units, which corresponds to on the order of $N^{1/2}$ chains, each having $N$ monomer units. The number of close interchain contacts involving a given chain, $n_c$, is proportional to the length of the chain, $n_c \sim N$. Since this chain has contacts with $M \sim N^{1/2}$ other chains, the average number of contacts between a pair entangled chains is given by $n_c/M \sim N^{1/2}$. Thus, in a melt of long chains, each pair of entangled chains has a large number of contacts. In the course of these many contacts, the chains randomly wind around each other. As a result, the two chains cannot easily separate. One way for the chains to untangle is by reptative motions along their own backbones. An alternate approach is for each chain to move laterally. Of course the chains cannot pass through each other at contact points, but each chain can slide laterally along the backbone of the other chain in the pair. In this work we explore the consequences of this lateral motion. Lateral motion of each chain perpendicular to the backbone of the other chain is also possible. However, if the two chains are highly entangled, this perpendicular lateral motion is restricted by the winding of the chains around each other. Therefore, we make the simplifying assumption that the sliding of each chain along the backbone of the other dominates, except on short length scales.

We have explored this sliding motion of one chain along the backbone of another.[17,19] If a given contact point between the chains slides a root mean squared contour displacement $\bar{\ell}$ along the backbones of the chains in time $t$, then this $\bar{\ell}$ is proportional to the mean squared bead displacement,

$$g(t) \sim \bar{\ell}(t) \tag{1}$$

Notice that $g(t)$ is the average of the square of the three-dimensional displacement vector for a bead in the chain, while $\bar{\ell}$ is the square root of the mean squared contour displacement of the contact point along the chain backbones.

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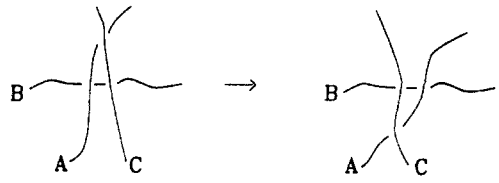


**Figure 1.** Chains A and C moving along the contour of chain B.

As one chain slides along the contour of another, this motion is impeded by the presence of other chains. An example of this interaction of three chains is pictured in Figure 1. As chain A slides along chain B, it encounters chain C. It is reasonable to assume that the motion of A along B is correlated to some extent with the motion along B of other nearby chains, such as chain C. However, the motion of chains A and C along chain B is not completely correlated. In Figure 1, chain A moves farther to the right along B than does chain C. Therefore, there is a cooperative component of motion of chains A and C along B and there is a noncooperative component. Since all chains are equivalent, it is also clear that the root mean squared contour displacement of A along C is the same as the root mean squared contour displacement of A along B.

Our objective is to evaluate the time dependence of the mean squared contour displacement of one chain along the backbone of another. Once this is accomplished, then (1) provides the mean squared bead displacement. This calculation is performed by evaluating the number of beads that must move cooperatively to produce a certain size contour length displacement $\bar{\ell}$. If this cooperative motion involves $n$ beads, the friction coefficient associated with this motion, $\zeta_n$, is proportional to $n$. The diffusion constant for this $n$ bead cooperative motion scales with $n$ as $D_n = K_B T/\zeta_n \sim 1/n$. This point is discussed more fully in the Appendix.

The number of beads that must move cooperatively to allow for lateral chain motion depends on the length scale for the motion. First consider two beads, which are $m$ beads apart in the same chain. The mean squared distance between these two beads is $\sigma_m^2 \equiv \langle(\Delta r_m)^2\rangle = mb^2$, where $b$ is the effective segment length. This expression assumes the chains can be modeled as Gaussian random coils, which is a good approximation in the melt, except over short distances.[23,24] The extent of correlation in the motion of the beads must be determined by the dimensionless ratio $\sigma_m^2/g$, since the only relevant length scales are provided by the bead mean squared displacement, $g$, and the mean squared distance between the two beads on the chain, $\sigma_m^2$. If $\sigma_m^2/g$ is small, the beads are near each other on the chain compared with the typical bead displacement, and the motion of the beads must be correlated. If the ratio $\sigma_m^2/g$ is large, then the motions of the beads are uncorrelated. Since $\sigma_m^2$ is proportional to $m$, this argument leads to the conclusion that $m_c$, the number beads in a chain that have correlated motions with any given bead, must be proportional to $g$,

$$m_c \sim g \tag{2}$$

Correlation is, of course, not an all or nothing quantity. More precisely, it is the correlation length measured along the contour of the chain which is proportional to $g/b$. This is discussed in the Appendix. The quantity $m_c$ is this correlation length divided by $b$.

Equation 2 states that the motion of a given bead requires the correlated motion of an $m_c$ bead segment in the same chain. The motion of this $m_c$ bead segment, which we refer to as segment a, is correlated with the motion of the other chains in contact with it. We argue above that a chain of length $N$ is in contact with $N^{1/2}$ other chains of the same length, if the chains are modeled as Gaussian random coils. The same argument holds for $m_c$ bead segments of Gaussian random coil chains. Therefore, there are $m_c^{1/2}$ chain segments of length $m_c$ that are entangled with segment a, and these segments have their motions correlated with the motion of segment a on the length scale considered.[25]

This argument gives on the order of $m_c \sim g$ beads in each of the $m_c^{1/2}$ nearby chains that must move cooperatively to produce the lateral motion on this length scale. Therefore, the total number of beads moving cooperative is given by $n_c \sim m_c m_c^{1/2} \sim g^{3/2} \sim \bar{\ell}^{3/2}$. The diffusion constant for this cooperative motion is given by

$$\begin{aligned} D_g &\sim 1/n_c \\ &\sim \bar{\ell}^{-3/2} \end{aligned} \tag{3}$$

Once the scaling of $D_g$ has been obtained, the time scale for the motion on this scale can be obtained. $D_g$ is the diffusion constant for the motion of chain A along chain B, accounting for the cooperative motion of the remaining chains that must be dragged along. The relationship between contour displacement, diffusion constant and time for the motion, $t_g$, is

$$\bar{\ell}^2 \sim D_g t_g \tag{4}$$

Substitution of (3) into (4) yields

$$t_g \sim \bar{\ell}^{7/2} \tag{5}$$

This is the relationship between the contour length scale and the time for the motion. Inverting provides the time dependence of $\bar{\ell}$

$$\bar{\ell}(t) \sim t^{2/7} \tag{6}$$

or, equivalently, of the bead mean squared displacement

$$g(t) \sim t^{2/7} \tag{7}$$

which follows from (1). This expression for $g(t)$ is not valid for very short times, since the Gaussian random coil approximation for the chains is not accurate over short length scales and because the model of each chain sliding along the backbones of neighbors is not appropriate on short scales. It is also not appropriate for contour length scales on the order of the chain length or longer. It is valid for the important intermediate regime.

The terminal time $\tau$ can be evaluated from the condition that $\bar{\ell}$ at $t = \tau$ must be on the order of the chain contour length, which is proportional to $N$. Combining $\bar{\ell}(\tau) \sim N$ and eq 6 gives[21]

$$\tau \sim N^{7/2} \tag{8}$$

in excellent agreement with experiment. At $t = \tau, g \sim N$, since $g \sim \bar{\ell}$. This gives $g(\tau) \sim R_G^2$ as expected, where $R_G$ is the chain radius of gyration. This result, together with (8), provides the scaling for diffusion constant for the *relative* center of mass motion of two entangled chains

$$\begin{aligned} D_{cm}^{rel} &\sim R_G^2/\tau \\ &\sim N^{-2.5} \end{aligned} \tag{9}$$

This contribution arises from the sliding of the chains along each other (i.e. relative motion of the chains) until the contacts between them are broken, which occurs when the contact points reach the chain ends.

There is also a contribution to $D_{cm}$ which arises from the *correlated* motions of all chains in a correlated

region.[21,26,27] We have shown previously[21] that this contribution scales as

$$D_{cm} \sim N^{-21/10} \tag{10}$$

if $\tau \sim N^{7/2}$. This contribution results from the correlated motion of all beads in a correlated volume $\xi^3$. The optimal correlation length,[21] which is the value of $\xi$ that maximizes this contribution to $D_{cm}$, is proportional to $\tau^{1/5}$. Since the diffusion constant is inversely proportional to the number of correlated beads, this yields $D_{cm} \sim \xi^{-3} \sim \tau^{-3/5}$, which leads to (10). This contribution to $D_{cm}$, eq 10, should dominate over the contribution in eq 9 for long chains due to the weaker scaling on $N$. This result $D_{cm} \sim N^{-2.1}$ is in excellent agreement with experimental observations.

## III. Discussion

The model for lateral chain motion presented in this paper provides excellent results for the scaling of the center of mass diffusion constant and the terminal time. In a separate paper[1] the application of this model is made to the evaluation of the relaxation modulus of monodisperse and bidisperse melts. The results are also in excellent agreement with experimental results.

The model considers the lateral motion of the chains. The scaling analysis presented accounts for the intrachain and interchain correlations for the motion of the beads. This analysis predicts that the lateral chain motion is slowed by the interchain interactions, but it is not suppressed, as assumed in the reptation model. The slowed lateral motion provides results in excellent agreement with melt polymer phenomenology. This is a mean field theory in that the averaged bead–bead correlations are employed in determining the lateral chain motion. This does not preclude the possibility of the presence of particularly knotted multichain configurations, which suppress the lateral motion. However, it does show that there is no need to make such an assumption in order to reproduce these experimental results.

The model presents a simplified picture of polymer melts in a number of ways. The lateral motion of each chain is taken to be primarily along the random coil contours of neighboring chains. Fluctuations in the distance from these contours of nearby chains can also contribute to the bead mean squared displacement. The assumption is that, except over short distances, the motion along the contours dominates over these lateral motions perpendicular to the contours of neighboring chains, due to the highly entangled nature of the configurations of each pair of neighboring chains. The model also only considers the lateral motion. Reptative motions can contribute to $g(t)$ as well. This competition between reptation and the slowed lateral motion is an important question. One simple argument would state that since the terminal time for reptation scales as $N^3$ and it scales as $N^{3.5}$ for lateral motion, then the reptative motion should "win" for sufficiently long chains. However, this $N^3$ scaling for reptation assumes that lateral motion is suppressed. If this is not the case, there are many more avenues open for lateral motion than reptation. This reptative scaling may not be appropriate for a chain which is exploring this large number of lateral configurational moves. Thus, it is unclear which mechanism should dominate in the melt at long times. We plan to study the competition between lateral and reptative motions in future work.

The presence of the plateau in the relaxation modulus and the crossover from short chain Rouse-like behavior to long chain behavior at a critical chain molecular weight are often taken to be signatures of the suppression of lateral motion.[2] In a separate manuscript[28] we present the results of computer simulations which study chain relaxation within a computational model. This model incorporates the sliding lateral motion of the chains along the other chains with which they have contacts. These simulations clearly indicate the presence of a plateau in the relaxation within this lateral motion based simulation model.

The lateral motion model presented in this work is not capable of reproducing the crossover to short chain behavior. It is clearly a long chain model. In polymer systems the chain ends are more mobile than beads near the chain center. As a result the ends do not provide significant barriers to the lateral chain motion. This feature is not incorporated in this model. For short chains, pairs of nearby chains are not highly entangled. In this case the lateral motion need not be along the contours of these neighboring chains. Furthermore, reptative and lateral motions should both be important for short distance motion. If all these features were incorporated in the model, one would expect to see the crossover to Rouse-like behavior for short chains. We plan to address these considerations in future work.

One final point is worth considering. We evaluated the number of beads that must have their motions correlated as a function of the mean squared bead displacement $g$. This result is then employed to calculate the time dependence of the motion of one chain along another, which in turn provides the time dependence of $g$. Can there also be a three-dimensional cooperative motion of all these beads that have their motions correlated (as opposed to the correlated motions along chain contours considered here)? The answer to this question is that there can be such a motion, but it cannot grow in time faster than the bead motion due to the sliding along the contours of nearby chains, which is considered in this work. If this three-dimensional cooperative motion did have a stronger time dependence, then the sliding motion would become insignificant at later times. If this sliding motion is negligible, then the system behaves like a cross-linked system and the three-dimensional chain motions are not possible over long distances. As a consequence, three-dimensional cooperative motions are possible, but they cannot dominate the motions considered in this model.

In summary, we have presented a scaling argument for the lateral chain motion. A major consequence of this argument is that the lateral chain motion contribution to the bead mean squared displacement behaves as $g \sim t^{2/7}$ for times less than the terminal time. In addition, the model predicts that the terminal time scales as $\tau \sim N^{3.5}$ and the dominant contribution to the center of mass diffusion constant for long chains scales as $D_{cm} \sim N^{-2.1}$.

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## Appendix

In this appendix, the diffusive motion of collective modes is explored. Let us first consider the motion on the time scale $t_s$ of the center of mass of all beads in a region of space, $V$. We assume that a correlation length can be defined for the motion of the beads at time $t$. If the spacial dimension of the region $V$ is on the order of the correlation or longer, then the center of mass motion of the beads in $V$ is only weakly correlated with the motion of beads outside the region on this time scale. If this is the case,

then the center of mass motion is well approximated as diffusion for times $t < t_s$

$$\langle(\Delta\xi_1)^2\rangle = 6D_\xi t \tag{A1}$$

where

$$\xi_1 = \frac{1}{N}\sum_j \mathbf{r}_j \tag{A2}$$

The summation in (A2) is over all beads in $V$ at $t = 0$. As time increases, the length scale for bead motion increases. This can cause the correlation length to increase with time. If at some time greater than $t_s$ the center of motion of the beads in $V$ is significantly correlated with the motion of beads outside $V$, then the simple diffusion law (A1) may not apply. However, for $t < t_s$ the correlations are short ranged compared to the length scale of $V$, and (A1) is a reasonable approximation. (It is exact if correlations between beads in the region and outside it are ignored.)

The diffusion constant $D_\xi$ can be evaluated by considering the motion at very short times, as long as we consider the particle motion to be Brownian on all time scales, including very short time scales. At very early times, the length scale for bead motion is very short and all interparticle correlations can be ignored. In this case

$$\begin{aligned}\langle(\Delta\xi_1)^2\rangle &= \frac{1}{N^2}\sum_{j,k}\langle\Delta\mathbf{r}_j\cdot\Delta\mathbf{r}_k\rangle \\ &= \frac{1}{N^2}\sum_j\langle(\Delta\mathbf{r}_j)^2\rangle \\ &= \frac{1}{N}6D_0t\end{aligned} \tag{A3}$$

where $D_0$ is the single particle diffusion constant for times when $\langle(\Delta\mathbf{r}_j)^2\rangle$ is much less than the mean squared distance between particles. The last expression assumes that all beads are equivalent, and it employs $\langle(\Delta\mathbf{r}_j)^2\rangle \equiv 6D_0t$ for all $j$ at very short times. Of course, in real systems the motion is not Brownian for distances much less than the interparticle distance. However, if we model the motion as Brownian on all length scales, this does not effect the results on longer scales for which the Brownian model is appropriate. This extension of the Brownian model to very short length scales provides a simple way of calculating the mode diffusion constant.

Now consider the motion of an individual bead, bead 1, for $t < t_s$. At very short times its motion is diffusive and $\langle(\Delta\mathbf{r}_1)^2\rangle = 6D_0t$. For times on the order of $t_s$, the motion of bead 1 is significantly correlated to the motion of the other beads in $V$, if the correlation length is on the order of the spacial dimension of $V$. In this case one might expect $\langle(\Delta\mathbf{r}_1)^2\rangle$ to be on the order of $\langle(\Delta\xi_1)^2\rangle$; that is, $\langle(\Delta\mathbf{r}_1)^2\rangle \sim 6D_0t/N$ for $t \sim t_s$. Clearly, the interparticle correlations slow the bead motion.

The coordinate of bead 1 can be expressed as a sum of $\xi_1$ and a displacement from $\xi_1$

$$\mathbf{r}_1 = \xi_1 + \xi_2 \tag{A4}$$

where $\xi_2 = \mathbf{r}_1 - \xi_1$. We assume

$$\langle\Delta\xi_1\cdot\Delta\xi_2\rangle = 0 \tag{A5}$$

for $t < t_s$. This is the case, for instance, in an equilibrium isotropic system, as long as the correlations between the beads inside $V$ and those outside $V$ are ignored. From $\xi_2 = \mathbf{r}_1 - \xi_1$, we have

$$\langle(\Delta\xi_2)^2\rangle = \langle(\Delta\mathbf{r}_1)^2\rangle + \langle(\Delta\xi_1)^2\rangle - \frac{2}{N}\sum_{j=1}^{N}\langle(\Delta\mathbf{r}_1)^2\rangle C_{1j}(t) \tag{A6}$$

at time $t$, where the normalized correlation function $C_{1j}(t)$ is given by

$$C_{1j}(t) = \langle\Delta\mathbf{r}_1\cdot\Delta\mathbf{r}_j\rangle/\langle(\Delta\mathbf{r}_1)^2\rangle \tag{A7}$$

Combining (A6) with $\langle(\Delta\mathbf{r}_1)^2\rangle = \langle(\Delta\xi_1)^2\rangle + \langle(\Delta\xi_2)^2\rangle$, which follows from (A5), we obtain

$$\langle(\Delta\xi_2)^2\rangle = \langle(\Delta\xi_2)^2\rangle + 2\langle(\Delta\xi_1)^2\rangle - \frac{2}{N}\sum_{j=1}^{N}\langle(\Delta\mathbf{r}_1)^2\rangle C_{1j} \tag{A8}$$

Rearranging we find

$$\langle(\Delta\mathbf{r}_1)^2\rangle = N\langle(\Delta\xi_1)^2\rangle/\sum_{j=1}^{N}C_{1j} \tag{A9}$$

Suppose we now take $V$ to be very large and ignore the correlations between beads inside $V$ and those outside $V$. Ignoring these correlations has a negligible effect on the motion of bead 1 at times for which the correlation length is much less than the spacial dimension of $V$. (For instance, we could take $V$ to be macroscopic.) The quantity $N\langle(\Delta\xi_1)^2\rangle = 6D_0t$ is independent of the size of $V$. We can define the number of correlated beads at time $t$ as

$$N_c(t) = \sum_j C_{1j}(t) \tag{A10}$$

where the sum is the overall beads in $V$. Combining (A9) and (A10) yields

$$\langle(\Delta\mathbf{r}_1)^2\rangle = 6D_t t \tag{A11}$$

where

$$D_t = D_0/N_c(t) \tag{A12}$$

These expressions become independent of the size of $V$ for large $V$. These expressions show that the diffusion constant for the motion of a bead is inversely proportional to the number of beads that have motions which are correlated with the motion of bead 1.

Equation A11 actually provides a lower limit for $\langle(\Delta\mathbf{r}_1)^2\rangle$, since there may be other collective modes besides center of mass modes that may provide a larger contribution to $\langle(\Delta\mathbf{r}_1)^2\rangle$. An example of a collective mode, which might be important, is a mode for a back-flow circulation. In such a mode, as the beads in a region move in one direction, beads from a neighboring region flow in the vacated volume. The mode involves a closed circulation on some length scale due to this type of collective motion.

Collective modes of this type can be defined by

$$\xi_1 = \frac{1}{N}\sum_j \mathbf{A}_j\cdot\mathbf{r}_j \tag{A13}$$

where $\mathbf{A}_j$ rotates vector $\mathbf{r}_j$ and multiplies it by a constant, which we expect to be of order unity. The multiplicative constant can, in the most general case, vary from bead to bead. As before $\xi_2$ is defined as $\mathbf{r}_1 - \xi_1$, and (A5) is required to be satisfied. If (A5) is not satisfied for a given $\xi_1$, then a new mode $\xi'_1$ can be defined as $\xi'_1 = B\xi_1$. The mode that corresponds to $\xi_2$ is given by $\xi'_2 = \mathbf{r}_1 - \xi'_1 = \xi_2 + (1 - B)\xi_1$. By appropriately choosing $B$, $\xi'_1$ and $\xi'_2$ can be found which obey $\langle\Delta\xi'_1\cdot\Delta\xi'_2\rangle = 0$, as long as $\langle\Delta\xi_1^2\rangle \neq$

0. The argument leading to (A9)–(A12) follows as before, except that $C_{1j}(t)$ is now defined by

$$C_{1j}(t) = \langle \Delta\mathbf{r}_1 \cdot \mathbf{A}_j \cdot \Delta\mathbf{r}_j \rangle / \langle \Delta\mathbf{r}_1^2 \rangle \qquad \text{(A14)}$$

In order for the motion of this mode to obey simple diffusion for $t < t_s$, the beads involved in the mode must be largely uncorrelated with the beads not involved in the mode. If this is not the case, the changing extent of correlation slows the mode as time increases. In order for these correlations to be small for all $t < t_s$, the length scale associated with the mode must be on the order of the correlation length at time $t_s$ or greater. As a result, the correlations are small between bead 1 and those beads for which the $\mathbf{A}_j$'s provide significant rotations. In this case, the sum over $C_{1j}$ is not too different from the sum of $C_{1j}$ for the center of mass modes, and the value calculated for $\langle(\Delta\mathbf{r}_1)^2\rangle$ is not changed too much from the value for the center of mass modes.

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(25) This picture of the correlated motion corresponds to the assumption that the length scale for the correlated motion of chain segments is proportional to the length scale for the total motion. If $g_c$ is the correlated component of $g$, this assumption can be expressed as $g_c \sim g$. If the motion of one chain is correlated with the motion of the nearby chain segments over a length scale determined by $g_c$, then the number beads whose motion is correlated in each of these segments must be proportional to $g_c$. The argument is exactly the same as the argument for the number of correlated beads in a single chain. This gives the number of beads in each nearby chain whose motion is correlated as scaling as $m_c \sim g$. This is the result used in the scaling argument in the text. If this assumption that $g_c \sim g$ were not true, $g_c$ would have to have a weaker scaling with respect to $g$. This would ultimately lead to a weaker scaling of $\tau$ on $N$ than the $N^{3.5}$ scaling obtained in this work. (In previous work[17,19] it was assumed that there is no interchain correlation, $g_c \sim 0$, except at short times. This leads to $\tau \sim N^{3.0}$.) A milder scaling of $g_c$ on $g$ results in the interchain correlations being negligible on longer length scales. Since there are more interchain contacts between each pair of chain segments on longer length scales, it seems unlikely that this is the case. It is also worth noting that the noncooperative component of $g$, $g_{nc}$, must be proportional to $g$. This is required by the equivalence of all chains. In Figure 1, A must slide along C on the average the same distance it slides along B, leading to a noncooperative component of the motion along B that is of the same order of magnitude as the total motion.
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