Effect of Many Chain Interactions on Lateral Motion in Polymer Melts: A Model for the Dynamics of Linear Chain Systems

Michael F. Herman* and Ping Tong

Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

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ABSTRACT: A model is presented for the lateral motion of linear polymer chains in a monodisperse melt. Because each pair of neighboring chains in a melt is highly entangled and randomly wound around each other, the lateral motion of each chain is taken to occur primarily along the contours of neighboring chains. This lateral motion is impeded by interactions with other nearby chains. Some obstacle chains constitute significant barriers to lateral motion, while others do not, depending on the local configurations of a chain. A given chain may constitute an impassable barrier on one length scale, and not pose an impassable barrier on longer length scales. An expression is developed for the fraction of barriers which constitute impassable barriers as a function of the length scale for chain motion. The cooperative motion of mutually impassable chains is considered in the model. A scaling analysis is applied to this model, leading to the prediction that the mean-squared bead displacement for the polymer chains scales as $t^{2/7}$. The corresponding terminal time scales with chain length as $N^{7/2}$. A calculation of the center of mass diffusion constant, which is based on the correlated motion of all chains in a certain region, yields $D_{cm} \sim N^{-2.1}$. The relaxation modulus is also evaluated and found to be in very good agreement with experimental data.

I. Introduction

In this paper we develop a model for the dynamics of linear chain polymer melts. In a monodisperse melt, each chain is entangled with on the order of $N^{1/2}$ other chains, where N is the number of monomer units per chain. There is also on the order of $N^{1/2}$ contacts between a pair of entangled chains. A pair of chains is depicted schematically in Figure 1. In the course of the interchain contacts, these two chains wind randomly around each other. Because the two chains are highly intertwined, they cannot readily separate. Relative motion of the two chains can occur by means of reptation, in which each chain moves along its own backbone. An alternative mechanism is for each chain to move laterally along the backbone of its neighboring chains. Of course, a mixture of the two types of motions is also a possibility.

The reptation model[1-22] assumes that the presence of the neighboring chains so impedes the lateral motion as to totally suppress it, except over short distances. This model has been successful in describing a wide range of experimental results for polymer systems in the melt and concentrated solutions.[23-33] Despite this general success of the reptation model, there are a number of reasons to explore alternative models and to investigate the basic question of whether the constraints due to the neighboring chains are sufficient to suppress the lateral chain motion. The shear viscosity is observed experimentally to scale with chain length as $N^{3.4}$, rather than N^3 as predicted by reptation. While a number of explanations[9,34,35] have been offered to explain this discrepancy, it remains an open question as to whether this difference in scaling represents a real deficiency in the reptation model or not. Recent computer simulations[36-43] have also raised questions concerning the validity of the reptation hypothesis, although the interpretation of these simulations is open to some debate. Moreover, since the main justification for the reptation model lies in its ability to reproduce phenomenology, it is certainly of interest to explore whether other models[44-51] reproduce the phenomenology as well.

In previous work[48-51] we have explored a model based upon the assumption that the lateral chain motion is not suppressed in the melt. In that model the motion of each chain occurs primarily along the backbones of neighboring chains. It is assumed that the barriers to this motion due to other chains can simply be incorporated into a friction coefficient for the motion of one chain along the contour of another. In contrast, the present work models the effect of the barriers due to other chains explicitly. We find that these barriers inhibit the relative motion of the chains, but the cooperative motions of the chains are sufficient in this model to provide lateral chain motion which reproduces the main scaling relations for polymer melts.

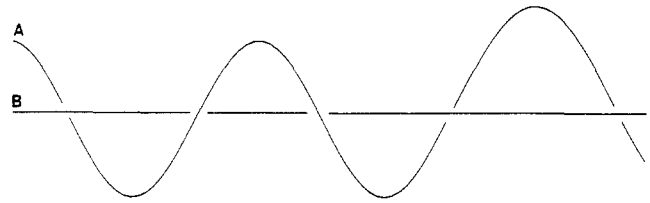

Figure 1. Schematic drawing of two entangled chains. In a real melt both chains assume Gaussian random coil configurations. Chains are randomly wound around each other. Lateral motion of chain A results in motion along the contour of chain B at the contact points. The various points in A can move laterally in different directions, altering the chain configuration.

The model presented in this work considers the lateral motion of each chain along the contours of its neighbors. As a chain moves along these neighboring contours, it encounters additional chains. These additional chains pose obstacles to the lateral motion of the chain of interest. Some obstacles pose effective barriers only over rather short length scales and can be easily circumvented by chain motion of any larger length scale. This is described in Figure 2. We associate a contour length l with each obstacle. In the model presented, an obstacle of length l constitutes an impassable barrier to lateral motion of a chain, if the length scale for chain motion is less than l. On the other hand, it does not pose an impassable barrier when chain motion on longer length scales is considered. As time increases, the length scale of chain motion increases, and the fraction of obstacles which form impassable barriers decreases.

If a barrier is impassable on some length scale, this presents a barrier only to the relative motion of the chains, not to the cooperative chain motion. This cooperative

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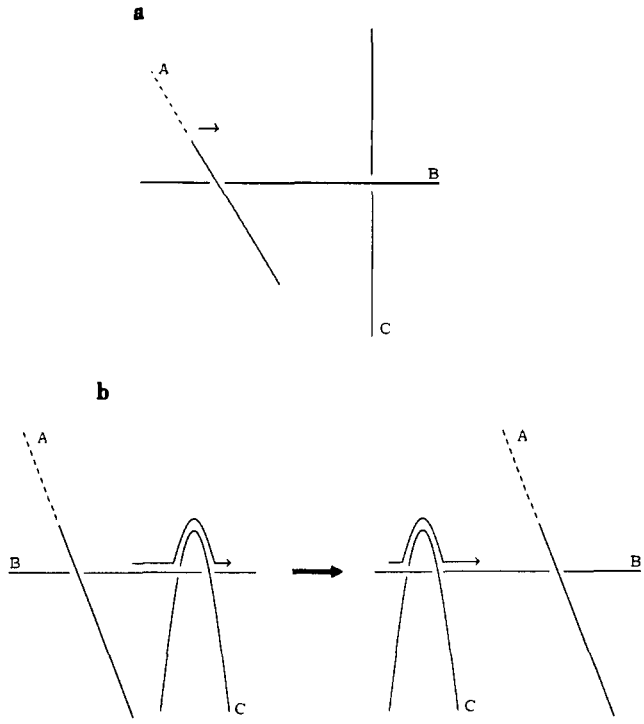

Figure 2. The lateral motion of chain A along the contour of B is impeded by contact with chain C. On the length scale shown in a, chain C poses an impassable barrier to the motion of A. The same set of chains is shown in b on a much larger length scale. On this length scale, the motion of chain A can result in it passing over the obstacle, chain C.

motion of the chains leads to chain displacements over longer distances. On these longer length scales more chains constituting impassable barriers are encountered. As this occurs, the effective cooperative motion involves a greater number of chains. This results in a slowing of the lateral chain dynamics. As the chain motion occurs over longer length scales, a larger fraction of the barriers become passable. This feature facilitates the lateral motion.

These are the main features which are incorporated into the model. A scaling analysis is applied to this model. This predicts a bead mean-square displacement that behaves as $g \sim t^{2/7}$. As a consequence, the terminal relaxation time predicted by this model scales as $N^{7/2}$. When the correlated motions of all chains in a region of the melt are considered, the center of mass diffusion constant is found to scale as $N^{-2.1}$. These predictions are all in excellent agreement with experimental observations.[1] The relaxation modulus in the terminal region is also calculated within this model, and it is found to be in very good agreement with experimental data.

The outline of this paper is as follows. Section II.A presents the basic concepts upon which the model is based and develops a reasonable distribution of length scales for the obstacles imposed by neighboring chains. The model for the cooperative motion of the chains which are mutually impassable is presented in section II.B, and a scaling analysis of this model is presented. The scaling behavior of the center of mass diffusion constant is explored in section II.C, and the shape of the relaxation modulus is calculated in section II.D. The results are summarized and the simplifications inherent in the model are discussed in section III.

II. Theory and Results

A. Distribution of Barriers to Motion along Chain Contours. In Figure 1, we present a highly simplified view of two chains in a monodisperse melt. On course, both chains have Gaussian random coil configurations.[52,53] We have drawn chain B stretched out to aid in visualizing the situation. Because of the large number of interchain contacts, the two chains cannot simply diffuse apart. There are two ways that the chains can untangle. The chains could reptate away from each other, or they could move laterally along each other. In the melt, these two mechanisms leads to models which have differences. In real systems, both motions could occur simultaneously. Here we focus primarily on the lateral motion in order to understand the consequences of this mechanism.

As chain A slides along the backbone of chain B, it encounters other chains which impede the progress of this lateral motion. Two possible situations are depicted in Figure 2. In Figure 2a, chain A encounters a third chain, chain C, which presents an impassable obstacle to its motion along B on the length scale presented in the figure. In Figure 2b, however, the local configuration of chain C is such that it does not impose an impassable barrier. Chain A can pass over C and continue along B until it encounters a barrier which is impassable.

The question of whether an obstacle imposes an impassable barrier or not depends on the length scale of motion that is being considered. The contour length of the obstacle (e.g., chain C in Figure 2) between successive contacts with another chain (chain B in Figure 2) provides an appropriate length for deciding whether a barrier is passable, when compared with the length scale for chain motion during a given time interval. To employ this idea in a model for melt dynamics, we need the distribution of segment lengths of a chain between consecutive contacts with another chain. We construct this distribution $\rho_N(l)$ by requiring that it normalized

$$1 = \int_{l_m}^{bN} \rho_N(l)\, dl \tag{1}$$

and that the mean distance between contacts is of order $N^{1/2}$

$$aN^{1/2} = \int_{l_m}^{bN} \rho_N(l) l\, dl \tag{2}$$

where a is an unknown proportionality constant with dimension of length and b is the segment length. In (1) and (2), l_m is the minimum distance between successive contacts. The second condition, (2), is equivalent to the statement that a chain has $\sim N^{1/2}$ contacts. This is a consequence of the fact the $R_G \sim N^{1/2}$, so that each chain is in contact with all other chains in a volume of order $V_G \sim R_G^3 \sim N^{3/2}$. Assuming that the monomer density is independent of chain length, then the chain density is $\sim 1/N$, giving $N^{1/2}$ chains in V_G. Each chain has a total of on the order of N contacts with other chains, giving an average of $\sim N^{1/2}$ contacts with each of the $N^{1/2}$ chains in V_G.

Since we are treating the chains as ideal Gaussian random coils, it is reasonable to assume that $\rho_N(l)$ has a simple scaling dependence on l. In this case, condition 2 implies $\rho_N(l) \sim l^{-3/2}$. Applying condition 1, it is readily shown that the form

$$\rho_N(l) = {}^1/_2(a/b^{1/2}) l^{-3/2}/(1 - aN^{-1/2}/b) \tag{3}$$

exactly satisfies both (1) and (2) if l_m and a are related by $l_m = a^2/b$. In real polymer systems, one would not expect the simple scaling form for $\rho_N(l)$ to be valid at small l, due to short-range correlations in chain configuration.[52,53] Since the dominant contribution (highest power of N) to (2) is determined by the upper limit of the integration, additional shorter range correction terms (i.e., terms which decay faster than $l^{-3/2}$) do not contribute to the leading contri-

bution in N to (2). However, these correction terms can contribute to the normalization integral (1) and, therefore, they would alter the relationship between l_m and a. In this work we ignore these short-range corrections and employ (3) for $\rho_N(l)$. The short-range corrections are only important at relatively short times and do not affect the important scaling behaviors predicted by the model.

When another chain, chain C, is encountered as chain A slides along chain B, chain C imposes a barrier to this motion. If we are considering the motion of chain A along chain B over a contour length l, then we treat all chain segments of C with length greater than l as constituting impassable barriers on this length scale. The fraction of barriers that are impassable, when considering motion on a contour length scale of l, is given by

$$F(l) = \int_l^{bN} \rho_N(l_1)\, dl_1 = (a/b^{1/2})[l^{-1/2} - (bN)^{-1/2}]/(1 - aN^{-1/2}/b) \approx a/(bl)^{-1/2} \quad (4)$$

where correction terms of order $N^{-1/2}$ have been ignored in the last expression.

Let l_0 be the mean distance between encounters by chain A with other barrier chains as it moves along chain B. If f is the fraction of chains forming impassable barriers, then the mean contour distance over which chain A is free to travel before encountering an impassable barrier is given by $l_1 = l_0/f$. In addition, f depends on l_1. Since each encounter with a chain segment of length greater than l_1 constitutes an impassable barrier in this model, we have $f = F(l_1)$. This, together with $l_1 = l_0/f$ and (4), yields

$$l_1 = b(l_0/a)^2 \quad (5)$$

as the mean contour distance over which chain A can move freely.

B. Model for Cooperative Chain Motion. Chain A encounters impassable barriers on average on the length scale l_1 as it moves along the contour of chain B. This does not mean, however, that the motion of A along B stops at this point. The relative motion of chains moving along the contour of chain B is inhibited by the impassable barriers they present to each other. However, there is still a cooperative component of the motion of these chains. To account for this cooperative motion along the contour of B, we consider the following model. Walkers are randomly placed along a contour. These walkers represent the impassable chains and the contour represents the contour of chain B. We choose the unit of length for the contour such that the initial density of walkers is unity. The walkers diffuse along the contour, but they are not able to pass through each other. In this way the walkers pose impassable barriers to the motion of their neighbors. The choice of length scale corresponds to setting l_1 of (5) to unity. This is equivalent to dividing all quantities with dimension of length by l_1, making them dimensionless quantities. We define $\bar{l}(t)$ to be the root-mean-squared contour displacement for the walkers; that is, $\bar{l}(t) = \langle \sum_j l_j(t)^2/N_w \rangle^{1/2}$, where $l_j(t)$ is the time-dependent contour displacement of the jth walker and N_w is the number of walkers. This quantity $\bar{l}(t)$ provides the length scale of the motion of the walkers on the contour at any given time. When $\bar{l}(t) > 1$, randomly chosen walkers are designated as phantom walkers. Other walkers can pass through a phantom walker. Once a walker is designated as a phantom walker, it is no longer an impassable barrier to other walkers. The number of walkers chosen to be phantom walkers on any given time step is specified so that the number of nonphantom, impassable walkers divided by the initial number of walkers $F[\bar{l}(t)]$, the fraction of obstacles that are impassable on the length scale $\bar{l}(t)$. We first consider the case in which the phantom walkers offer no resistance to the motion of the other walkers. Below we modify this point. In this discussion the term "walkers" is used to denote only the nonphantom walkers. The other walkers are always explicitly referred to as phantom walkers.

We can determine the dependence of $\bar{l}$ on t for this model by means of a scaling analysis. To simplify the scaling expressions, constants like the segment length b and the constant a in (2) are ignored, since they do not affect the scaling of $\bar{l}$ with t. In the Appendix this scaling argument is illustrated by applying it to the simpler case for which the number of walkers on the contour is held fixed, and the scaling predictions are compared to numerical results for that case. Here the more difficult case is considered in which the number of impassable walkers decreases with time. Let s be the mean contour distance between walkers. Since the density of walkers changes with time, s is a function of t. If $\bar{l} < 1$, then $s = 1$; otherwise $s = F^{-1}(\bar{l})$. When $\bar{l} > 1$, then the motion of the walkers must involve correlated displacements of a number of walkers, since $\bar{l} > s$. If we consider two walkers which are n walkers apart on the contour at time t, then the average distance between these two walkers in ns. If it is assumed that the distribution of walker positions along the contour is random at all times, then the mean-squared fluctuation about this average distance is given by $\sigma_n^2 = n\sigma_1^2$, where σ_1^2 is the mean-squared fluctuation in the distance between adjacent walkers on the chain. Also in this case, the distribution of distances between adjacent walkers is Poisson and $\sigma_1^2 = s^2$. This yields

$$\sigma_n^2 \sim ns^2 \quad (6)$$

If σ_n^2 is less than $\bar{l}^2$, then the motion of two walkers, n walkers apart on the contour, must be correlated. On the other hand, if $\sigma_n^2 > 2\bar{l}^2$, then the relative displacement of the walkers falls within the fluctuations for the distance between them, and their motions need not be correlated. Therefore, the minimum number of walkers whose motion must be correlated for walker displacements of order $\bar{l}$ is

$$m(\bar{l}) \sim \bar{l}^2/s^2 \sim \bar{l} \quad (7)$$

The last line of (7) follows from $s = F^{-1}(\bar{l}) \sim \bar{l}^{1/2}$.

The center of mass diffusion constant for a cluster of m walkers is inversely proportional to the numbers of walkers

$$D_m \sim 1/m \sim 1/\bar{l} \quad (8)$$

If we are in a regime for which there is a simple scaling relationship between $\bar{l}$ and time, then τ, the time required for the mean-squared displacement of the cluster to reach $\bar{l}^2$, can be evaluated from[54]

$$\bar{l}^2 \sim D_m\tau \quad (9)$$

Substitution from (8) into (9) yields

$$\bar{l}(t) \sim \tau^{1/3} \quad (10)$$

The model as presented so far misses an important feature. The phantom walkers are passable barriers on length scale $\bar{l}$ but were impassable on shorter length scales. Because of this, the passable barriers should slow the diffusion on shorter length scales than $\bar{l}$. In particular, they should slow the motion of the remaining nonphantom walkers on the length scale s, the mean distance between collisions with other nonphantom walkers. To incorporate

this feature into the model, we define a length scale dependent diffusion constant, $d(s)$, for the motion of the walkers over distances on the order of s. This can be defined as

$$d(s) \sim s^2/t(s) \tag{11}$$

where $t(s)$ is the time at which the mean-squared displacement of the walkers is s^2. We assume that we are in a regime for which a simple scaling relationship exists between $\bar{l}$ and t; that is, $\bar{l} \sim t^\alpha$, where α is a constant determined below. As long as the same scaling applies at the earlier time $t(s)$, we have $s = t(s)^\alpha$, Since $s = \bar{l}^{1/2}$, one finds that $t(s) = \bar{l}^{1/2\alpha}$. Substitution of this into (11) yields

$$d(s) \sim \bar{l}^{1-1/2\alpha} \tag{12}$$

The motion of a walker over the length scale $\bar{l}$ involves the correlated motion of $m(\bar{l})$ nonphantom walkers. This yields a correlation length of

$$\xi(\bar{l}) \sim m(\bar{l})s \sim \bar{l}^{3/2} \tag{13}$$

The corresponding correlation length for motion on the length scale s is $\xi(s) \sim s^{3/2} = \bar{l}^{3/4}$. Since the mean distance between nonphantom walkers is s, there are $\bar{l}^{3/4}/s \sim \bar{l}^{1/4}$ impassable walkers within this correlation length. The effects of these $\bar{l}^{1/4}$ impassable walkers is included in $d(s)$. Because of this fact, $d(s)$ is not quite the diffusion constant needed. We require a diffusion constant for walker motion on the length scale s that includes only the effect of the passable barriers, since the effect of the impassable walkers is included explicitly by their mutual impenetrability.

We can express $d(s)$ as

$$d(s) = \frac{1}{\bar{l}^{1/4}} d_0(s) \tag{14}$$

An expression of the form of (14) corresponds to dividing the complete set of walkers, impassable and phantom, within the correlation length $\xi(s)$ into $\bar{l}^{1/4}$ groups. Each group contains one impassable walker and the average number of phantom walkers closer to it than any other impassable walker. The diffusion constant $d_0(s)$ is the diffusion constant for the center of mass motion of one such group on the length scale s, while $d(s)$ is the diffusion constant for the motion of the entire set of $\bar{l}^{1/4}$ groups. Therefore, $d_0(s)$ is the diffusion constant for the motion of a single impassable walker between collisions with the other impassable walkers, including the slowing effect of the phantom walkers. This is the diffusion constant we need. From (12) and (14) we find

$$d_0(s) \sim \bar{l}^{(5/4-1/2\alpha)} \sim t^{(5\alpha/4-1/2)} \tag{15}$$

where $\bar{l} \sim t^\alpha$ has been employed.

The τ in eq 10 is the time in a model which completely ignores phantom walkers. We can choose the time scale so that the diffusion constant for the motion of the nonphantom walkers between collisions is unity in this case. Changes in τ can be related to changes in t for a model which employs $d_0(s)$ as the diffusion constant for the impassable walkers by means of the expression

$$d\tau = d_0(s)\, dt \tag{16}$$

Equations 15 and 16 give

$$\tau \sim t^{(5\alpha/4+1/2)} \tag{17}$$

Substitution of this result into (10) yields

$$\bar{l} \sim t^{(5\alpha/12+1/6)} \tag{18}$$

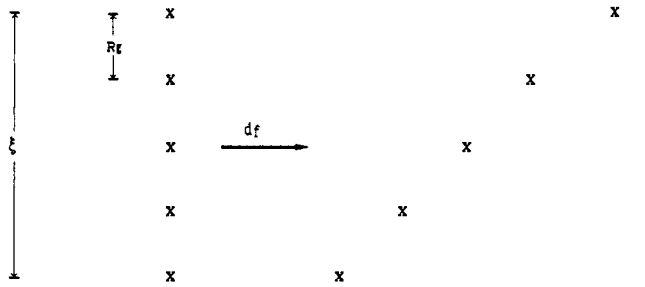

Figure 3. Illustration of the effect of correlated chain motion. The ×'s indicate the locations of the centers of mass of selected chains, which are spaced about a radius of gyration, R_G, apart. The total distance between the first and last chain is taken to be on the order of the correlation length ξ. In time t_f, each chain moves on the order of R_G, relative to the chains which are separated from it by a distance of $\sim R_G$. If the motion is correlated over the entire length ξ, then the relative displacement between the first and last chain is on the order of ξ.

Since α is defined by $\bar{l} \sim t^\alpha$, α must be $^2/_7$, giving

$$\bar{l} \sim t^{2/7} \tag{19}$$

The quantity of interest is not the mean-squared contour displacement $\bar{l}^2$, but rather the mean-squared three-dimensional bead displacement, $g(t)$. The relationship between $g(t)$ and $\bar{l}$ has been considered in detail previously for a model in which the chains slide laterally along the random walk contours of neighboring chains.[50] This relationship is

$$g(t) \sim \bar{l} \tag{20}$$

in the case of a monodisperse sample. This result, combined with (19), yields

$$g(t) \sim t^{2/7} \tag{21}$$

for the current model. The scaling of the terminal time is obtained by evaluating the time when $\bar{l}(t)$ is on the order of the chain length or, equivalently, when $g(t)$ is on the order of the chain radius of gyration. This provides the time scale on which contacts between chains are broken. Since $\bar{l}(t)$ scales as $t^{2/7}$, the terminal time, which is obtained from $\bar{l}(t_f) \sim N$, scales as

$$t_f \sim N^{3.5} \tag{22}$$

C. Center of Mass Diffusion Constant. In models for polymer dynamics,[1] the center of mass diffusion constant is commonly evaluated from

$$D_{cm}^{(1)} \sim R_G^2/t_f \tag{23}$$

where R_G is the chain radius of gyration. This equation states that, since the chains untangle in time t_f, the mean-squared displacement in this time should be on the order of R_G^2. Substituting $R_G^2 \sim N$ and (22) into (23) gives the scaling

$$D_{cm}^{(1)} \sim N^{-2.5} \tag{24}$$

This is a somewhat higher N dependence than is observed for polymer melts.

Since (23) is based on the time it takes for chains to untangle, $D_{cm}^{(1)}$ is really the diffusion constant for the relative motion of chains that are entangled. It has been pointed out by Fixman[34] that a different scaling can appear when the correlated motion of the chains is considered. In Figure 3, an argument is described for D_{cm} based on the cooperative motion of all chains in a region defined by a length scale ξ. This length scale is determined below. In time t_f, those chains that were initially within R_G of each

other have mean-squared displacements of order R_G^2 relative to each other. This is the basis of (23). However, if the centers of mass for two chains are a distance of $\xi \sim mR_G$ from each other, then they have a maximum relative mean-squared displacement of order ξ^2, if the motion of the entire region is correlated, as shown in Figure 3. The region defined by the length scale ξ contains a number of chain monomer units proportional to the volume of the region, which is of order ξ^3. If we define D_ξ to be the diffusion constant for the correlated motion of the entire region, then it is reasonable to assume that D_ξ should be inversely proportional to the number of monomers in the region. Therefore, we expect

$$D_\xi \sim 1/\xi^3 \tag{25}$$

Since ξ^2 is the maximum mean-squared displacement in time t_f due to the cooperative motion of this region, the actual mean-squared displacement is given by the smaller of ξ^2 or $6D_\xi t_f$. The value of the correlation length ξ, which maximizes the mean-squared displacement, is obtained when

$$\xi^2 = 6D_\xi t_f \tag{26}$$

Substitution of (25) into (26) yields

$$\xi \sim t_f^{1/5} \sim N^{7/10} \tag{27}$$

This correlated motion provides a contribution to the center of mass motion of the chains. Equations 25 and 27 give the scaling of this contribution to the center of mass motion to be

$$D_{cm}^{(2)} = D_\xi \sim N^{-2.1} \tag{28}$$

For long chains this cooperative contribution to the center of mass motion dominates over the contribution presented in (24), due to the milder scaling with chain length.

D. Linear Viscoelastic Response. If lateral motion occurs, then the stress in a system cannot be supported by the orientational memory of a tube. Rather it must be supported by the contacts between chains. After a strain has been applied, the set of chains in contact with any given chain is not an equilibrium distribution of chains. In particular the centers of mass of these chains are distributed in a way that reflects the applied strain. This set of contact chains are in contact with still other chains, and so on throughout the entire polymer system. The only way for this nonequilibrium distribution of contacts to completely relax is for the initial contacts between the chains to break as the chains slide along each other.[49,51]

In this picture, the stress relaxation modulus in the postplateau region can be modeled as being proportional to the fraction of initial interchain contacts which have not been broken. A contact breaks when one chain reaches the end of the other chain involved in the contact. Therefore, the stress relaxation modulus for a monodisperse sample of identical chains is given by[49,51]

$$G(t) = G_0 P_s(t)^2 \tag{29}$$

where $P_s(t)$ is the probability that one of the chains has not reached the end of the other chain. $P_s(t)$ is squared in (29) because the probability that a contact between chains A and B has not broken equals the probability that A has not reached the end of B multiplied by the probability that B has not reached the end of A.

There remains the task of calculating $P_s(t)$. The total diffusion constant for walker motion is the product of D_m from (8) and $d_0(s)$ from (15). Combining these, together with $\bar{l} \sim t^\alpha$ and $\alpha = {}^2/_7$, one finds that the total walker diffusion constant is $D_w(t) \sim t^{-3/7}$. The density at time t for a walker which is initially located at the point x_0 on the contour is governed by the diffusion equation with a time-dependent diffusion constant $D_w(t)$. This is equivalent to the equation

$$\frac{\partial}{\partial \tau}\rho(x,x_0,\tau) = \frac{\partial^2}{\partial x^2}\rho(x,x_0,\tau) \tag{30}$$

where τ is related to the time t by

$$\tau = \int_0^t D_w(t_1)\, dt_1 \tag{31}$$

(This τ is not the same as τ in eqs 9, 10, 16, and 17.) If the walkers are uniformly distributed on a contour length L with absorbing boundary conditions, then the fraction of walkers obeying (30) which have not encountered an end of the contour before τ is given by

$$P(\tau) = \sum_{j=1,3,5,\ldots} \frac{8}{j^2\pi^2} \exp(-j^2\pi^2\tau/L^2) \tag{32}$$

Solving (31) and substituting τ as a function of t into (32) yields

$$P_s(\tau) = \sum_{j=1,3,5,\ldots} \frac{8}{j^2\pi^2} \exp[-j^2(t/t_T)^{4/7}] \tag{33}$$

where $t_T^{4/7} \sim L^2$. Since $L \sim N$, this confirms that the terminal time for viscoelastic relaxation scales as $N^{7/2}$.

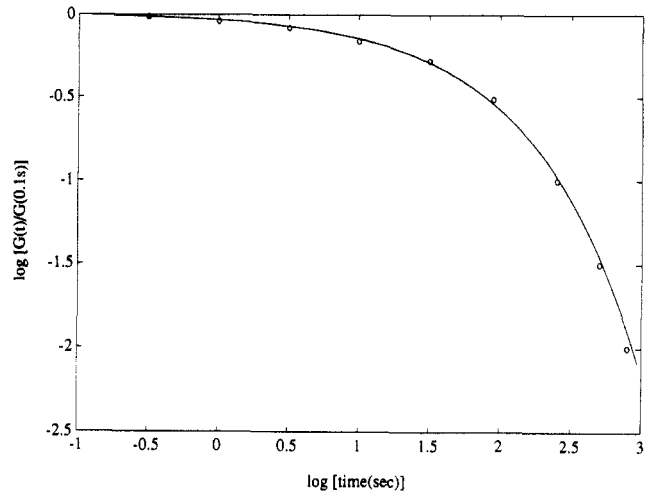

Figure 4. log–log plot of the relaxation modulus versus time. The solid line is the result from (29) and (33). The circles are experimental data taken from ref 55.

In Figure 4 we plot $G(t)$ evaluated from (29) with $P_s(t)$ obtained from (33). Experimental data for polyisoprene relaxation taken from the work of Fuller and co-workers[55] is also included for comparison. The results of the model obviously reproduce the experimental relaxation data very well. Given the simplicity of this model, the level of agreement may be somewhat fortuitous. Nevertheless, these exceptionally good results are very encouraging.

III. Discussion and Summary

In this paper we have developed a model for lateral chain motion in a monodisperse melt of linear polymer chains. Each chain is entangled with on the order of $N^{1/2}$ surrounding chains. Each pair of entangled chains is highly intertwined and wound around each other. In our model we assume that each chain in an entangled pair of chains moves along the contour of the other chain, and in this way they can eventually disentangle. As a chain moves

along the contours of neighboring chains, it encounters other chains which pose obstacles to its motions. These obstacles may constitute passable or impassable barriers to the chain motion along the contour. To designate a specific barrier as passable or impassable, a length scale must be specified. Each barrier appears impassable on short length scales and passable on sufficiently long length scales. We incorporate this feature in our model by associating a contour length with each barrier. The distribution of barrier lengths is equated with the distribution of contour lengths of a chain between successive contacts with another chain. To specify barriers as passable or impassable we compare the contour length associated with the barrier to the root-mean-squared contour length displacement for the motion of one chain along the contour of another at a given time.

As one chain moves along another chain, it cannot move past these impassable barriers. However, it can move cooperatively with them. We model this cooperative motion by studying the motion of impenetrable walkers on a contour. In this model we randomly specify an increasing fraction of the walkers as phantom walkers as time increases, so that the fraction of the barriers which are impassable decreases as the length scale for the motion along the contour increases. The root-mean-squared contour displacement of the walker can be associated with the mean-squared bead displacement for the polymer chains, $g(t)$, except for an unimportant proportionality constant. Our scaling analysis of this model predicts $g(t) \sim t^{2/7}$. This corresponds to a terminal time which scales as $t_f \sim N^{7/2}$. We evaluate a cooperative center of mass diffusion constant due to the correlated motion of all the monomer units in a certain correlation volume. This leads to $D_{cm} \sim N^{-2.1}$. All of these predictions agree very well with the known behavior of monodisperse polymer melts. We also evaluate the relaxation modulus in the terminal region due to a step strain. This calculation is based on the premise that the interchain contacts support the stress in the melt, and the relaxation modulus at time t is proportional to the fraction of contacts which were present when the step strain was applied and remain unbroken at time t. The shape of the relaxation modulus calculated in this fashion is in very good agreement with experimental data.

This model is highly simplified in a number of ways. The model treats each chain segment along a chain contour as a simple random walker. This does not account for the memory effects due to the fact that the segment is part of a long chain. For instance, if a bead in a chain in a Rouse model has a displacement in one direction during a time interval, then the remainder of that chain tends to pull it in the opposite direction to some extent on average. By treating each chain segment along the contour of interest as a simple walker, we are assuming that the lateral chain motion is so slowed by the presence of the obstacles that these memory effects have time to relax, and consequently they do not affect the lateral dynamics. Local reptative motions of a chain along its own backbone are likely to be important in this chain memory relaxation.

While local reptative motions may be important, our model assumes that the lateral motions are sufficient on longer length and time scales to distort any initial tube. If the system loses memory of the initial tube due to the lateral motion, then the reptation picture no longer provides a reasonable description of the chain motion, and the present model may provide a more useful description. At each time step, there are on the order of N times as many different lateral motions available to a chain compared with reptative motions. This greater number of lateral motions available to the chain may result in the lateral motion dominating the chain dynamics on long time scales, as long as the lateral motion is not completely suppressed by the obstacles imposed by neighboring chains. This may be the case even if the terminal time for pure reptation is much shorter (i.e., it scales as N^3) than the terminal time for lateral motion.

In this model each obstacle is treated as a contour of a single chain with a specific length. In a real system, as a chain slides along a barrier contour, it encounters other obstacle chains, which it must then follow. This sequence of obstacle chains together presents a contour for a chain to follow which has a random walk configuration (with some short length correlation). Therefore, the total obstacle imposed by this sequence of chains should affect the motion of the chain of interest in a manner which is not greatly different than the effect of a random walk contour of a single chain.

Probably the most significant simplification of the model presented here is that each obstacle is treated as a separate entity. In a real polymer melt all the chains in a region are highly entangled. This model clearly does not account for the full complexity of the mutual entangling of all the obstacles to the motion of each chain in the system. Within the model, we have shown how the cooperative motion of a chain and the nearby obstacles can give rise to lateral motion, even if a finite fraction of the obstacles are impassable barriers on the relevant length scale at a given time. In future work, we hope to examine how the intertwining of the obstacles affects this result.

Another feature of this model that warrants comment is that the correlation length for the motion of the walkers on the contour scales as $l^{3/2}$. For $l > (bN)^{2/3}$, this corresponds to the motion of walkers on a contour which is correlated over distances longer than the chain contour length bN. This may appear to be a cause for some concern. However, the picture of the chains moving on a single contour is highly simplified. In fact, a chain moves along one contour, encounters a barrier, moves along the contour of the barrier chain, encounters another barrier, and so on. As it moves along this sequence of chain contours, it returns to the original contour from time to time. As it does so, it progresses along that original contour. Given that the chain actually moves from the contour of one chain to another and that all of the neighboring chains are so intertwined, it seems reasonable that the end of any one chain would not significantly limit the extent of the correlations, although it may lead to extra contributions to $g(t)$ in the spirit of the constraint release contribution in the reptation model.

There are other limitations of the model as well. The length scales for the barrier chains are treated as static quantities, while in fact the contour length of barriers vary with time. Furthermore, even if lateral motion dominates in a system over long time and length scales, reptation motions should still be important for local motions. This could affect $g(t)$, at least at short times.

In our earlier lateral motion model[48-51] we included correlations in the motion of beads along the same chain but assumed that other nearby chains only inhibit the lateral motion of one chain along the backbone of a neighbor for short times. Because of this assumption the effect of the barriers to this lateral motion could be incorporated by means of a simple friction coefficient for the motion of a chain along the contour of another. In the work presented here, a model for the barriers to lateral motion is presented which introduces the correlations

between different chains as they move along the contour of the same chain. On the other hand, it is assumed that intrachain correlations do not affect the lateral motion. In this sense these two models explore different important aspects that must be accounted for in a model for lateral chain motion. There are three important features of these lateral motion models. Two of these are the intrachain correlations and the interchain correlations. The third feature is that the lateral motion of each chain is modeled as occurring along a random coil contour. This results in the slowing of the lateral motion through the relationship $g(t) \sim \bar{l}(t)$. The models presented here and previously[50] consider the interchain correlation and intrachain correlation extremes, respectively. Intermediate possibilities also exist. The motion along each random coil contour takes place in three dimensions, which provides a chain with the flexibility to fluctuate closer and farther from the contour in question. It must do this as it works its way past the barriers. Because of these fluctuations, the present model may overestimate the interchain correlations. This might be compensated by intrachain correlations, leaving the model predictions substantially unchanged. Alternatively, if a model is considered which includes the maximum imaginable interchain and intrachain correlations, then the lateral chain motion would be considerably slower than is observed experimentally.

This model provides some important insights. In particular, it demonstrates how cooperative chain motion can result in significant lateral motion, even when the chains present impassable barriers to each other. This is an essential feature. Without this cooperative motion, the lateral motion would indeed be suppressed in the model. The length scale dependence of the fraction of obstacles constituting impassable barriers is another important feature of the model. If all obstacles were treated as impassable on all length scales, the model would give $g \sim t^{1/4}$ and $t_f \sim N^{4.0}$. Thus, this length scale dependence facilitates the lateral motion. The importance of correlated motions for the center of mass diffusion constant is also an important feature of this model.

In summary, we have presented a model for the dynamics of linear chain polymer melts. The model incorporates the constraining effect that neighboring chains have on the lateral motion of a given chain, although this feature is not included in its full complexity. The cooperative motion of the various chains results in a lateral chain motion. The behavior which results from this lateral motion for the bead mean-squared displacement, terminal relaxation time, center of mass diffusion constant, and the relaxation modulus are explored within this model and found to be in excellent agreement with experimental results.

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Appendix

In this appendix the scaling analysis employed in section II.B is applied to the simpler problem in which no walkers are removed as time progresses. The results are compared with numerical simulations. Since no walkers are removed, the diffusion constant for the motion of a walker between encounters with other walkers is a constant. Also s, the mean distance between walkers, is a constant, and we set this to unity. As is the case for the model presented in section II.B, the minimum number of walkers whose motion must be correlated on the length scale $\bar{l}$ is $m(\bar{l}) \sim l^2/s^2$. Since $s = 1$ in the case considered here, we find

$$m(\bar{l}) \sim \bar{l}^2 \tag{A1}$$

Therefore the diffusion constant for correlated motion is

$$D_m \sim 1/m \sim 1/\bar{l}^2 \tag{A2}$$

The relationship between $\bar{l}$ and t is given by[54]

$$\bar{l}^2 \sim D_m t \tag{A3}$$

Combining (A2) and (A3) yields

$$\bar{l}^2 \sim t^{1/2} \tag{A4}$$

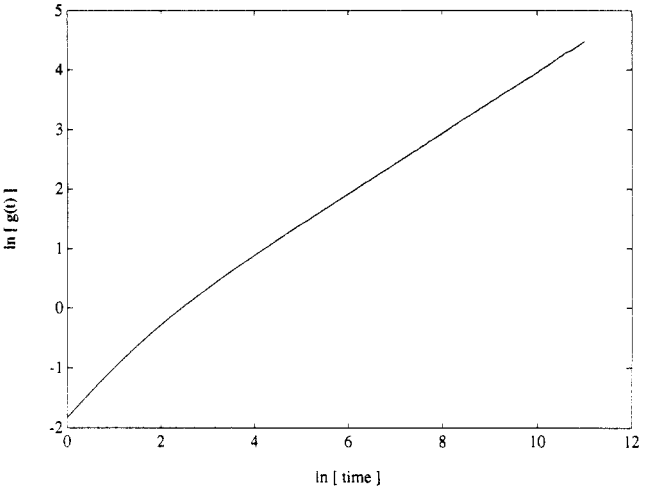

Figure 5. log–log plot of the mean-squared contour displacement versus t for impenetrable walkers on a circle. The mean contour distance between walkers is unity. The calculation is for 500 walkers on the circle and is averaged over 1000 circles.

In Figure 5, we present numerical results from a random walk simulation for 500 walkers randomly placed on a circle with a circumference of 500. The time step is chosen to be one attempted move of each walker. The move of a walker consists of randomly choosing a displacement of the walker in the interval −1 to 1. If this displacement results in this walker passing the position of another walker on the circle, then the attempted displacement is rejected and the walker is given zero displacement on this move. Otherwise the displacement is accepted. In this way, the walkers are not allowed to pass through each other. The results are averaged over 1000 circles. The numerical results clearly show an $\bar{l}^2 \sim t^{1/2}$ behavior after a short crossover region corresponding to the walker motion over length scales less than the mean distance between walkers.

The correlation length for motion on the length scale $\bar{l}$ is given by $\xi(\bar{l}) = m(\bar{l})s$, as in section II.B. This corresponds to

$$\xi(\bar{l}) \sim \bar{l}^2 \tag{A5}$$

for the case considered here. When $\xi(\bar{l}) \sim N$, the motion of all beads on the circle is correlated and this motion must have the simple diffusion form

$$\bar{l}^2 \sim D_N t \tag{A6}$$

The crossover occurs when $\bar{l}^2 \sim \xi(\bar{l}) \sim N$. Since $\bar{l}^2 \sim t^{1/2}$, the crossover time t_c is given by

$$t_c \sim N^2 \tag{A7}$$

Substituting the crossover values $\bar{l} \sim N$ and $t_c \sim N^2$ into

(A6) shows that

$$D_N \sim 1/N \tag{A8}$$

as must be the case since the correlated motion includes all N beads on the circle. We have not carried the numerical calculations out to long enough times to see the crossover to the free diffusion behavior.

This relatively simple example illustrates the use of the length scale dependent number of correlated walkers $m(\bar{l})$ in the evaluation of the diffusion constant for the correlated motion of these walkers. This diffusion constant is then utilized in the evaluation of $\bar{l}(t)$ from $\bar{l}^2 \sim D_m t$.

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(54) The diffusion constant is a function of time through its dependence on the time-dependent mean contour displacement $\bar{l}$. If D is time dependent, the relationship between $\bar{l}^2$ and time is $\bar{l}^2 \sim \int_0^t D\, dt_1$. However, if $\bar{l}$ and D have simple scaling relationships with time, then $\bar{l}^2 \sim Dt$ has the same scaling as the integral of D over time, and this nonintegral form can be used to determine the correct scaling of $\bar{l}(t)$.
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