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Models for the dynamics of monodisperse polymer melts based on lateral chain motions

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A recently developed model for the dynamics of monodisperse polymer melts of linear chains is briefly reviewed. Within the simplifications inherent in the model, it is found that the obstacles to the motion of a given chain, which are imposed by neighboring chains, do not suppress the lateral chain motion. The model associates a length scale with each obstacle, and compares it with the length scale for chain motion. If the obstacle length is greater than the length scale for chain motion, the obstacle is deemed impassable. The cooperative motion of the mutually impassable obstacles is considered, and this gives rise to predictions that are in excellent agreement with experimental observations. If the model were modified to include the additional complexities of real polymer systems, various features of the model might change. The implications of a number of possible modifications in the model are explored. Specifically, the impact of varying the behavior of the function which determines the fraction of obstacles that are impassable is examined in detail. In addition, in the original model it is assumed that chain memory is relaxed due to the slowing of lateral chain motion by the obstacles imposed by neighboring chains. The effect of the opposite assumption of essentially no memory relaxation is also studied. Finally, the influence of limiting the extent of the correlations between the motions of various chain segments because of finite chain length is also considered. It is found that these features have effects that can largely cancel each other. As a result, a range of lateral motion models, which are consistent with the known phenomenology of these systems, are possible.

1. Introduction

In this work, we discuss a model for the dynamics of a monodisperse polymer melt. For simplicity, we consider only the case of linear polymer chains. The dominant model for melt polymer dynamics over the past 10–15 years has been the reptation model [1–22], although a number of alternative models have appeared recently [23–31]. The reptation model assumes that the lateral motion of each chain is so hindered by the surrounding chains that it is essentially suppressed for distances longer than some value. If this is the case, then the chain motion on longer length scales must occur by motion of the chain along its own backbone. The reptation model has been quite successful in describing a great many observations concerning the dynamics of relaxation of polymer melts [32–42]. Despite this general success, there are reasons to examine the basic premise of the reptation model more closely,

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and to consider if other models are also reasonable. First of all, reptation hypothesis has never been proven on the basis of a more fundamental description of the polymer system. Its justification rests on its ability to describe phenomenology. This does not preclude the possibility of alternative models which also describe phenomenology. These are some experimental observations for which is it ambiguous whether the reptation model provides an adequate description. For example, the terminal relaxation time is found experimentally to scale as $N^{3.4}$, where N is the number of monomer units per chain. The reptation model predicts an $N^{3.0}$ behavior. Various explanations for this discrepancy have been advanced [9,43,44] and it is not clear whether this observation represents a real deviation from the reptation prediction or not.

We have recently developed alternative models [27–32] which do not assume that the lateral chain motion is suppressed, and which therefore probe the consequences of lateral chain motion. We have found that it is possible for lateral motion models to reproduce the phenomenology of these systems [27–30]. In this paper, we briefly describe a model [31] which considers the lateral chain motion without making an assumption about whether it is suppressed by the surrounding chains. It treats the surrounding chains as barriers, and associates a length scale with each barrier. If the length scale for a barrier is less than the mean chain displacement, then the barrier does not block the lateral motion, otherwise is does block the lateral motion. Since the mean chain displacement is a function of time, so is the fraction of obstacles that are effective barriers to the lateral chain motion. There are effective barriers on all length scales less than the chain radius of gyration. This impedes the relative motion of the chains. However, there are still cooperative motions, and we analyze these cooperative motions by means of a scaling argument. This analysis predicts that the cooperative motions result in lateral motion on all length scales, within the assumptions of the model. The mean squared monomer displacement is found to scale as $g(t) \sim t^{2/7}$, and the terminal time scales as $N^{7/2}$. The center of mass diffusion constant is predicted to scale as $N^{-2.1}$, when cooperative motions are included. These predictions are in very good agreement with experimental results and computer simulations.

While this model contains many features which should be important in real polymer systems, it still provides a quite simplified picture of the polymer dynamics. In particular, the model treats each obstacle as separate from all other obstacles. Within the context of this simplification, it predicts that the lateral motion is not completely suppressed due to the cooperative motions in the melt, and demonstrates that a model based on lateral chain motion can reproduce experimentally observed behavior. In real systems, many of the local obstacles encountered by a chain are actually different segments of the same neighboring chain. Furthermore, all the neighboring chains surrounding a designated probe chain are highly entangled with each other as well as with the probe chain. This intertwining of the various obstacles to the motion of the probe chain must be accounted for in order to definitely address the question of whether the lateral motion is suppressed or not in the melt.

A realistic theory of these systems including this level of complexity has not yet been developed. In this paper, we explore the range of behaviors of our current lateral model as various features of the model are modified. This work provides an understanding of the sensitivity of the model to the various features considered. As additional levels of complexity are added to these models in the future, this study should aid in determining whether the new models can provide predictions in agreement with experiment.

In section 2.1 of this paper, the lateral motion model is briefly reviewed. Section 2.2 explores the sensitivity of the model to changes in three features. The first feature (section 2.2.1) involves modifications in the form of the function which determined the fraction of obstacles that are impassable as a function of length scale. The second feature (section 2.2.2) concerns the treatment of chain memory. In the original model, it is assumed that chain memory is essentially relaxed on the time scale for lateral motion. This assumption is based on the fact that the lateral motion is significantly slowed by the obstacles imposed by neighboring chains, allowing time for the memory relaxation. The effect of the converse assumption of no memory relaxation is discussed. The third feature explored (section 2.2.3) involves the impact on the model predictions if the length scale for correlations between motions of different chain segments is limited to the chain radius of gyration. In the original model, the correlation lengths are longer than this at later times. We find that these different modifications of the model result in changes in the predictions of the model that largely cancel. As a result, a range of lateral models are qualitatively consistent with the phenomenology of polymer systems.

2. Theory

2.1. DESCRIPTION OF THE MODEL FOR LATERAL CHAIN MOTION

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. Each pair of entangled chains has on the order of $N^{1/2}$ interchain contacts on average. In the course of these many interchain contacts, a pair of chains wind randomly around each other. Figure 1 presents a schematic picture of this. Because two chains are highly interwined, they cannot readily separate. The relative motion of the two chains can occur by means of reptation, in which each chain moves along its own backbone. Alternatively, each chain could move laterally along the backbone of its neighboring chains. A mixture of the two types of motions is also a possibility.

The model discussed here 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 which pose obstacles to the lateral motion of the chain of interest. Some obstacles are effective barriers only over short length scales and can be easily circumvented by chain motion on longer length scales. This is described in fig. 2. In the model discussed here, a contour length l is associated with

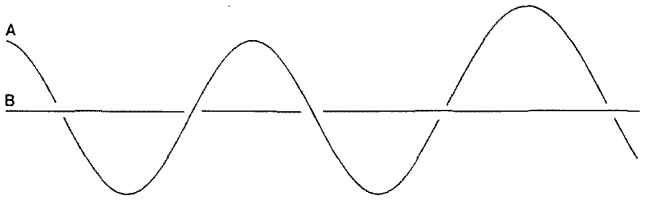

Fig. 1. Schematic drawing of two entangled chains in a melt. In a real melt, both chains have Gaussian random coil configurations. Chains are randomly wound around each other.

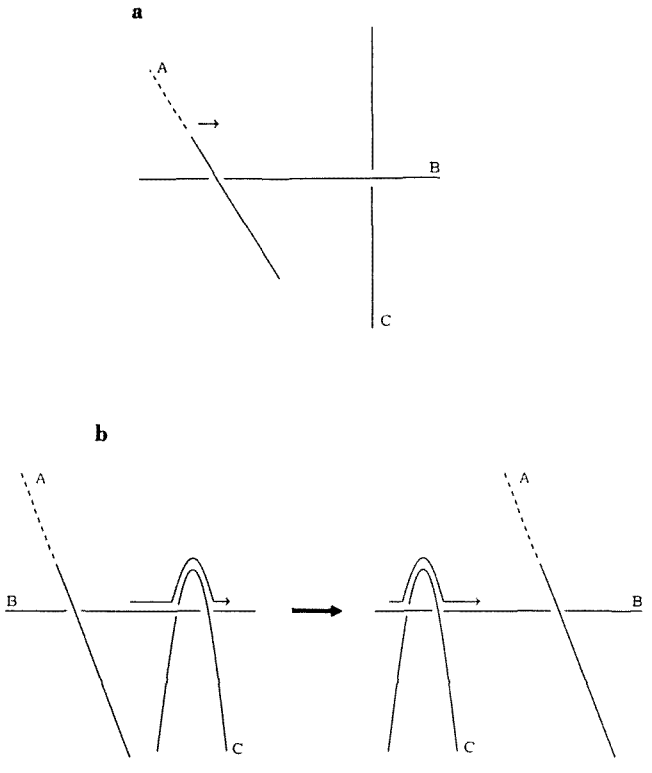

Fig. 2. The lateral motion of chain A along the contour of chain B is impeded by contact with chain C. On the length scale shown in (a), chain C poses an impassable barrier to the motion of A. The same set of chains is shown in (b) on a much larger length scale. On this length scale, the motion of A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

each obstacle. An obstacle of length l constitutes an impassable barrier to the 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 represents a barrier only to the relative motion of the chains, not to the cooperative chain motion. This cooperative motion of the chains leads to chain displacements over longer distances. On these longer length scales, the effective cooperative motion involves a greater number of chains. This slows the lateral chain dynamics. As the chain motion occurs over longer length scales, a larger fraction of the barriers becomes passable. This feature facilitates the lateral motion.

These are the main features of the model. Notice that while the model explores the lateral chain motion, it does not assume that the lateral motion must occur. In fact, neighboring chains pose impassable barriers to the lateral motion on any length scale of chain motion shorter than the chain radius of gyration. If it were not for the cooperative motion of the chains, the lateral motion would be entirely suppressed.

A contour length is associated with each barrier to the motion of one chain (chain A) along the contour of a second chain (chain B). (The chain labels refer to fig. 2.) The contour length employed in the model is the contour length of the barrier chain, chain C, between successive contacts with chains B. The distribution of contour lengths for the barriers $\rho_N(l)$ can be evaluated by assuming that ρ_N is normalized and that it gives an average l which is of order $N^{1/2}$. This latter condition is equivalent to requiring that there be order $N^{1/2}$ contacts between a pair of chains on average. These conditions are consistent with the distribution [31]

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

where a is a constant, and the segment length b has been set to unity.[1)]

Since we model each chain in the melt as moving along the contours of the nearby chains, then the mean squared contour displacement $\langle l^2 \rangle$ can be calculated at each time for the motion of one chain along another at a contact point. If the contour length associated with a given barrier is greater than $\bar{l}(t) = \langle l^2 \rangle^{1/2}$, then the lateral motion of a chain is not sufficient to move it past this barrier. In this case, the barrier is considered impassable, and the other chain cannot proceed it along a contour. Conversely, if the barrier contour length is less than $\bar{l}(t)$, then the barrier is considered passable, and any other chain can move past it. The fraction of barriers which are impassable at any time is given by the integral of $\rho_N(l)$ from $\bar{l}(t)$ to N. This fraction has the form

[1)] Since the segment length b has been set to unity, the contour lengths such as l, $l(t)$, s are actually dimensionless contour lengths l/b, l/b and s/b, respectively. Essentially, the unimportant factor of b has been dropped to simplify the equations.

$$F(\bar{l}) \sim \bar{l}^{-1/2}. \tag{2}$$

We model this as a set of Brownian walkers on a contour. The walkers represent segments of various chains as they progress along the contour of a specific chain. Randomly chosen walkers are removed as time progresses, so that the fraction of walkers remaining on the contour at any time is given by $F[\bar{l}(t)]$. The walkers that remain at any given time represent the impassable barriers at the time. The average distance between walkers at time t is given by $s = F(\bar{l})^{-1}$. The walkers that have been removed up to time t represent barriers which are passable at t, but were impassable at some earlier time. Since these restrict the chain motion along the contour on shorter length scales, they slow the diffusive motion at t, even though they are passable. This can be accounted for by evaluating the diffusion constant for motion on the interwalker length scale s. The appropriate diffusion constant is given by

$$d_s \sim s^{3/2}/t_s, \tag{3}$$

where t_s is the time when the mean-squared displacement of the walkers is s^2. The justification for this form for d_s is presented elsewhere [31], and it is discussed when considering a generalization of the model in section 2.2.1.

We have applied a scaling analysis to this model [31]. It predicts that the mean-squared contour displacement of the walkers behaves as $t^{4/7}$. While the models treat the chains as moving along contours of neighboring chains, it is the three-dimensional motion of the chains which we ultimately need to consider. The contours of chains in a melt are well approximated by Gaussian random coils [45,46]. This can be used to deomonstrate that $g(t)$, the mean-squared (three-dimensional) displacement of a point on a chain, is related in this model to $\bar{l}(t)$ by [31]

$$g(t) \sim \bar{l}(t). \tag{4}$$

Since $\bar{l}^2 \sim t^{4/7}$, the scaling analysis of the model predicts

$$g(t) \sim t^{2/7}. \tag{5}$$

At sufficiently long times, the center of mass component dominates and this $t^{2/7}$ behavior cross over to a $g \sim t$ simple diffusion form.

Another important quantity in polymer dynamics is the terminal relaxation time, which defines the longest time scale for linear viscoelastic response. In this model, and in essentially all other models for polymer melts, the scaling of this quantity is obtained by equating it with the time when $\bar{l}(t)$ is on the order of the chain contour length. This is equivalent to the time for which $g(t)$ is on the order of the squared chain radius of gyration R_G^2. If $g(t) \sim t^{\alpha}$, then the terminal time t_f must scale as N^{γ}, where $\gamma = 1/\alpha$. Therefore, the scaling analysis predicts $t_f \sim N^{7/2}$.

Another important quantity is the diffusion constant for the chain center of mass motion. We have considered contributions to this diffusion constant from the relative motion of neighboring chains and from the correlated motion of all chains in a region of the melt [31]. We find that the contribution due to the correlated motion should dominate for large N. A similar observation has also been made by Fixman [47]. If the centers of mass of two chains are located within a chain radius of gyration of each other, then the two chains are entangled. In time t_f, the mean-squared relative displacement of the two chains is on the order of R_G^2. This is essentially the definition of t_f. If two chains have centers of mass located a distance $\xi > R_G$ apart, and if the motion of the chains is correlated over distances of order ξ, then the maximum mean-squared relative displacement of these two chains is on the order of ξ^2. This requires correlated motion of all chains in a volume of order ξ^3, and the diffusion constant for the correlated motion of all chains in the volume D_ξ should be inversely proportional to the number of monomers in the volume.[2] This gives $D_\xi \sim \xi^{-3}$. The mean-squared displacement in time t_f due to correlated motion over a distance ξ is given by the smaller of ξ^2 and $6D_\xi t_f$. The ξ which maximizes this is obtained from

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

The dependence of ξ on N can be obtained by substituting $t_f \sim N^{7/2}$ and $D_\xi \sim \xi^{-3}$ into (6). Substitution of this result back into D_ξ yields a contribution to the chain center of mass diffusion constant which scales as [31]

$$D_{c.m.} \sim N^{-2.1}. \tag{7}$$

This model incorporates a number of significant features. While it investigates the lateral chain motion, it does not assume that the lateral motion must occur. The cooperative motion of the chains makes the lateral motion possible, even though nearby chains present impassable barriers to the lateral chain motion on all length

[2] A collective mode of this type will be similar to the center of mass mode for the n monomers within the correlated volume. This mode can be written as $y = N^{-1}\sum_i c_i x_i$, where x_i are the individual monomer coordinates. For the center of mass, all the c_j's are unity. In the present case, the c_j's may vary some over the correlated volume, but are of order unity. For a very short time step τ, the motions of the different monomers in the volume are nearly independent. Therefore, $\langle y^2\rangle = N^{-2}\sum_{j,k}\langle c_j x_j c_k x_k\rangle \approx N^{-2}\sum_j c_j^2\langle x_j^2\rangle = N^{-1}\langle c^2\rangle\sigma^2$, where $\sigma^2 = \langle x_j^2\rangle$ and $\langle c^2\rangle = N^{-1}\sum_j c_j^2$. Since all the c_j's are of order unity, $\langle c^2\rangle$ is also of order unity. The diffusion constant for the collective mode is defined by $\langle y^2\rangle/2\tau$, and is of order $1/N$. Short-range correlations could be included, but these do not affect the scaling and become insignificant as $\tau \to 0$. At longer times, the interactions between the chains may or may not slow the collective motion. Since the collective mode involves correlated motion over the distance ξ^2, a mean-square displacement greater than ξ^2 is not possible in time t_f [31]. Therefore, if $6D_\xi t_f$ is greater than ξ^2, the intrachain interactions must slow the motion. For this reason, the mode which provides the maximum displacement occurs when eq. (6) is satisfied.

scales. The length scale dependence of the fraction of neighboring chains which present impassable barriers is also an important feature. Without this, the lateral motion would be slower and the terminal time longer. This model predicts a terminal time that scales as $N^{3.5}$, compared with $N^{3.0}$ for pure reptation. This means that the terminal time for reptation must be shorter for longer chains. However, this does not require that reptation must dominate, since there are many more avenues for lateral motion.

2.2. GENERALIZATIONS OF THE MODEL

This model presents a simplified picture of polymer dynamics. Probably the most significant simplification is that the model treats each neighboring chain segment as being independent of all others. In the real system, a large number of the chain segments in contact with a specific probe chain belong to the same entangling chain. Furthermore, the various chains entangling the probe are also entangled with each other. More complex models need to be developed and studied in order to understand the impact of these features on the lateral chain motion. While we do not attempt a complete study of these questions here, we do explore the range of behaviors possible within the current model. The first feature considered here is the changes in the predictions of the model as the function $F(l)$ is varied. This function is the fraction of neighboring chain segments which pose impassable barriers as a function of length scale. The form of this function is one feature of the model that could change if the additional complexities in the nature of the barriers are accounted for. We limit $F(l)$ to the simple scaling functional form $F(l) \sim l^{-a}$, where a is treated as a parameter of the model. The value $a = 1/2$ corresponds to the model discussed above and elsewhere [31].

Another feature explored in this section concerns the use of simple random walkers to model the motion of the chain segments along the contours of neighboring chains. The motion of real chain segments would have some memory of the history of their motion. If a point on a chain moves in one direction, then on average the remainder of the chain exerts a pull in the opposite direction. The present model ignores these memory effects. This corresponds to the assumption that the lateral chain dynamics is sufficiently slowed by the barriers to lateral motion that the memory function is essentially completely relaxed. Here, we employ a Rouse model with a bead friction coefficient evaluated from our lateral motion model to investigate the influence of chain memory.

Another feature of the model is also considered. In the original model described above, the correlation length for walker motion on the length scale $\bar{l}$ scales as $\bar{l}^{3/2}$. If $\bar{l} > N^{2/3}$, this correlation length is longer than the chain contour length. The question arises as to whether this is reasonable. In a real system, a chain moves along one chain until it encounters another which blocks its progress. Then it moves along that one and so on. This motion along a sequence of chain contours is not significantly different in nature than the simplified motion along a single contour

employed in the model. However, in this picture of sequence of contours, it is not clear whether there should be a limit on the range of correlations for the motions along the contours. In this section, we investigate the effect of limiting the maximum correlation length to the chain contour length in the model.

2.2.1. Varying $F(t)$

Here we consider the generalized model which is the same as described above except that the fraction of obstacles (segments of neighboring chains) which are impassable when considering chain motion on a length scale l is given by

$$\begin{aligned} F(l) &= 1 \qquad && l < l_0; \\ &= (l/l_0)^{-a} && l > l_0. \end{aligned} \tag{8}$$

The parameter l_0 is a minimum length for the obstacles, which we set to unity. The exponent a is treated as a variable parameter. As before, a model for the motion of random walkers on a contour is studied. The walkers pass through each other. The quantity $\bar{l}(t) = \langle l^2 \rangle^{1/2}$ is the root-squared displacement of the walkers along the contour. Walkers are removed from the simulation such that the fraction of the original number of walkers present at any time is given by $F(\bar{l})$. The remaining walkers correspond to the fraction of obstacles which are impassable at that time. The obstacles which are passable still slow the lateral chain motion, since they were impassable on shorter length scales and thus hindered the motion. This is accounted for by defining a length scale dependent diffusion constant analogous to d_s of (3) for the diffusive motion of the walkers between encounters with other remaining walkers. A specific definition of d_s is given below. However, we first consider the simpler model in which the individual walker diffusion constant is unity at all times. The time t in the model with a time-depenent walker diffusion constant can be related to the time τ in the simpler model with a diffusion constant of unity by the relationship

$$d_s \, \mathrm{d}t = \mathrm{d}\tau \tag{9}$$

for each short interval. Equation (9) specifies that the change in $\bar{l}^2$ be the same in the two models during the interval. Integrating this expression gives τ as a function of t.

To solve for the dependence of $\bar{l}$ on τ, we apply the following scaling argument. For a given value of $\bar{l}$, the mean distance between adjacent walkers is $s = F(\bar{l})^{-1} = \bar{l}^a$, and the mean distance between two walkers, which are n walkers apart along the contour, is ns. If we assume that the walkers are distributed randomly along the contour at all times, then the mean-squared fluctuation in the distance between adjacent walkers is s^2, and the corresponding quantity for a pair of walkers n

walkers apart is $\sigma_n^2 = ns^2$. If the mean-squared displacement of the walkers $\bar{l}^2$ is greater than σ_n^2, then the displacement of the pair of walkers cannot be independent; they must be correlated. On the other hand, if $\bar{l}^2$ is less than σ_n^2, then the motion of the pair of walkers could be independent, since it falls within the squared fluctuation in the distance between the walkers. Therefore, the minimum number of walkers whose motion must be correlated for displacements on the length scale $\bar{l}$ is

$$m(\bar{l}) \sim \bar{l}^2/s^2 \sim \bar{l}^{(2-2a)}. \tag{10}$$

This quantity $m(\bar{l})$ is the number of walkers for which $\sigma_n^2 \leq \bar{l}^2$. The correlation length for walker motion on length scale $\bar{l}$ must than be the mean distance between walkers $m(\bar{l})$ walkers apart,

$$\xi(\bar{l}) \sim m(\bar{l})s(\bar{l}) \sim \bar{l}^{(2-a)}. \tag{11}$$

The diffusion constant for the correlated motion of m walkers is the diffusion constant for the center of mass of these walkers. This is inversely proportional to m,

$$D(\bar{l}) \sim \frac{1}{m} \sim \bar{l}^{2(a-1)}. \tag{12}$$

The τ corresponding to a specific value of $\bar{l}$ can be obtained from

$$\bar{l}^2 \sim D(\bar{l})\tau, \tag{13}$$

which gives

$$\tau \sim \bar{l}^{(4-2a)}. \tag{14}$$

Inverting this expression, we find

$$\bar{l} \sim \tau^{1/(4-2a)}. \tag{15}$$

Now we return to the evaluation of d_s, the diffusion constant for the motion of a walker between collisions with other remaining walkers. The effective diffusion constant for walker motion on the length scale $\bar{l}$ can be evaluated as

$$d_0(\bar{l}) \sim \bar{l}^2/t. \tag{16}$$

If we assume that t and $\bar{l}$ are related by the simple scaling form

$$\bar{l} \sim t^{\alpha}, \tag{17}$$

then (16) together with (17) yields

$$d_0(\bar{l}) \sim \bar{l}^{(2-1/\alpha)}. \tag{18}$$

The corresponding diffusion constant for motion on the length scale of the mean distance between walkers s, is

$$d_0(s) \sim \bar{l}^{(2a-a/\alpha)}, \tag{19}$$

where $s = \bar{l}^a$ has been employed. The correlation length for motion on the length scale s is obtained from (11),

$$\xi(s) \sim s^{(2-a)} \sim \bar{l}^{(2a-a^2)}. \tag{20}$$

As long as $a < 1$ and $s > 1$, this correlation length is greater than s. Consequently, $d_0(s)$ includes the effect of some walkers that have not been removed. The number of remaining walkers within the correlation length is

$$n_s = \xi(s)/s \sim \bar{l}^{(a-a^2)}. \tag{21}$$

The diffusion constant $d_0(s)$ can be written as

$$d_0(s) \sim \frac{1}{n_s} d_s. \tag{22}$$

Writing $d_0(s)$ in the form (22) corresponds to breaking the total set of walkers within $\xi(s)$ into n_s groups. The quantity d_s is the diffusion constant for the center of mass of one group, while $d_0(s)$ is the diffusion constant for the center of mass for the entire set of n_s groups. The diffusion constant d_s is the diffusion constant for a single remaining walker together with the surrounding removed walkers on the length scale s. Here we are treating the removed walkers as phantom walkers in the model. This is the diffusion constant we use for the motion of a remaining walker between contacts with other remaining walkers.

Equation (22) can be solved for d_s to give

$$d_s \sim n_s d_0(s) \sim \bar{l}^{(3a-a^2-a/\alpha)} \sim t^{(3\alpha a-\alpha a^2-a)}. \tag{23}$$

Equation (9) together with (23) yields

$$\tau \sim t^{(3\alpha a-\alpha a^2-a+1)}. \tag{24}$$

Substitution of this result into (15) gives

$$\bar{l} \sim t^{(3\alpha a-\alpha a^2-a+1)/(4-2a)}. \tag{25}$$

Comparison with (17) shows that the exponent on t in this last expression must equal α. Solving for α yields the scaling result for $l(t)$,

$$\bar{l}(t) \sim t^{1/(4-a)}. \tag{26}$$

For the case where $a = 1/2$, which is the model presented previously [31], this gives $\bar{l} \sim t^{2/7}$. If $a = 0$ and the all barriers remain impassable, then $\bar{l}$ behaves as $t^{1/4}$.

The terminal time t_f is associated with the time when $\bar{l} \sim N$. This corresponds to a scaling of

$$t_f \sim N^{(4-a)}. \tag{27}$$

As a varies from 0 to 1, this expression for t_f decreases from 4.0 to 3.0.[3)] We have previously shown [31] that if $t_f \sim N^{\gamma}$, then the contribution to the center of mass diffusion constant from cooperative motions scales as $N^{-3\gamma/5}$. Therefore, for this generalized model, we find

$$D_{\text{c.m.}} \sim N^{-3(4-a)/5}, \tag{28}$$

which varies from $N^{-2.4}$ to $N^{-1.8}$ as a varies from 0 to 1.

2.2.2. *Chain memory effects*

The second feature of the model which we examine is the effect of chain memory on the motion along the contour. The model described in section 2.1 treats the motion of each walker as diffusive and, therefore, ignores these memory effects. One way of rationalizing this approximation is to view each chain as moving by lateral steps along the contours of neighboring chains. The chains also move along their own backbones by steps of approximately the same size. If a chain takes a specific lateral step, then on average this causes the chain to stretch somewhat. If this stretching is relieved by other reptative or lateral motions prior to the next lateral move of this point on the chain, then there is no memory and a lateral step in either direction along the contour of the neighboring chain is equally likely. If the stretching is not relieved before the next lateral move of this point on the chain, then a move back to the original position is more likely than a move farther in the same direction. If the time steps for lateral and reptation motions are the same, then the memory is not significantly relaxed on the scale of a single step and this slows the lateral motion.

[3)] Throughout this paper, t_f refers to the terminal time for lateral motion. The reptation model predicts a terminal time which scales as $N^{3.0}$. It might at first seem that the "faster" reptation must dominate for large enough N. The assumption here is that there are so many more avenues for lateral motion than for reptation that the chain spends its time exploring the lateral motions. If this is the case, then the lateral motion model may provide a more reasonable description of the chain dynamics than tube models.

The presence of barriers to lateral motion slows the mean lateral displacement on length scales longer than the mean distance between barriers. However, it does not affect the reptation motion. For motion on some contour length scale $\bar{l}$, the reptation time for chain relaxation scales as $\bar{l}^2$, since the reptation motion is Rouse-like motion along the chain backbone [1]. The time scale for lateral motion, if memory effects are ignored, scales as $\bar{l}^{7/2}$ for the model described in section 2.1, and it scales as $\bar{l}^{(4-a)}$ for the generalized version in section 2.2.1. Memory effects can only lengthen the times for lateral motion. Therefore, the lateral displacements do not have to be very large before the reptation relaxation time is much smaller than the lateral displacement time. Under these conditions, the reptation motion should relax the chain memory except on quite short length scales.

The fact that reptation motion is more rapid than lateral motion on most length scales does not imply that reptation dominates the dynamics. If lateral motion is not totally suppressed by the obstacles posed by neighboring chains, then there are many more lateral pathways available to a chain than there are reptation pathways. The reptation motion facilitates the lateral motion by relaxing the chain memory, allowing the chain to move laterally in different directions at different points along the chain. Questions still remain as to whether the reptation motion is able to simultaneously facilitate the lateral motion at all points along a chain on all length scales. Alternatively, the reptation motion may be so fast that it actually dominates the chain motion on some length scales. These are questions we plan to study in future work.

Since it is uncertain whether local reptative motions are sufficient to simultaneously relax the chain memory at all points along a chain, it is useful to consider the possible effect of chain memory on the current model by studying the extreme case in which there is no memory relaxation. We can estimate the memory effects by treating the chain as a Rouse chain [1] and replacing the usual friction coefficient with a length scale dependent friction coefficient derived from the behavior of the lateral chain motion. The friction coefficient in the Rouse model is the friction coefficient for the motion of a chain bead (monomer). It does not include the effect of the bond interactions with neighboring beads in the same chain. Since the friction coefficient does not include these intrachain interactions, it should be calculated in the present case from the lateral chain model without memory effects, since the memory effects arise from intrachain interactions. Since $g \sim \bar{l} = \langle \bar{l}^2 \rangle^{1/2}$,

$$\frac{\mathrm{d}}{\mathrm{d}t} g_0 \sim \frac{1}{2\bar{l}_0} \frac{\mathrm{d}}{\mathrm{d}t} \langle l^2 \rangle_0, \tag{29}$$

where the subscript zero indicates that memory effects are ignored. We can define a friction coefficient ζ_l for the lateral motion along the contours of neighboring chains from

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle l^2 \rangle_0 \sim K_B T / \zeta_l . \tag{30}$$

The corresponding friction coefficient for three-dimensional bead motion ζ_{3D} can be defined from

$$\frac{dg_0}{dt} \sim K_B T/\zeta_{3D} . \tag{31}$$

These can be related using (29), yielding

$$\zeta_{3D} \sim \zeta_l \bar{l}_0 . \tag{32}$$

The friction coefficient for lateral motion ζ_l can be identified with $K_B T/D_{TOT}(\bar{l})$, where $D_{TOT}(\bar{l})$ is the total diffusion constant for walkers on the contour in the model presented in section 2.2.1. This is given by $D_{TOT}(\bar{l}) = D(\bar{l})d_s \sim \bar{l}^{(a-2)}$, where (12) and (23) have been employed, and α in (23) has been replaced with $1/(4-a)$, its value in the absence of memory effects. This expression for D_{TOT} gives $\zeta_l \sim \bar{l}^{(2-a)}$. Inserting this into (32) yields

$$\zeta_{3D} \sim \bar{l}^{(3-a)} . \tag{33}$$

The mean-squared displacement of $g(t)$ for a Rouse model (ignoring the center of mass contribution) has the form [1]

$$g(t) \sim \sum_p \frac{1}{p^2} \left\{ 1 - \exp\left[-p^2 A \int_0^t dt_1/\zeta_{3D}(t_1) \right] \right\}$$

$$\sim \sum_p \int_0^t dt_0 \, \zeta_{3D}(t_0)^{-1} \exp\left[-p^2 A \int_0^{t_0} dt_1/\zeta_{3D}(t_1) \right] , \tag{34}$$

where p labels the normal modes of the Rouse chain and A is a constant which scales as N^{-2}. The friction coefficient depends on time through its dependence on $\bar{l}$. For large N, the sum over modes can be approximated as an integral over p. The result is

$$g(t) \sim \int_0^t dt_0 \, \zeta_{3D}^{-1}(t_0) \left[\int_0^{t_0} dt_1/\zeta_{3D}^{-1}(t_1) \right]^{-1/2} . \tag{35}$$

If we take $g(t) \sim \bar{l}(t) \sim t^{\alpha}$, then $\zeta_{3D} \sim t^{(3-a)\alpha}$. Substitution of these expressions into (35) yields a condition on α, which can be solved to give $\alpha = 1/(5-a)$. Therefore, this model for the memory effects predicts

$$\bar{l} \sim t^{1/(5-a)}, \tag{36}$$

$$t_f \sim N^{(5-a)}, \tag{37}$$

$$D_{c.m.} \sim N^{-3(5-a)/5}. \tag{38}$$

Notice that only the friction coefficient for lateral motion has been employed in this calculation. Therefore, only relaxation times appropriate for the lateral motion have been allowed, and relaxations due to faster motions along the chain backbone have been excluded.

2.2.3. *The effect of restricting the correlation length for lateral motion*

In this section, we explore the consequence of restricting the length over which correlations are allowed in the model. Since the correlation length for motion on the length scale $\bar{l}$ is given by $\xi(\bar{l}) \sim \bar{l}^{(2-a)}$, this correlation length becomes larger than the contour length of a chain $L \sim N$, when $\bar{l} \sim N^{1/(2-a)}$. This corresponds to the time $t_0 \sim N^{(4-a)/(2-a)}$. If we do not allow correlations over distaces longer than L, then the $\bar{l} \sim t^{1/(4-a)}$ behavior crosses over to simple diffusion behavior $\bar{l}^2 \sim D_0 t$, when $t = t_0$. The diffusion constant D_0 is the total diffusion for lateral motion at t_0. This is given by $D(\bar{l})d_s$ evaluated at time t_0. When the result $\alpha = 1/(4-a)$ is substituted into into (23), one obtains $d_s \sim \bar{l}^{-a} = s^{-1}$. A consequence of this is that the total diffusion constant is inversely proportional to the correlation length and that

$$D_0 \sim \frac{1}{N} \tag{39}$$

for $t > t_0$.

We can summarize the behavior of $g(t) \sim \bar{l}(t)$ for the model if we limit the correlation length to the chain contour length as

$$\begin{aligned} g(t) &= t^{1/(4-a)} && t < t_0; \\ &= \left(\frac{1}{N} t\right)^{1/2} && t > t_0, \end{aligned} \tag{40}$$

where $t_0 \sim N^{(4-a)/(2-a)}$. The terminal time is found from $g(t_f) \sim N$, which gives

$$t_f \sim N^3. \tag{41}$$

The cooperative contribution to the center of mass diffusion constant scales as

$$D_{c.m.} \sim N^{-9/5}. \tag{42}$$

It is worth noting that there is also a non-cooperative contribution to $D_{c.m.}$ which scales as N^{-2}, as in the reptation model [31].

3. Discussion and summary

In this paper, we have described a recently presented model for the dynamics of monodisperse polymer melts. The model studies the lateral chain motion and finds that, within the simplifications inherent in the model, the lateral motion is not suppressed by the obstacles presented by neighboring chains, although it is slowed. The model predicts behaviors for the monomer mean-squared displacement, the terminal relaxation time, and the center of mass diffusion constant which are in excellent agreement with experimental results and computer simulations [48–50].

The model greatly simplifies the problem by treating each obstacle to lateral motion as being independent of all others. In reality, the obstacles are highly interconnected and intertwined in a melt. In the model considered here, as chain A moves along the contour of chain B, it encounters a barrier chain, chain C. It then moves along the contour of chain C. In actual polymer melts, it would soon encounter a chain D, move along the contour of that chain, encounter a chain E, and so on until it encountered the contour of chain B again. In this model, we consider only simple barriers made up of a single chain, chain C. We find the model provides reasonable results despite this simplification. One possible explanation is that the barrier presented by the sequences of chains, chain C, chain D, chain E, and so on, has the form of a random walk contour, which has short-range correlations but looks like a Gaussian random coil over longer distance. Therefore, the effect of the complex barrier composed of chains C, D, E, ... is not substantially different from the simple barrier, chain C, employed in the model. On the other hand, it may be that in the real system the complete set of intertwining chain contours results in topological constraints that are not present in the simple model presented here. Further work is needed to study this point.

In this paper, we study the sensitivity of the model to changes in various aspects of it. We vary the form of the function $F(l)$, which gives the fraction of obstacles that pose effective barriers to lateral motion as a function of length scale. This is certainly one feature of the model that could change as added complexities are included. We restrict our study to an $F(l)$ of the form l^{-a}, where a is considered a variable parameter. The value $a = 1/2$ corresponds to the original model. The scaling analysis applied to this generalized model predicts a mean-squared monomer displacement which behaves as $g(t) \sim t^{1/(4-a)}$, a terminal time which scales as $t_f \sim N^{(4-a)}$, and a center of mass diffusion constant which scales as $D_{c.m.} \sim N^{-3(4-a)/5}$.

Chain memory effects have been ignored in the original model. This corresponds to assuming that these are effectively relaxed by local chain motions on the time scale for the hindered lateral motion. We explore the consequences of this assumption by making the alternate assumption that memory effects are not relaxed to any significant extent. The memory is then incorporated into the model through the use of a Rouse model for the chain dynamics, which employs a friction coefficient evaluated from the lateral chain motion. When these memory effects are included, the model predicts $g(t) \sim t^{1/(5-a)}$, $t_f \sim N^{(5-a)}$ and $D_{c.m.} \sim N^{-3(5-a)/5}$.

Finally, we consider the effect of limiting the maximum range of correlations betwen the motions of the chains. In the original model, the relative chain motions are correlated over a distance which becomes longer than the chain radius of gyration before the terminal relaxation is reached. In it unclear whether this is reasonable. Therefore, we explore the behavior of the model if we limit the maximum correlation length. We find that $g(t)$ crosses over from the $t^{1/(4-a)}$ behavior to a $(t/N)^{1/2}$ behavior at a crossover time $t_0 \sim N^{(4-a)/(2-a)}$. The terminal time behaves as N^3, and the cooperative contribution to $D_{\text{c.m.}}$ scales as $N^{-9/5}$. These predictions ignore memory effects.

From these studies, it is clear that a range of lateral models are reasonably consistent with the experimentally observed behaviors. If $F(l) \sim l^{-a}$, then an increase in the parameter a facilitates the lateral motion, while decreasing a slows lateral motion. Inclusion of chain memory slows lateral chain motion, and limiting the maximum correlation length for relative motions of the chains facilitates the lateral chain motion. This study provides some insight into the range of possibilities within the lateral model for chain motion. For instance, if a more complex and realistic model for the distribution of barriers to lateral motion results in a modified $F(l)$, this could be offset by memory effects or by limiting the range of correlations. Memory effects and limitations on the correlation length shift the behavior of the model in opposite directions and, therefore, could be present but largely cancel in some systems. The real challenge for the future is to develop models which incorporate the complexities due to the connections between and intertwining of various barriers. Since both reptative and lateral motions lead to predictions in general agreement with known polymer phenomenology, it is only by means of this type of detailed theory that a truly clear picture of the mechanisms of polymer dynamics in the melt can be obtained.

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