Using Force Field Simulations for the Evaluation of the Monomer Parameters for the Calculation of Diffusion Constants for Long Chain Polymer Melts

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ABSTRACT: Force field simulations are employed in the evaluation of the monomer interaction diameter used in the lateral motion (LM) model for the dynamics of polymer melts. Interaction diameters are obtained for polystyene (PS), polyethylene (PE), poly(ethylene oxide) (PEO), and poly(dimethylsiloxane) (PDMS) from two- and three-chain configurations. It is found that these interaction diameters result in diffusion constants using the LM model that are in good agreement with experimental data. If the interaction diameter is known, the only adjustable parameter in the diffusion constant calculations is the bare monomer diffusion constant, D_0. The calculation of D_0 from short chain, short time force field molecular dynamics simulations is attempted for PE, PEO, and PDMS. The bare diffusion constant obtained for PE is found to provide accurate diffusion constants for long chain melts from LM calculations with no adjustable parameters. Values for D_0 were not obtained from the simulations performed for PEO and PDMS, because the monomers do not move significantly on the time scale of the simulations for these polar systems.

I. Introduction

Several theoretical models for the dynamics of polymer melts have been developed.[1−33] Much of the theoretical research concerning the dynamics of polymer melts and concentrated solutions employs the reptation[15−17] picture of each chain moving within a confining tube, which is assumed to mimic the constraining influence of the surrounding chains. In recent years, several other theories of the dynamics of polymer melts have been presented. These include the mode−mode coupling model of Schweizer and co-workers,[18−20] the generalized Rouse model of Hess,[21,22] the kinetic theory approach of Bird and Curtiss,[23,24] the hydrodynamic scaling model of Phillies,[25−27] the models developed by Loring and co-workers,[28−32] which treat the effect of the surrounding chains as fluctuating transient barriers to the chain motion, and the approach of Douglas and Hubbard,[33] which considers the motions of clusters of chains in the melts.

We have also presented a theory of polymer melt dynamics in a series of publications over the past several years.[1−14] This theory, which we refer to as the lateral motion (LM) model, assumes that the lateral motion is not completely suppressed. This theory takes into account the restrictions on the lateral motions due to the noncrossability of the chains and the correlations in the chain motions that must accompany the lateral motion of the chains. The coupling between lateral and reptative chain motions is also considered. It has been shown[8] in previous work that good agreement is obtained between the predictions of the theory and the results of published computer simulations,[34,35] if purely theoretical estimates are employed for all parameters in the theory except the bare monomer diffusion constant. Furthermore, very accurate quantitative agreement with the simulation data is achieved with modest changes in just a few of these theoretically estimated parameters.[13,14] Using parameters that have been modified on the basis of comparison with simulation data, excellent agreement has also been found[13,14] between the predictions of the theory and experimental[38,39] diffusion constant data for polyethylene (PE), poly(ethylene oxide) (PEO), and poly(dimethylsiloxane) (PDMS) melts.

The structure of the monomer unit for the polymer is defined in the theory[13] by the monomer length, b, the Kuhn length, b_1, the monomer diameter, σ, and the bare monomer diffusion constant, D_0. The length, b, can be defined as the distance from an atom along the chain backbone in one monomer unit to the same atom in the next monomer. However, in this work, we define it as the average distance per bond along the chain backbone, and the number of monomer units per chain is taken to be the number of bonds along the backbone. The monomer size and shape are characterized by b and σ, while b_1 reflects the stiffness of the backbone. The diameter σ for the polymers considered in previous work[13,14] was estimated on the basis of force field parameters. For PE, the σ employed is a typical force field interaction diameter for a united atom $-CH_2-$ group. For PEO the diameter is chosen as the average of two $-CH_2-$ force field diameters and one $-O-$ force field diameter. For PDMS, a diameter is defined for the $-Si(CH_3)_2-$ group such that the area of a circle with this diameter equals the cross-sectional area of the group, where this cross-sectional area is evaluated using force field diameters and bond lengths.[13] The diameter associated with this group is then averaged with the force field diameter for $-O-$ to get a single σ for this chain. The use of force field parameters in obtaining the σ values for these systems results in very good agreement between the molecular weight dependent diffusion constant predicted by the theory[13,14] and the published experimental data.[38,39]

The bare monomer diffusion constant plays the same role in this theory as (the inverse of) the monomer friction coefficient does in many other theories. This parameter was treated as an adjustable parameter in the comparisons[8,13,14] with the simulation data for

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monomer mean-squared displacements (MSDs) and center-of-mass MSDs and in the comparison with the experimental diffusion constant data. This is the only freely adjustable parameter in the calculations. The monomer length, b, and the Kuhn length, b_1, were taken to have their known values for the experimental and simulation systems.

In this paper, two questions are examined numerically. The first question is whether an average monomer diameter, σ, can be defined in a useful and meaningful manner for polymers with pendant groups attached to the chain backbone. Polystyrene (PS) is chosen as the system to investigate this question. An average distance between chains is estimated using a currently available force field program, and then this estimated σ is employed in the calculation of the molecular weight dependence of the diffusion constant. The second question explored is whether the sole remaining adjustable parameter, D_0, can be determined from force field molecular dynamics calculations. In many-chain dynamical simulations,[34] the monomer MSD has been found to be essentially independent of chain length at early times, if the same monomer density is employed for all chain lengths. This suggests that it may be possible to determine D_0 from relatively short time and relatively short chain simulations of the melt. Since we are interested in short chain and short time simulations, a small simulation box with periodic boundary conditions should be sufficient. The main question is whether current force fields are adequate to accurately reproduce the dynamics of the polymer melt at appropriate temperatures and densities. This question is examined for PE, PEO, and PDMS melts.

II. Theory

In this section, a summary of the theory is provided. A more complete discussion of the theoretical development can be found elsewhere.[13] Pairs of chains, which have their centers of mass near each other in a melt, have a large number of contacts between them. It can be shown[7] that the average number of contacts between a pair of nearby chains, each containing N monomers, scales as $N^{1/2}$. To disentangle from each other, each chain in the entangled pair can reptate along its own contour and slide laterally along the backbone of the other chain. As each chain moves laterally along the backbone of the other chain, this motion is hindered by the presence of the other nearby chains. Thus, the lateral motion of one chain along the backbone of another requires significant correlation with the motion of other chains in the melt.

It can be shown quite generally that the particle mean-squared displacement in a system of equivalent particles, which have correlated motions, is given by[6,7]

$$g(t) \sim \frac{D_0}{N_c(t)}\, t \tag{1}$$

where D_0 is a constant, which we refer to as the bare diffusion constant. $N_c(t)$ is defined by

$$N_c(t) = \sum_{j=1}^{N_{\mathrm{tot}}} \frac{\langle \Delta \mathbf{r}_j(t) \cdot \Delta \mathbf{r}_1(t) \rangle}{\langle \Delta \mathbf{r}_1(t)^2 \rangle} \tag{2}$$

where N_{tot} is the number of particles in the system. $N_c(t)$ is, roughly, the number of particles (or monomer units in the polymer system) that have displacements correlated with the displacement of a given particle. The particle MSD given by eq 1 can be thought of as the center-of-mass MSD of the correlated group of particles. At early times, when the particle displacements are small, the motion of one particle does not influence the motion of particles far away. In this case, the motion of this particle is correlated only with the motion of nearby particles. At later times, when the particle displacements are larger, then the motion of this particle is correlated with the motions of a larger group of particles. Consequently, $N_c(t)$ increases as $g(t)$ increases. This results in subdiffusive motion, the time dependence of which is determined by the $g(t)$ dependence of $N_c(t)$.

In a polymer melt at early times, when the monomer MSD, $g_r(t)$, is small, the lateral motions of the segments are not greatly restricted by the interchain contacts. Only the intrachain correlations are important in this regime. The number of monomers in one Gaussian chain, which have correlated lateral displacements with the lateral displacement of some particular monomer in this chain, is proportional to the monomer MSD, $g_r(t)$.[4,7] Thus, in the early time regime $N_c(t) \sim g_r(t)$. Inserting this into eq 1 leads[7] to the Rouse-like result $g_r(t) \sim t^{1/2}$ at early times.

As $g_r(t)$ becomes larger, there comes a time when the contacts between pairs of chains restrict the motion such that the lateral displacements of each chain take place primarily along the backbones of the surrounding chains in the melt.[7] Furthermore, there must be correlation in the melt between the lateral displacements along any chain contour of all the chains entangled with that chain.[7] Thus, interchain correlations become an important contribution to $N_c(t)$ at this crossover time, which is independent of chain length. We refer to the crossover value of $g_r(t)$ as g_{c1} and the crossover time as t_{c1}. The crossover value of $g_r(t)$ has been shown to scale as $g_{c1} \sim b_1{}^4/\sigma^2$, where σ is the monomer diameter, and the proportionality constant has been determined[13] from computer simulations, giving $g_{cl} = 1.09 b_1{}^4/\sigma^2$. When interchain correlations have been accounted for in $N_c(t)$ and the lateral motions of the chains are restricted to take place along the curvilinear backbones of the surrounding chains, the $g_r(t)$ that results has been shown[4] to scale as $g_r(t) \sim t^{2/7}$, and the proportionality constant is determined by the continuity of $g_r(t)$ at t_{c1}.

The discussion up to this point has not considered the coupling between the lateral motions and reptative motions. The extent of correlation with the motions of neighboring chains that must accompany a given lateral motion of a particular chain is reduced, if there is reptative motion along the chain backbone toward the point of the lateral motion, since this allows this chain to move around the neighboring chains. This reduction in the correlations would result in a lower $N_c(t)$ and a greater MSD according to eq 1. The greater lateral motions allow the chain to explore a greater volume of the chain configurational space. This can be modeled[7,13] as producing a thermodynamic force dragging the chain along its backbone toward its middle, to increase the lateral motions and the configurational space available to the chain. At each point along the backbone, this reptative drift toward the chain center is converted, on average, into additional lateral displacements. This reptative drift increases the breaking of the interchain contacts as the chain is dragged past the surrounding chains. This results in a crossover to less entangled motion on the time scale of the contact breaking time due to this drift. This crossover time scales as $t_x \sim N^{14/5}$. For times greater than this contact breaking time, the mean-squared displacement due to the lateral motion of the monomers scales[7,13] as $g_r(t) \sim t^{2/5}$, rather than the $t^{2/7}$ dependence employed before t_x. This results in a terminal time, defined as the time when the monomer mean-squared displacement relative to the surrounding chains is on the order of the squared chain radius of gyration. This time scales as $\tau \sim N^{3.3}$.

In a recent publication,[14] an alternate treatment of the reptative–lateral coupling has been presented, in which the reptative and lateral motions are mixed during each small time step. Since this treatment allows for the continuous mixing of the reptative and lateral motions, it may provide a more reasonable treatment of this coupling. However, the center-of-mass diffusion constant obtained using this treatment[14] is essentially indistinguishable from that obtained using the thermodynmic force model,[7,13] although the form of the monomer MSDs differ for the two approaches. Since we are only interested in diffusion constant data in this work, the thermodynamic model[7,13] is completely adequate for this work.

Another feature of our theoretical development is the inclusion of long-range correlated motions,[6,7,13] which allows for the correlated motion of a chain together with all the surrounding chains within some correlation length. This long length scale correlated motion can result in larger mean-squared displacements than the motion of the chains relative to their surroundings, because this relative motion is slowed by the entanglements with the surrounding chains. This correlated contribution scales as $g_c(t) \sim g_r(t)^{3/8}t^{1/4}$. [Throughout this paper, the subscript r has been placed on the contribution to the monomer MSD, $g_r(t)$, from displacements of a monomer relative to its local surroundings in order to distinguish it from long-range correlated contribution, $g_c(t)$.] The evaluation of the prefactor is discussed elsewhere.[7,13]

The center-of-mass motion of the chains relative to the surroundings is determined[7,13] by treating the chain as several independently moving units, each with a number of monomers given by $n_c(t) \sim g_r(t)$. There are $n_{seg} = N/n_c(t)$ of these units per chain. The displacements of these units are taken to be independent of each other with a mean-squared value equal to $g_r(t)$. This gives a contribution to the center-of-mass MSD of $g_{cmr}(t) \sim g_r(t)/n_{seg} \sim g_r(t)^2/N$. There is also a contribution to the center-of-mass mean-squared displacement from the long-range correlated motions corresponding to $g_c(t)$. The number of monomers in the same chain with correlated displacements for this type of motion, $n_c^c(t)$, is given by the length of a Gaussian chain that fits within the correlation length, $\lambda_c(t)$, for this motion at time t. While the details of the analysis can be found elsewhere,[7,8,13] the result for this contribution is $g_{cmc}(t) \sim g_c(t)^3/Ng_r(t)$, as long as $\lambda_c(t) < R_G$ or, equivalently, when $n_c^c(t) < N$. At some $t = t_{c2}$, $n_c^c(t_{c2}) = N$ for sufficiently long chains, and all monomers in the chains have correlated displacement for this type of motion at this and all subsequent times. Therefore, $g_{cmc}(t)$ crosses over to $g_{cmc}(t) = g_c(t)$ for $t > t_{c2}$. These two contributions, $g_{cmr}(t)$ and $g_{cmc}(t)$, to the center-of-mass MSD yield contributions to the center-of-mass diffusion constant that scale with chain length as $D_{cmr} \sim N^{-2.3}$ and $D_{cmc} \sim N^{-2.1}$, respectively. The diffusion constant has commonly[17,38] been considered to scale as N^{-2} to $N^{-2.1}$. However, Lodge has recently argued that the data for seven polymer systems is in better agreement with a $N^{-2.3}$ dependence.[39] In the context of the LM theory, this would suggest that D_{cmr} is the larger contribution to the diffusion constant in these systems for the range of molecular weight considered.

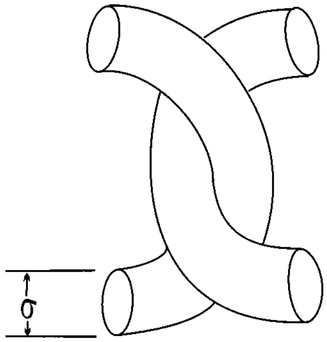

Figure 1. Short segments of two chains represented as semiflexible cylinders.

III. Numerical Calculations

A. Evaluation of Interaction Diameter. In this section, we investigate whether the interaction diameter can be defined for polystyrene chains using a commercially available force field program[41] and whether the molecular weight dependence of the diffusion constant obtained by the LM theory with this interaction diameter is in agreement with published experimental results.[40] Unlike our earlier studies involving PE, PEO, and PDMS,[13] the σ parameter cannot easily be estimated from the interaction parameters employed in force fields, due to the presence of the phenyl side group. The LM theory models the chains as semiflexible cylinders, which have a diameter σ as illustrated in Figure 1, and with the Kuhn length determining the chain stiffness. This diameter plays an important role in the theory because g_{c1}, the value of the monomer MSD when the dynamics crosses over from the early time Rouse-like behavior to the entangled behavior, depends on σ, as discussed in section II. The prefactor in the g_{c1} expression in the theory is chosen by comparing of the predictions of the theory with computer simulations for chains with spherical monomers.[34] The σ in this evaluation of the prefactor is taken to be the Lennard-Jones interaction diameter, which was employed in the simulations. Thus, the σ in the theory corresponds to a Lennard-Jones interaction diameter for the monomers in the chain. Real polymers are not simple tubes with one diameter. The monomers can have more complicated shapes. For PE, the choice of the united atom $-CH_2-$ interaction diameter for σ worked very well, and an average of the interaction diameters for the different groups along the chain backbone gave good results for PEO and PDMS.[13] These were polymers with relatively simply shaped monomers. Here we investigate whether an average σ can be obtained for PS, a polymer with phenyl side groups, from simple two- or three-chain force field calculations and whether the molecular weight dependent diffusion constant predicted by the theory using this σ is in good agreement with experimental data.

To estimate σ for PS, the commercially available software Cerius[2] from Molecular Simulations Inc. was

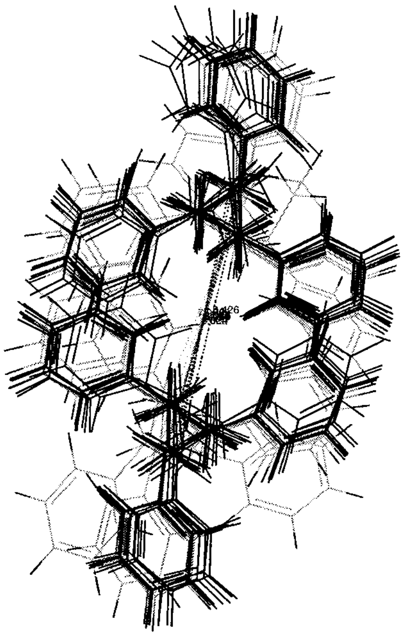

Figure 2. View of two-chain PS configuration down chain backbones. Printed out from the Cerius^2 modeling system.

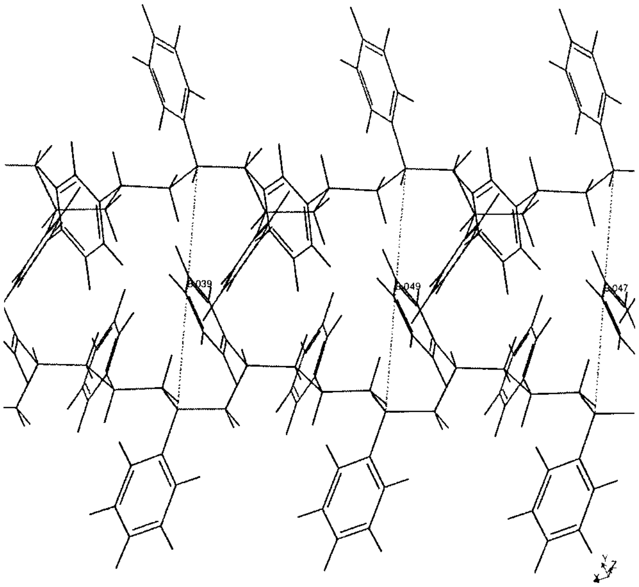

Figure 3. View of two-chain PS configuration. Printed out from the Cerius^2 modeling system.

employed to generate a 40 monomer unit PS chain, where a monomer unit is defined as $-CH(C_6H_5)CH_2-$. Two identical chains were then placed in very close contact of each other, so that the corresponding atoms of the two chains almost overlapped. The system energy was then relaxed by molecular mechanics minimization using the PCFF force field[41] available in Cerius^2. When the relaxation of the two chains was complete, the distances between corresponding atoms along the chain backbones were measured, and the mean value of those measurements was used as an estimate of the interaction diameter σ. Figure 2 presents a view down the backbones of the chains after the relaxation is complete. A side view is shown in Figure 3. The two chains in the relaxed configuration shown in Figures 2 and 3 are approximately mirror images of each other. A value of $\sigma = 8.04$ Å is estimated from this two-chain configuration. By varying the initial relative positions of the chain, it is possible to obtain another relaxed configuration where one of the chains is approximately rotated by 60° about the axis of its backbone and the chains are approximately parallel to each other. An estimate of the interaction diameter of $\sigma = 9.55$ Å is obtained from this configuration. In addition to the two-chain relaxations, a similar relaxation was performed with three PS chains, placed initially almost on top of each other. The value of σ estimated from the relaxed three-chain configuration is 7.53 Å.

Lateral motion model calculations of the molecular weight dependence of the center-of-mass diffusion constant were performed using each of these estimates of σ. The bare monomer diffusion constant, D_0, is treated as an adjustable parameter. All aspects of the theory, other than the choice of σ, are the same as in the previous PE, PEO, and PDMS calculations.[13] As in the previous calculations, the known bond length for bonds along the backbone is utilized for b and the Kuhn length b_1 is calculated from the experimental characteristic ratio C_∞. The values of the parameters employed in the calculations are given in Table 1. Figure 4 compares the calculated LM theory results with published data for the self-diffusion constant.[40] There is good agreement between the experimental data and our theoretical prediction for all three values of σ. This indicates that, even though values estimated for σ vary by 10–20% for this system, depending on the number and orientation of the chains employed, very reasonable values of the diffusion constant are obtained for any value of σ within the range suggested by the force field calculations.

To further test whether this simple method for estimation of the average interaction diameter is suitable, we have applied it to PE, PEO, and PDMS, for which we have already obtained good results estimating σ directly from force field parameters.[13] In each of these cases, a two-chain configuration was relaxed using the molecular mechanics minimization (Cerius^2) using the PCFF force field.[41] Each chain contains 40 monomers. (One monomer is $-CH_2CH_2-$ for PE, $-CH_2CH_2O-$ for PEO, and $-Si(CH_3)_2O-$ for PDMS.) A σ of 4.17 Å was obtained for PE, a σ of 4.88 Å was obtained for PEO, and a σ of 5.77 Å was obtained for PDMS. These values are somewhat higher than earlier estimates[13] of 3.85, 3.7, and 4.57 Å for PE, PEO, and PDMS, respectively, especially in the cases of PEO and PDMS. The molecular weight dependent diffusion constant for PE predicted using a σ of 4.17 Å differs only very slightly from the previous results.[13] The differences between diffusion constants obtained for PEO and PDMS using the values of σ from the two chain calculations and the diffusion constants from previous calculations[13] are similar to the differences in the PS diffusion constants in Figure 4 for the various values of σ. The PDMS diffusion constant data are shown in Figure 5. The agreement with the experimental data, while not as accurate as the previous results, is still good.

B. The Bare Diffusion Constant *D_0*. The bare diffusion constant D_0 is the only adjustable parameter in the LM theory calculations of the monomer and center-of-mass MSDs and of diffusion constants. The early time $g_r(t)$ is essentially independent of chain length in the LM model, and this has also been observed in simulations,[34] when the same density is employed for all chain lengths. This suggests that it might be possible to obtain the bare diffusion constant for chains of any

Table 1. Polymer-Dependent Parameters Used in LM Model Calculations of Diffusion Constants[a]

parameter	PE	PEO	PDMS	PS
bond length b (Å)	1.54	1.49	1.64	1.54
kuhn length b_1 (Å)	10.7	6.26	9.84	15.4
interaction diameter (Å)	3.85, 4.17	3.7, 4.88	4.57, 5.77	7.53, 8.04, 9.55
D_0 (cm^2/s)	2.4×10^{-5}	1.7×10^{-5}	1.75×10^{-5}	4.5×10^{-7}
temp T (K)	448	373	333	498
density (units/Å^3)	0.0330	0.0430	0.0150	0.0110
av unit weight (g/mol)	14.0	14.7	37.0	52.0

[a] The density and average unit weight are defined in terms of units along the chain backbone. PEO, for example, has two $-CH_2-$ units and one $-O-$ unit per monomer.

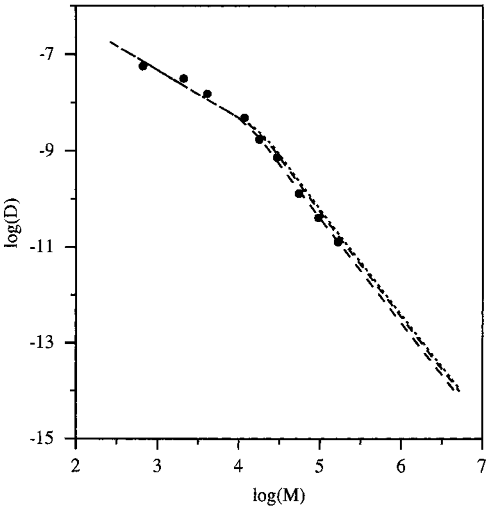

Figure 4. Log–log plot of the LM model center-of-mass self-diffusion constant (in cm^2/s) vs molecular weight for PS. Interaction diameters of 7.53 Å (dotted line), 8.04 Å (short-dashed line), and 9.55 Å (long-dashed line) are used in the calculations. The symbols are the experimental results of Fleischer.[40]

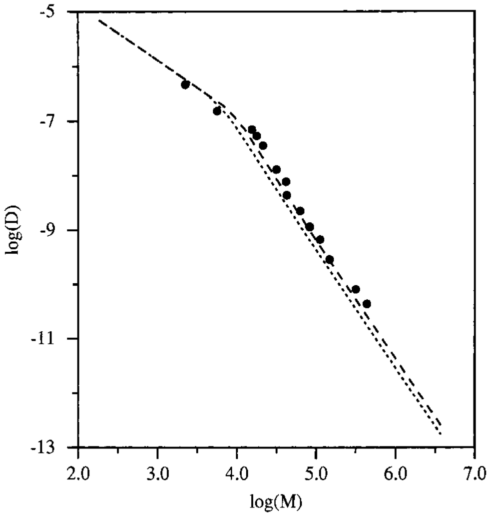

Figure 5. Log–log plot of the LM model center-of-mass self-diffusion constant (in cm^2/s) vs molecular weight for PDMS. Interaction diameters of 4.57 Å (dashed line) and 5.77 Å (dotted line) are employed in the calculations. The symbols are the experimental results of Appel and Fleischer.[39]

length from short chain, short time simulations. If we are only interested in short chain, short time simulations, small sample sizes with periodic boundary conditions should be sufficient. To test the feasibility of evaluating the bare diffusion constants from molecular dynamics calculations, PE simulations were performed using the commercially available software Cerius^2, from Molecular Simulations Inc.[41]

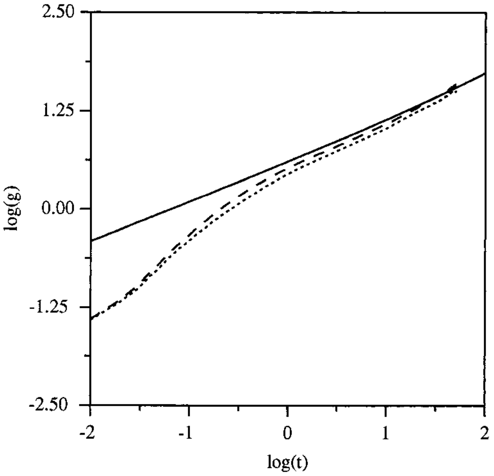

Figure 6. Log–log plot of the monomer MSD (in Å^2) vs time (in ps) for PE simulation. The dotted line is the MSD for the middle monomer in each chain, and the dashed line is the MSD for all monomers. The solid line is the monomer MSD from the LM model calculation with $\sigma = 3.85$ Å.

Figure 6 compares the calculated time-dependent MSDs from the molecular dynamics simulations using the COMPASS force field[41] for PE with the predicted results from the LM model employing the D_0 (and σ) value used earlier in the comparisons with the experimental data.[13] Results were also obtained using the PCFF force field[41] for this system, and the MSDs were found to be similar to the COMPASS results. The PE simulation shown in Figure 6 consists of 50 chains, each 10 monomers ($-CH_2CH_2-$) long. The simulation temperature is set to $T = 448$ K, which is the same as in the experimental systems to which our predictions are compared. (See Table 1.) The 50 chain PE system with the desired density was constructed in a cubic cell with periodic boundary conditions. The long chain melt density is employed, rather than the experimental melt density for chains of the length used in the calculations. The aim here is to use short chain simulations to evaluate a bare monomer diffusion constant appropriate for long chain systems, and this is predicated on the assumption that the early time dynamics is independent of chain length. In previous simulations[34] of many-chain systems, the early time dynamics is found to be quite independent of chain length, if chains of different length are simulated at the same density. The initial configuration constructed by the Cerius^2 software for the system was relaxed using the molecular mechanics energy minimization routines, to obtain a suitable starting configuration for a molecular dynamics simulation. After the relaxation was completed, momenta were chosen for all particles from the Boltzmann distribution, and a constant-volume/constant-temperature dynamics was performed with a time step of 0.001 ps. The calculations were quite CPU intensive. The simulation shown in Figure 6, which has a total time of 50 ps, for example, took 270 h of CPU time on a SGI/CRAY Origin2000 computer system.

There have been extensive simulations of alkane melts, using force fields which have been specifically designed for simulations of alkanes.[42-46] The LM model treats the chains as Rouse-like for all times shorter than the crossover time, t_{c1}. The monomer MSDs in Figure 6 and in the previous alkane simulations[42-46] display ballistic behavior at very short times and then crossover to a more Rouse-like behavior. Although the local chain stiffness results in deviations from Gaussian statistics for short chains, which necessarily precludes true Rouse-like behavior for short chains at short times,[42-46] the hope here is that the bare diffusion constant, D_0, can be determined by comparison of the LM model predictions with an *approximately* $g_r(t) \sim t^{1/2}$ regime in the monomer MSD from the simulations.

The monomer MSD for PE shown in Figure 6 does display a $t^{1/2}$ behavior, and the MSD in this regime is in excellent agreement with the LM model MSD obtained using the same D_0 that was employed in the PE diffusion constant calculations.[13] The bare diffusion constant, which would be determined from these simulations, would clearly provide accurate results for long chain PE diffusion constants in the melt *using no adjustable parameters*. Since the PCFF force field was found to yield a monomer MSD that is very close to the COMPASS result, this would also provide excellent PE diffusion constants for long chain melts. Paul et al.[45] have evaluated the monomer MSD for the $C_{100}H_{202}$ melt at $T = 509$ K. If the expression[36,45] for the segmental friction temperature dependence, $\zeta(T) \propto \exp[1326/(T - 149)]$, for alkane melts is employed to correct for the temperature difference, the D_0 that would be obtained from this $C_{100}H_{202}$ melt would be very similar to that predicted by the simulations reported here.

Molecular dynamics simulations were also performed for PEO and PDMS. The PEO simulation contained 20 chains, each 5 monomers ($-CH_2CH_2O-$) long. The PDMS simulation consisted of 30 chains, each having 10 monomers [$-Si(CH_3)_2O-$]. In contrast to the PE results, the PEO and PDMS simulations do not display a time regime where the monomer MSD has an approximately $t^{1/2}$ dependence, and it is not possible to extract an estimate of D_0 from these simulations. The monomers in these two simulations only move a little around their initial positions on the time scale considered in the simulations. These simulation systems seem to behave more like glasses at the temperature and density considered than like melts, at least on the short time scale of the simulations.

IV. Discussion

There are four polymer specific parameters in the lateral motion model for melt dynamics: the average backbone bond length, b, the Kuhn length, b_1, the monomer interaction diameter, σ, and the bare monomer diffusion constant, D_0. The first two of these are related to the polymer structure and configuration in a well understood manner. The latter two are not so well understood. In this paper, we make a first attempt to determine whether these two parameters can be evaluated numerically using current force fields. The interaction diameter is estimated in this work by generating two or three chains using a commercially available force field program,[41] placing them very close to each other, and allowing the program to relax the configuration. The interaction diameter is then obtained by averaging over a set of short interchain atom−atom distances. This procedure for estimating σ provides values which vary by ∼10−20%, depending on how many chains are used, the initial orientation of the chains before the relaxation step, and the choice of the atom−atom distances over which the average is taken. While this procedure only provides an estimate of this parameter, which is good to about 10−20%, it is considerably simpler than attempting to evaluate σ from much larger and computationally more intensive many chain simulations with significant configurational averaging. The computational effort required for a large simulation is considerable, particularly for a system like PS with a fairly large monomer unit. Furthermore, while a large-scale simulation would remove the ambiguity due to the dependence of σ on the initial configuration in the method employed here, it is also not precisely clear how to unambiguously estimate σ from a large simulation.

Three estimated values of σ for PS were obtained by varying the number and initial orientation of the chains. When these are used in LM model calculations, it is found that the diffusion constant results do not differ greatly for the three calculations and that the calculated diffusion constants are in good agreement with published experimental data[40] for the molecular weight dependence of the diffusion constant in all cases.

The estimated values of σ from this procedure for PE, PEO, and PDMS are somewhat higher than those used in earlier calculations.[13] This is particularly true for PEO and PDMS. The diffusion constant results using the estimated σ are very close to the earlier calculations for PE and in very good agreement with experiment. The diffusion constant results for PEO and PDMS, although not quite as good as PE, are still in reasonably good agreement with experiment. The higher values of σ obtained here (as compared with our earlier estimates) result in part from the fact that the two chain configurational minimization employed should tend to set the distance between corresponding atoms along the chain backbones near the minimum in their pairwise interaction, which is at $2^{1/6}\sigma$ for the Lennard-Jones potential, rather than at σ. Furthermore, there is a wider range of distances between the corresponding atoms on the backbones of the two chains for PEO and PDMS than for PE and PS, where the range is quite narrow. If we had estimated σ from only the few shortest interchain atom−atom distances, the estimated values of σ would be about 4.6 Å for PEO and 5.1 Å for PDMS, which are closer to the values employed in the earlier calculations. (The values of σ for PE and PS estimated in this way would not change very much from those used above.) If these were employed in the LM model calculations, smaller deviations from the earlier calculations and from experiment would be expected.

There are two contributions to the diffusion constant in the LM model: one from the relative motion of neighboring chains and the other from the correlated motion of a chain with the surrounding chains. These both scale as $D_{c1}(N_{c1}/N)^a$, where a is about 2.3 for the first contribution and 2.1 for the second.[13,14] Since $D_{c1} \sim N_{c1}^{-1}$ and $N_{c1} \sim \sigma^{-2}$, these contributions scale as $\sigma^{2(1-a)}$. Thus, a 10−20% error in σ would result in about a 20−50% error in the diffusion constant. While this size error is certainly not negligible, the ability to predict the diffusion constant of a polymer system over a wide range of molecular weights to this level of accuracy (with the bare monomer diffusion constant from short chain data as the only experimental input) is a reasonable accomplishment, and the LM model diffusion constants evaluated in this work agree reasonably well with the experimental data for all values of σ considered. As more experience is gained in numerically evaluating the monomer diameter from force field calculations, it is hoped that it will be possible to improve the numerical procedure employed and to further reduce the uncertainties in the value of the parameters obtained.

Our attempts to evaluate D_0, the bare monomer diffusion constant in the LM model, from short chain, short time, small sample size molecular dynamics calculations had mixed results. In the case of PE, the value of D_0 provided by molecular dynamics calculations is very close to that which was employed in the LM theory calculations. Thus, *the LM model is capable of providing highly accurate diffusion constants for long chain PE melts with no adjustable parameters*. In contrast, it was not possible to extract a value for D_0 from the molecular dynamics calculations for PEO and PDMS, since the monomers simply rattle around their initial positions on the time scale of the simulations.

One possible explanation for the PEO and PDMS molecular dynamics results is that the force fields employed in the molecular dynamics calculations are not sophisticated enough to accurately represent the dynamics of the many-chain polymer system with polar monomers, such as PEO and PDMS, at the temperatures and densities considered. The long chain melt density, which is used in these simulations, is slightly higher than the experimental density for short chains, such as those employed in this study. This higher than experimental density could also be contributing to the slowing down in the chain dynamics that we observe for PEO and PDMS. In addition, the zero time configuration for each system is chosen by minimizing the potential energy for the system, starting from a randomly generated configuration. This results in an initial energy that is less than the equilibrium average energy for the chosen temperature. Since the time-dependent dynamics are performed using a constant temperature molecular dynamics algorithm, the average system energy would relax to that corresponding to the equilibrium system at the chosen temperature. However, the runs performed are relatively short, and the fluctuating temperature calculated from the time-dependent average kinetic energy per particle is typically a few degrees below the desired temperature throughout the runs. This could also be contributing to the observed slowing of the dynamics. An alternative possibility is that the dynamics predicted by the force field program is reasonably accurate, that the monomers in the melt for these polar systems do largely rattle around relatively fixed positions on the relatively short time scale of the simulations, and that the motion would look Brownian on longer time scales than considered by the simulations. If this explanation is correct, the calculations presented in this work for PEO and PDMS indicate that much longer time scale simulations would be needed to evaluate the D_0 for polar systems such as these.

In conclusion, the force field calculations for the evaluation of monomer interaction diameters for PS, PE, PEO, and PDMS suggest that this LM theory parameter can be quite reasonably and easily estimated from two- or three-chain configurations, although further testing on a wider range of systems would certainly be useful. The force field molecular dynamics simulations performed for the C_{20} system in this paper, as well as other more extensive alkane melt simulations,[45] provide values for the bare monomer diffusion constant that would yield accurate long chain diffusion constant results using the LM model with no adjustable parameters. On the other hand, it was not possible to extract D_0 values for the polar PEO and PDMS systems from the very short time, short chain melt simulations considered in this work.

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