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Monte Carlo and molecular dynamics simulation of the glass transition of polymers

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Abstract. Two coarse-grained models for polymer chains in dense glass-forming polymer melts are studied by computer simulation: the bond fluctuation model on a simple cubic lattice is treated by Monte Carlo methods, and a continuum bead–spring model with a Lennard-Jones potential between the beads is treated by means of molecular dynamics. While the dynamics of the two models differ for short length scales and the associated timescales, the two models behave similarly on mesoscopic spatial and temporal scales. In particular, the mode-coupling theory of the glass transition can be used to interpret the slowing down of the undercooled polymer melt. For the off-lattice model, the approach to the critical point of mode coupling is studied both at constant pressure and constant volume. The lattice model allows a test of the Gibbs–Di Marzio entropy theory of the glass transition to be carried out, and our finding is that although the entropy does decrease significantly, there is no ‘entropy catastrophe’ where the fluid entropy would turn negative. Finally, a forward look at the effects of confinement on the glass transition in thin-film geometry is given.

1. Introduction

The glass transition from the supercooled melt to the amorphous solid is still a puzzle [1–4]. While the viscosity $\eta(T)$ increases by about 15 orders of magnitude (T_g is empirically defined by $\eta(T = T_g) = 10^{13}$ P) in a narrow temperature interval, the change in the static structure factor $S(q)$ (q is the scattering wavenumber) is rather minor; see e.g. [5]. What then is the physical basis of the phenomenon that many different systems show a nearly universal phenomenology of relaxation (e.g., the increase of the relaxation time τ or $\eta(T)$ ($\eta(T) \propto \tau$) described by the Vogel–Fulcher–Tammann (VFT) law, $\ln \tau \propto \ln \eta \propto E_{VF}/(T - T_{VF})$ [1]; relaxation functions obeying the Kohlrausch–Williams–Watts (KWW) law, $\varphi(t) \propto \exp[-(t/\tau)^\beta]$; etc [1])?

The answer to this question is controversial: e.g., there is the idea of an ‘entropy catastrophe’ static phase transition underlying the glass transition (the configurational entropy of the undercooled fluid vanishes at $T_0 < T_g$ [6], with possibly [7] $T_0 = T_{VF}$). Mode-coupling theory [2], on the other hand, yields a dynamical transition (apparently rounded [8]) from an ergodic fluid (atoms can easily escape from the cages formed by their neighbours) at a ‘critical’ temperature $T_c > T_g$ to a non-ergodic state (‘structural arrest’). Yet another concept attributes the increase of τ upon cooling to the increase of a glass correlation length [9], in analogy with spin glasses [10].

Polymer melts can be held in a very good metastable equilibrium in their supercooled state, and their glass transition temperatures occur in an experimentally convenient range;

hence a wealth of experimental data exist. Thus, it is desirable to approach these systems also by theoretical modelling via computer simulation [11]. However, due to the large size of these polymer coils (they exhibit non-trivial structure from the Å scale of covalent bonds up to the gyration radius which can be 100 Å) and the many decades of timescales spanned by the relaxation times of their motion, simulation of polymers is very difficult, and requires one to use simplified and efficient models [11]. Two such models will be defined and compared in the next section, while section 3 describes the tests of mode-coupling theory performed with these models. Section 4 briefly describes tests of other theories and also contains some concluding remarks.

2. Coarse-grained models for polymers on the lattice and in the continuum

The basic idea is to eliminate both the structural details on very small scales and the associated very fast dynamics by using a coarse graining along the polymer chemical sequence [11]: $n \approx 3\text{--}5$ successive chemical units are mapped into one effective bond, connecting two effective monomers. These effective bonds may be defined on a lattice as well as in the continuum. In the lattice case, the effective monomers are formed from all eight sites of an elementary cube on the lattice, and no site may belong to more than one monomer (excluded-volume interaction). Bond lengths in this ‘bond fluctuation model’ [11] are taken to be in the range from 2 to $\sqrt{10}$ lattice spacings, and bond vectors $\vec{b} = (\pm 3, 0, 0)$ (or permutations thereof) are taken to be in the ground state, while all other choices of the bond vector represent excited states, with an energy cost ε ($\varepsilon=1$; also $k_B \equiv 1$). This bond length potential may be thought of as representing the original atomistic intra-chain potentials in a coarse-grained way. Since this particular choice of the potential has the effect that each bond that is in the ground state blocks the four sites between its adjoining effective monomers from further occupation, it has the effect that free volume in the dense system is ‘wasted’ and a ‘geometric frustration’ is created—at high densities, not enough free volume is available that all bonds manage to get into their ground state as $T \rightarrow 0$ [12]. This model can be simulated very efficiently, and for chain lengths N as small as $N = 10$, properties typical of polymers (e.g., gyration radius $\langle R_g^2 \rangle^{1/2} \propto \sqrt{N}$) are reproduced. A density of $\phi = 0.533$ of occupied sites corresponds to a dense melt [12, 13].

The dynamics is introduced by randomly selecting a monomer of a chain and by attempting to move it by one lattice unit in a randomly chosen direction. Of course, the move is only carried out if the new position satisfies excluded-volume and bond length constraints, and the possible energy change is considered using the usual Metropolis criterion [11, 12]. It is thought that this ‘random hopping’ of effective monomers in a coarse-grained sense corresponds to the random hops of chemical bonds over barriers in the torsional potential, because by such moves pieces of a chain can rotate relative to each other, and thus are responsible for the relaxation of the chain configurations [11, 14]. If one carries out such a mapping of a realistic (i.e., atomistic) chain model on the bond fluctuation model literally, one obtains the estimate that one attempted Monte Carlo step (MCS) per monomer corresponds to 10^{-13} s, and the lattice unit corresponds to a distance of 2 Å [14]. Typically, runs are carried out for systems of $L \times L \times L$ with periodic boundary conditions and $L = 30$, averaging over 16–160 independent ‘replicas’ of the system over a time of up to 10^7 MCS. Thus, even for the time window of this coarse-grained model, we are restricted to $t \approx 1 \mu\text{s}$ (while molecular dynamics simulations of atomistic models can deal with $t < 1$ ns only). However, one important aspect is that one can equilibrate the system configurations also with artificial moves, which have no counterpart in the dynamics of real chains, such as the ‘slithering snake’ algorithm [11, 14], and thus gain several orders of magnitude in time due to faster relaxation. In this way, configurations of the

well-equilibrated melts are prepared at rather low temperatures, which serve as initial states for runs with the ‘random-hopping’ algorithm in studying the dynamics of these melts.

Alternatively, we treat a continuum model where an effective bond is represented by a (finitely extensible) spring, and the effective monomers are the beads of this bead–spring model. There is a Lennard-Jones interaction between any pair of beads cut off at a distance $r_c = 2 \times 2^{1/6}\sigma$ [15]:

$$U_{\text{LJ}}(r) = 4\varepsilon [(\sigma/r)^{12} - (\sigma/r)^6] + c \quad (1)$$

where the constant c is chosen such that $U_{\text{LJ}}(r_c) = 0$. Choosing here units of length and temperature such that $\sigma = 1$, $\varepsilon = 1$, the springs are described by

$$U(r) = -\frac{1}{2}kR_0^2 \ln [1 - (r/R_0)^2] \quad R_0 = 1.5 \quad k = 30. \quad (2)$$

While $U_{\text{LJ}}(r)$ has its preferred distance at a minimum for $r_{\text{min}} = 2^{1/6}$, the minimum of the potential between neighbouring monomers along the chain (given by the sum of equations (1) and (2)) occurs for $r_0 \approx 0.96$: although the bead–spring model is fully flexible, this incompatibility of r_0/r_{min} with any standard crystal structure prevents crystallization of our model, and thus creates the ‘frustration’ in the fluid necessary for the formation of a glass upon cooling.

This off-lattice model is simulated by NpT molecular dynamics, with the choice of chain length of $N = 10$, and altogether $M = 1200$ monomers in the system [15]. Note that the constant-pressure ensemble [16] is used for equilibration only—for a study of dynamic properties a clock is set to zero and runs are started at $T = \text{constant}$ (using a suitable Nosé–Hoover thermostat [17]), which produces a dynamical behaviour practically indistinguishable from that of the microcanonical ensemble [15].

Figure 1 shows that one obtains a structure factor $S(q)$ of the amorphous polymer melt very similar to that from experiment [5]. If one studies the volume $v(T)$ per effective monomer

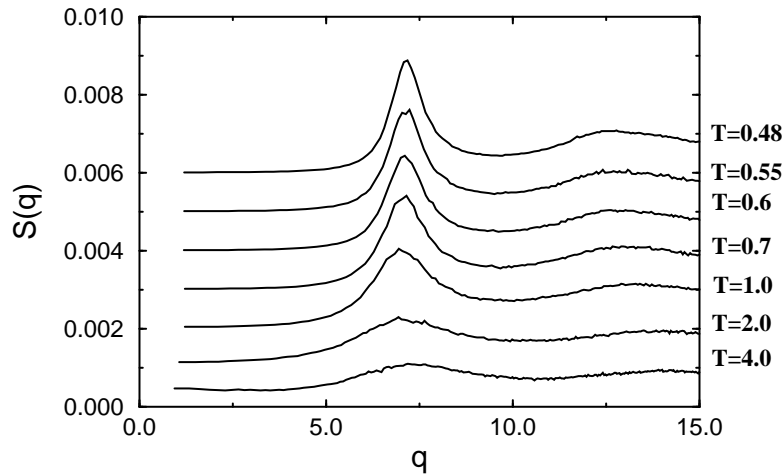


Figure 1. The structure factor $S(q)$ plotted versus wavenumber q , for a system of 120 off-lattice bead–spring chains with chain length $N = 10$, simulated in the NpT -ensemble at scaled pressure $p = 1$, with the choice of Lennard-Jones units $\varepsilon = 1$, $\sigma = 1$ (and $k_B = 1$). Note that the zero of the ordinate for each curve is shifted upward by 0.001 relative to the previous one. From Bennemann *et al* [15].

in a slow cooling run, starting at $p = 1$ from a well-equilibrated configuration at $T = 0.6$ and lowering T every 500 000 MD time steps by 0.02, one finds a rather well-defined kink at $T_g \approx 0.41$, while a fit of the self-diffusion constant to the Vogel–Fulcher law yields $T_{VF} \approx 0.33$ [18]. Thus, the model does exhibit a glass transition, as expected.

The bond fluctuation model also yields $S(q) \approx 0$ for small q due to the very small compressibility of the polymer melt, and then a broad peak similar to the ‘amorphous halo’ of figure 1 occurs, at $q \approx 3$ (in units of the lattice spacing for this model; physically this corresponds to about 1.5 \AA^{-1}) [13]. The peak position and shape also change very little with temperature. However, the second shallow and temperature-independent peak of figure 1 at still larger q , representing intra-chain correlations, is less well reproduced [13]. This is not surprising, since $q = 2\pi$ corresponds in real space to one lattice unit. A further disadvantage of the lattice model is that one can study the glass transition only at constant volume, while in the off-lattice model both constant-volume and constant-pressure studies were performed [18].

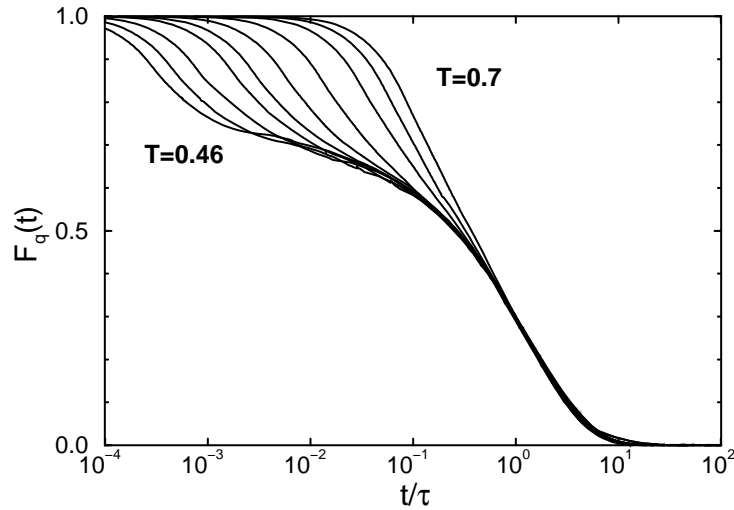


Figure 2. The dynamic structure factor $F_q(t)$ of the off-lattice model at scaled pressure $p = 1$ plotted versus a rescaled time t/τ_q (where τ_q is defined from $F_q(t = \tau_q) = 0.3$) for $q = 6.9$, the peak position of the static structure factor at low T (cf. figure 1). Only temperatures in the range $0.46 \leq T \leq 0.7$ are included, as indicated. From Bennemann *et al* [15].

3. Testing the mode-coupling theory (MCT) of the glass transition

Figure 2 shows the intermediate incoherent dynamic structure factor $F_q(t)$, defined as

$$F_q(t) = \frac{1}{M} \sum_{i=1}^M \langle \exp\{i\vec{q} \cdot [\vec{r}_i(t) - \vec{r}_i(0)]\} \rangle \quad (3)$$

where the sum is over all M monomers in the system (which are at the positions $\vec{r}_i(t)$ at time t). Pronounced two-step relaxation is seen; the second step (‘ α -relaxation’) satisfies the time–temperature superposition principle, while the first step (‘ β -relaxation’) does not [15]. The relaxation time τ_q is compatible both with the Vogel–Fulcher law with $T_{VF} \approx 0.33$ and

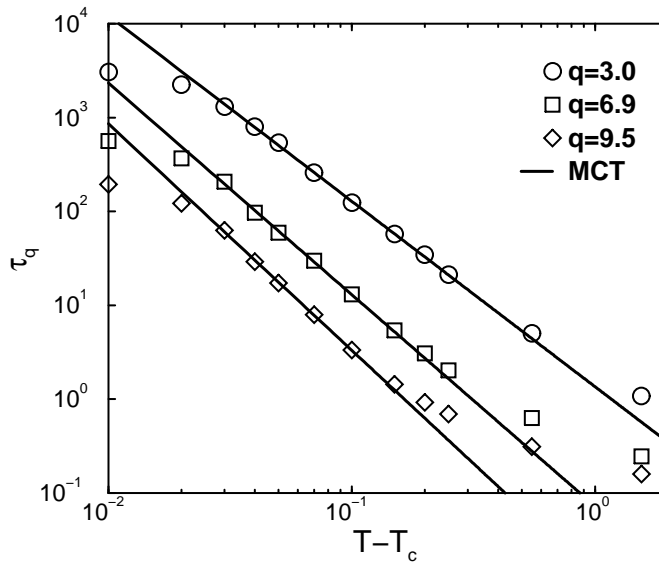


Figure 3. A log–log plot of the relaxation time τ_q versus $T - T_c$ with $T_c = 0.45$, for a pressure $p = 1$ and three values of q . The straight lines indicate the power laws $\tau_q \propto (T - T_c)^{-\gamma_q}$ with exponents $\gamma_q = 2.3, 2.1$ and 2.0 (from top to bottom). From Bennemann *et al* [18].

with a power law (figure 3), but with a q -dependent exponent γ_q [18]. While the consistency with a power law is evidence in favour of MCT [2], the q -dependence of the exponent γ_q is evidence against it. In addition, one sees that the data deviate from the power law both for $T/T_c - 1 \gtrsim 0.4$ (as expected, since this is not the asymptotic region) and for $T/T_c - 1 \lesssim 0.04$ (which can be attributed to ‘hopping processes’ by which effective monomers can escape from the cage formed by their neighbours; it is possible that an extended version of the theory [8] could describe the rounding of the ergodic–non-ergodic transition). Thus, the observability of the idealized MCT [2] is restricted to about one decade in $T/T_c - 1$, showing the limitations of this theory when applied to polymers [15, 18, 19].

In the α -regime, $F_q(t)$ can be fitted to the KWW law with an exponent β_q that is also weakly q -dependent ($\beta_q = 0.70 \pm 0.08$ for $q = 6.9$ [15]; for a detailed analysis of this q -dependence, see reference [19]). The predictions of MCT for the β -regime can also be tested in detail, and they compare rather favourably with those from MCT [19], although the same caveat over the restricted ‘temperature window’ where MCT is applicable again applies.

This analysis can be repeated for several pressures and thus one can trace out a ‘critical line’ $T_c(p)$ in the (T, p) plane separating the high-temperature state of the melt above T_c from the low-temperature state below T_c (figure 4). By carrying out simulations at constant pressure and at constant density, which lead to the same point $(T_c(p), p)$ on the line, one finds that $\tau_q \propto (T - T_c)^{-\gamma_q}$ does indeed hold with the same T_c and the same γ_q for both paths in the (T, p) plane. This underscores the physical significance of the MCT critical line.

Also the bond fluctuation model has been compared to MCT, both in its idealized [20] and in its extended [21] version. While a fit of various relaxation times and of the self-diffusion constant to the VFT law is nicely compatible with the data and yields $T_{VF} \approx 0.125 \pm 0.005$ [22], the MCT fits both [20, 21] yield $T_c \approx 0.15$, and power-law behaviour occurs over a similar temperature interval to that for the continuum model. One characteristic difference

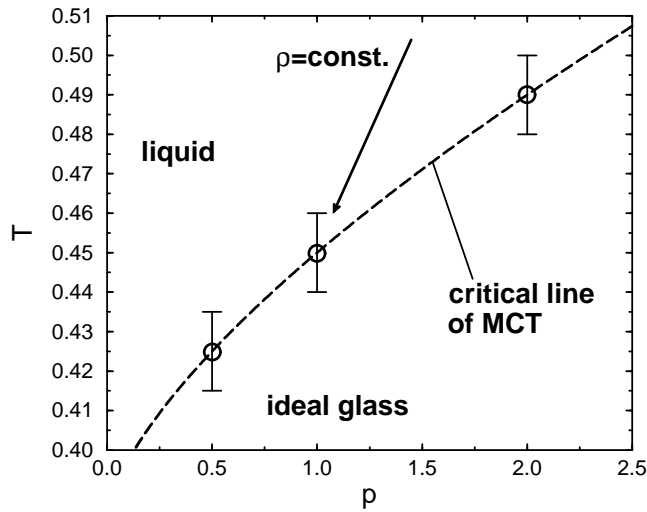


Figure 4. The critical line $T_c(p)$ in the (T, p) plane, for the off-lattice bead-spring model. In idealized MCT, the low-temperature state below T_c would be a frozen phase, a kind of ‘ideal glass’. In reality, this phase is still fluid, but the dynamics is dominated by different relaxation mechanisms (so-called ‘hopping processes’) compared to those for $T > T_c$. From Bennemann *et al* [18].

between the two models concerns the β -relaxation regime. While in the off-lattice model the first decay of the structure factor $F_q(t)$ (figure 2) is due to small-amplitude motions (over distances of the order of 10% of the distances between effective monomers and their nearest neighbours), no such small-scale motion is possible in the bond fluctuation model: either a monomer hops a lattice unit, or it cannot hop at all. This distinction also shows up when we compare the time dependence of the scaled mean square displacements of monomers for the two models (figure 5). Both the lattice model and the continuum model are thought to correspond essentially to the same physical system, a dense melt of short polymers, on a coarse-grained level. This implies that on mesoscopic scales (length scales of the order of the distance between effective monomers or larger) these different coarse-grained models should yield very similar results. On comparing suitably scaled data, this is indeed found to be the case (figure 3). Note that the regime where MCT is applicable corresponds to displacements smaller than the distances between monomers, and that the dynamics is Rouse-like at larger scales.

4. Comments on other theoretical concepts and some concluding remarks

A particular advantage of the lattice model is that the slithering snake algorithm allows us to obtain equilibrium properties of the model at fairly low temperatures, and the configurational entropy $S(T)$ can also be computed [23] and compared to the Gibbs–Di Marzio theory [6]. Indeed, one finds that $S(T)$ decreases to about a third of its high-temperature value $S(\infty)$ as T approaches T_g , but the curve $S(T)$ versus T near T_g bends and apparently saturates at a non-zero value at lower temperatures. Conversely, if one extracts the quantities that are used in the theory [6] directly from the simulation and inserts them into the (approximate!) theoretical formula [6, 23], one finds an ‘entropy catastrophe’ ($S(T)$ becoming negative) at $T \lesssim 0.18$. This unphysical result, however, is easily traced back to the underestimation of

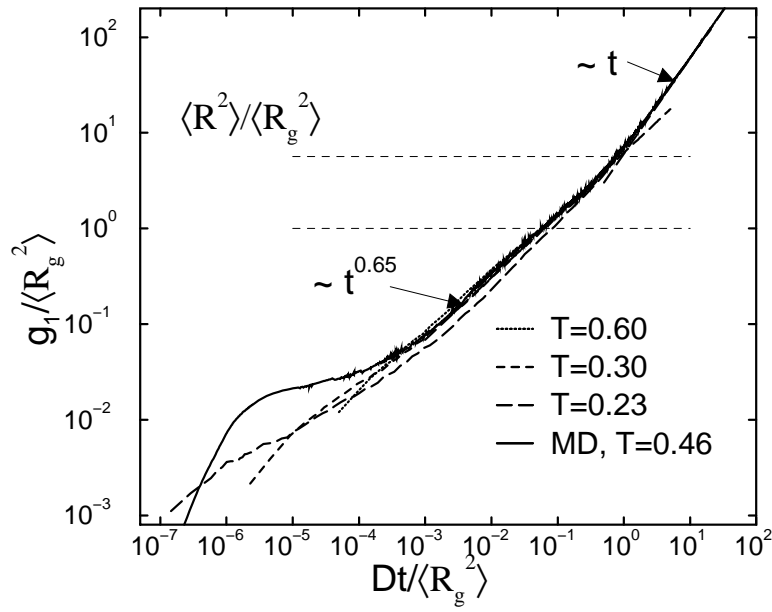


Figure 5. Comparison of the mean square displacement $g_1(t) (\equiv \langle [\vec{r}_i(t) - \vec{r}_i(0)]^2 \rangle)$ of inner monomers plotted versus scaled time ($Dt / \langle R_g^2 \rangle$, D being the self-diffusion constant and $\langle R_g^2 \rangle$ the mean square gyration radius of the chains) for the off-lattice model (the curve marked MD) with the corresponding Monte Carlo results for the bond fluctuation model at three temperatures.

$S(\infty)$ by the mean-field calculations of Gibbs and Di Marzio [6]. The ‘entropy catastrophe’ [6] is then an artefact of this mean-field theory, and one should not attribute physical significance to it. In such a manner, simulations can go beyond experiment in testing theories, because the theoretical input parameters can be unambiguously extracted from the simulation. Comparison between theory and simulation is possible without adjustable parameters.

However, it is interesting to note that the Adam–Gibbs equation [7], $D/D_0 \propto \exp\{-E_{\text{act}}/TS(T)\}$, where D_0 is the self-diffusion constant at very high temperatures and E_{act} some activation energy, provides a very good description of the diffusion constants found in the simulation when one uses also the $S(T)$ found in the simulation (figure 6). At the same time, the absence of any finite-size effect in figure 6 is at odds with the idea of attributing the slowing down implied by the decrease of $D(T)$ to an increasing glass correlation length $\xi(T)$ [9], via $\tau(T) \propto [\xi(T)]^z$ with z a dynamic exponent [10]: if such a hypothesis held, one would expect a reduction of the linear dimension, L , of the simulation box to decrease $\xi(T)$ (since $\xi(T) \leq L$) and hence $\tau(T)$, and in turn $D(T)$ should increase with decreasing L . Figure 6 proves the absence of such finite-size effects, contrary to the behaviour in two spatial dimensions [24]. This finding is surprising, since a growing static length can be extracted both from the pair correlation function in the melt [25] and from surface effects near hard walls [26]. It hence appears that there is a growing length identified in [25, 26], but that it is not responsible for the slowing down close to T_g (at least in three dimensions). Of course, there is no contradiction with experimental results which find that T_g for thin films (or pores) changes when the linear dimension of the film (or pore, respectively) is varied: depending on the boundary conditions at the surface, the local mobility of monomers in the surface region changes, and this effect is the more pronounced on freezing the smaller the linear dimension.

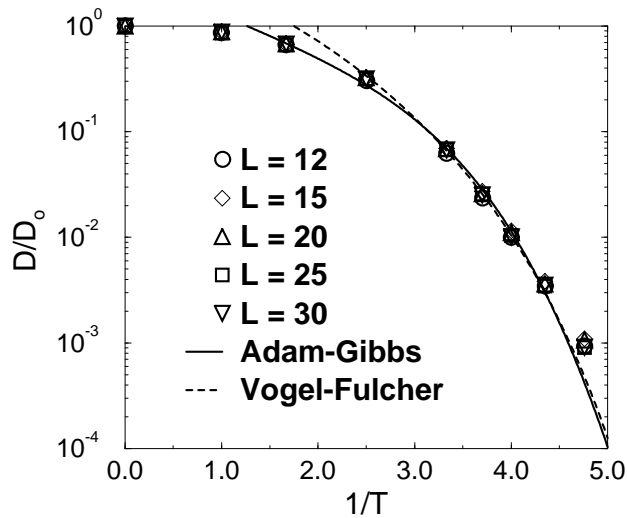


Figure 6. The self-diffusion constant of the bond fluctuation model plotted versus inverse temperature, for $L \times L \times L$ lattices with periodic boundary conditions and several lattice sizes L . The solid and the broken curves are fits to the Vogel–Fulcher and Adam–Gibbs equations, respectively. Data taken from Binder *et al* [25].

No such surface effect is present with the periodic boundary conditions of figure 6, of course. In experiments on the glass transition in confined systems, finite-size effects and surface effects can never be clearly separated, unlike in simulations where one can show that there is no finite-size effect (figure 6) at least in the temperature region studied here, although surface effects do exist [26].

Returning to MCT, we emphasize that idealized MCT does provide a good description of a large number of simulation data, but only over a rather restricted range of temperatures (about one decade in $T/T_c - 1$) and corresponding times (or viscosities: typically the range $10^0 < \eta(T) < 10^2$ P if $\eta(T_c) = 10^3$ P: the huge range from $10^3 \leq \eta \leq 10^{13}$ P is outside the scope of the theory). Correspondingly, only a small intermediate regime of small monomer displacements in figure 5 is described—neither the initial increase that depends on the microscopic properties of the model, nor the regime of hopping processes that lead to a Rouse-like relaxation of coil configurations (before ultimately ordinary diffusion sets in) are covered by the theory. Since there occur smooth crossovers between the various regimes, a reliable assessment of the validity of MCT for polymer melts near T_g is difficult. A more complete theory (that unifies e.g. MCT and the Rouse model) would be very welcome.

Acknowledgments

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