Cooling rate dependence of the glass transition temperature of polymer melts: Molecular dynamics study

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A coarse-grained bead spring model of short polymer chains is studied by constant pressure molecular dynamics (MD) simulations. Due to two competing length scales for the length of effective bonds and the energetically preferred distance between nonbonded beads, one observes a glass transition when dense melts are cooled down (as shown in previous work, at a pressure \( p = 1 \) the mode coupling critical temperature is at \( T_c \approx 0.45 \) and the Vogel–Fulcher temperature is \( T_0 \approx 0.33 \), in Lennard-Jones units). The present work extends these studies, estimating a cooling-rate-dependent glass transition temperature \( T_g(\Gamma) \) by cooling the model system from \( T = 0.6 \) down to \( T = 0.3 \), applying cooling rates from \( \Gamma \approx 10^{-3} \) to \( \Gamma \approx 10^{-6} \) (in MD time units), and attempting to identify \( T_g(\Gamma) \) from a kink in the volume versus temperature or potential energy versus temperature curves. It is found that \( T_g(\Gamma) \) lies in the range \( 0.43 < T_g(\Gamma) < 0.47 \), for the cooling rates quoted, and the variation of \( T_g(\Gamma) \) for \( \Gamma \) is compatible with the expected logarithmic variations. We will show why a detailed distinction between competing theories on these cooling rate effects would need an excessive amount of computer time. To estimate also the melting transition temperature \( T_m \) of this model, the system was prepared in a crystalline configuration as an initial state and heated up. The onset of diffusion, accompanied by an isotropization of the pressure tensor was observed for \( T_m \approx 0.77 \). This implies that the model is suitable for studying deeply supercooled melts. © 2002 American Institute of Physics. [DOI: 10.1063/1.1508366]

I. INTRODUCTION

Understanding the glass transition of undercooled fluids has been a long-standing challenge.\(^1\)–\(^7\) In particular, general agreement on the cause of the dramatic slowing down of structural relaxation in glass-forming fluids is still lacking: in particular, in "fragile" glassformers,\(^8\) such as polymer melts, the structural relaxation time \( \tau \) increases by about 15 orders of magnitude in a relatively narrow temperature interval above the glass transition temperature \( T_g \), while the static structure—in as much as it is revealed by static scattering of x rays or neutrons—changes only very little.\(^1\)–\(^8\) In view of these problems, it is tempting to apply molecular dynamics (MD) simulation methods\(^9\)–\(^14\) to study the glass transition behavior of suitable model systems, since these computer simulation methods allow us to give much more detailed information on both structure and dynamics than any experiment on real materials: in the computer experiments, full information on the trajectories of all the particles is accessible.

However, one must pay attention to the fact that for any chemically realistic model of a material, the integration time step \( \delta t \) of the MD technique must be chosen, typically, as small as \( \delta t = 1 \) fs = \( 10^{-15} \) s, and thus even very long runs (of the order of \( 10^7 \) or \( 10^8 \) time steps) hardly exceed a time interval of \( 10-100 \) ns. It is not really clear that on such short time scales the physical mechanisms of the glass transition can already emerge fully. For example, the "glass transition" that was claimed to be seen in an atomistic model for poly-

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Jones (LJ) mixture, a schematic model system for fragile glass formers,\textsuperscript{20} has revealed distinct cooling rate effects on the time scales accessible for MD simulations.\textsuperscript{21} While polymer melts are model systems for the study of the glass transition,\textsuperscript{1–8} and also of great technological importance,\textsuperscript{2–6} we are not aware of any previous work addressing the cooling rate dependence of $T_g$ (MD) for polymers (one Monte Carlo study of the bond fluctuation model\textsuperscript{22} did address this problem, but it is clear that the translation of the Monte Carlo time step into a physical time is a delicate matter.\textsuperscript{7,11,23} and the Monte Carlo method cannot fully describe the short-time dynamics of particles confined by cages formed by their neighbors, but only the later stages of glassy relaxation\textsuperscript{7}).

Thus, the present work is intended to fill this gap, using the same coarse-grained bead spring model of polymers\textsuperscript{24} that has been used before so successfully for a test of mode coupling theory,\textsuperscript{24–26} for analysis of the relation between glassy dynamics and the behavior of the Rouse modes\textsuperscript{27} for a study of dynamical heterogeneity and growing dynamic correlations,\textsuperscript{28} for analyzing the effect of confinement on the glass transition,\textsuperscript{29–31} etc. In Sec. II, we briefly summarize the main theoretical predictions on the cooling rate dependence of $T_g$, and their problems. Section III recalls the model that is treated and briefly comments on the simulation technique, while Sec. IV presents our main results. Section V gives results on a complementary problem, namely, the estimation of the melting/crystallization temperature $T_m$ of our model: this is done by preparing a guessed initial crystallization state and heating it up until significant onset of diffusive motions is found. Finally, Sec. VI summarizes a few conclusions.

II. THEORETICAL CONCEPTS ON THE COOLING RATE DEPENDENCE OF THE GLASS TRANSITION TEMPERATURE: BRIEF REVIEW

Let us assume that the fluid is kept at a temperature $T_i$ which is sufficiently high (e.g., near the melting temperature $T_m$ of the crystal), where the structural relaxation time $\tau$ is very small, and thus the fluid is in thermal equilibrium. Then, at a time $t=0$ the temperature is reduced to a temperature $T_f<T_g$ in a time $t_f$, either linear in time

$$T(t) = T_i - \Gamma t, \quad t \leq t_f, \quad \Gamma = (T_i - T_f)/t_f,$$

or by a stepwise cooling in $n$ small steps $\Delta T$ of duration $\Delta t$ such that $n \Delta T = T_i - T_f$ [Figs. 1(a) and 1(b)]. Then one may define the cooling rate $\Gamma = \Delta T/\Delta t$. One assumes that both case (a) and (b) in Fig. 1 lead to a similar physical behavior, as long as $n \gg 1$, and also it is required that the temperatures $T_i, T_f$ are sufficiently close to each other such that quantities like the volume $V$ (at constant external pressure and particle number $N$) of the fluid (or its enthalpy $H$) vary essentially linear with temperature in the chosen interval [as long as the fluid stays in metastable equilibrium: when the system falls out of equilibrium and freezes into the glass, a pronounced deviation from linearity occurs, as indicated in Fig. 1(c)]. Cooling-rate-dependent glass transition temperatures $T_g(\Gamma)$ can then be defined in terms of the intersection point between the straight line fitted to the (common) fluid branch and the straight line fitted to the solid branch [note that the volume $V(T_f)$ of the amorphous solid at $T_f$ does depend on the cooling history, and it is a controversial issue whether or not a meaningful limit $V_{\text{ideal glass}}(T_f) = \lim_{T \to 0} V(T_f)$ distinct from the fluid volume $V_{\text{fluid}}(T_f)$ exists].

Now one concept frequently invoked to explain the behavior as sketched in Fig. 1(c), is to say that the undercooled fluid falls out of equilibrium when the characteristic time $t_{\text{exp}}$ associated with the slow cooling process [Figs. 1(a) and 1(b)] becomes equal to the structural relaxation time $\tau$. As-
assuming a Vogel–Fulcher–Tammann\(^1\text{–}^7,32\) relation for the latter,
\[ \tau(T) = \tau_\infty \exp\left[\frac{E_A}{(T-T_0)}\right], \]
where \(\tau_\infty\), \(E_A\) are constants, and \(T_0\) is the Vogel–Fulcher–Tammann temperature, where formally \(\tau(T)\) would diverge, the equality \(\tau(T_\infty) = t_\exp\) yields
\[ T_g = T_0 + E_A / \ln(t_\exp / \tau_\infty). \]

However, the problem now is to clarify the precise relation between the time constant \(t_\exp\) characterizing the experiment, and the cooling rate \(\Gamma\). If we take \(t_\exp = t_f\), this implies [Eq. (1)] \(t_\exp = (T_i - T_f) / \Gamma\), and hence,
\[ T_g = T_0 - E_A / \ln(\Gamma \tau_\infty / (T_i - T_f)), \]
while if we take \(t_\exp = \Delta t = \Delta T / \Gamma\) [Fig. 1(b)], we instead obtain
\[ T_g = T_0 - E_A / \ln(\Gamma \tau_\infty / \Delta T). \]

While both expressions agree in predicting that there should be a relation \(T_g = T_0 \propto 1 / \ln \Gamma\), the appearance of temperature intervals, which reflect a somewhat arbitrary choice \((T_i - T_f)\) or \(\Delta T\), respectively, is somewhat disturbing. However, since \(\Gamma\) has the dimension [temperature/time], the argument in the logarithm necessarily must involve a temperature, in order that a dimensionless argument of the logarithm can be obtained. Of course, also Eq. (2) and the constants \(\tau_\infty\), \(E_A\) appearing there are of an empirical character, and if one wishes to use Eq. (4) or (5) to describe measured data, one can use \(\tau_\infty / \Delta T\) or \(\tau_\infty / (T_i - T_f)\) as an effective fit parameter. In this spirit, Eq. (4) or (5) has been used successfully.\(^{19}\)

A physically more reasonable but also more complicated procedure due to Narayanaswamy\(^{33}\) invokes the principle of “thermoreologial simplicity,” which implies that the fictive temperatures \(T^* (T_1)\) and \(T^* (T_2)\) of two cooling processes with different cooling rates can be related to each other by special shifting procedures. For details, we refer the interested reader to the original publication;\(^{33}\) the final result for the shift of the glass transition temperature is a linear relation with the cooling rate \(\Gamma\):
\[ \Delta T_g \propto \ln(\Gamma \tau_\infty / (T_i - T_f)) + \text{const}. \]

Unlike Eqs. (3)–(5) by this treatment no specific Vogel–Fulcher–Tammann form [Eq. (2)] is invoked here, and this may seem an advantage, since Eq. (2) is rather questionable. On the other hand, Eq. (6) cannot hold for an arbitrarily wide range of cooling rates \(\Gamma\), since \(\ln(\Gamma) \rightarrow -\infty\) for \(\Gamma \rightarrow 0\). In contrast, Eqs. (4) and (5) have built in that \(T_g(\Gamma) \rightarrow T_0\) in this limit.

It is clear that for a precise description of the volume or enthalpy relaxation during cooling processes of the type described by Figs. 1(a) and 1(b), a rather complete understanding of the slow relaxation phenomena near the glass transition is needed: even if one considers small deviations from (metastable) equilibrium only, this is a formidable problem.\(^{1–7,16,20}\) For the nonlinear processes occurring during cooling, the problem of finding a compelling theoretical framework is even more complicated. However, in the context of experiments or computer simulations the question to obtain \(T_g(\Gamma)\) from procedures such as shown in Fig. 1(c) is perfectly well defined in an operational sense. Thus, we shall take the predictions \(T_g \propto \text{const} + 1 / \ln \Gamma\) or \(T_g \propto \text{const} + \ln \Gamma\) only as heuristic working hypothesis to analyze our simulation data.

### III. MODEL AND SIMULATION TECHNIQUE

While various attempts to simulate the glass transition of atomistically realistic models of polymer chains, which include bond angle potentials between subsequent C–C bonds as well as torsional potentials, have appeared in the literature (e.g., Refs. 15 and 34–36), such calculations are too time consuming to allow simulations of several cooling rates over a sufficiently wide range of cooling rates, and hence, these studies could not investigate the problem addressed in the present paper. However, noting that the glass transition of polymer melts is a fairly universal phenomenon and polymers with rather disparate chemical structure show qualitatively very similar behavior, there is no need to account for full chemical detail, as long as we disregard problems such as prediction of \(T_g\) for specific materials. Thus, only generic features of polymers need to be kept: it is enough to treat a polymer as a flexible chain molecule where many subunits are linked together, and the interactions need to be chosen such that easy crystal formation is prevented. In fact, short chains with only \(N = 10\) subunits display already very well the Gaussian statistics of the end-to-end distance\(^{24}\) which is one of the hallmarks of polymers in the dense melt,\(^{37}\) and relax sufficiently fast at temperatures far above \(T_g\), so that the times \(\Delta t\) of our stepwise cooling procedure [Fig. 1(b)] can easily be chosen much larger than the Rouse time \(\tau_R\) of the chains\(^{37,38}\) at \(T_j\), at least in the case of our lowest cooling rates (since we vary \(\Gamma\) over three decades, for the highest cooling rates \(\tau_R\) and \(\Delta t\) are comparable).

All subunits (called “effective monomers” in the following) of the chains interact with each other with a shifted and truncated LJ potential,
\[ U_{LJ}(r) = 4 \epsilon \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 + c, \quad r \leq r_c = 2 r_{\text{min}}. \]
where \(r_{\text{min}}\) denotes the distance \(r\) where \(U_{LJ}(r)\) has its minimum (Fig. 2), \(r_{\text{min}} = 2.18 \sigma\), and the constant \(C = 0.00775\) is chosen such that \(U_{LJ}(r = r_c) = 0\). For distances larger than the cutoff distance, \(U_{LJ} = 0\). Henceforth, all distances shall be measured in units of \(\sigma\), temperatures in units of \(\epsilon / k_B\), and times in units of \((m \sigma^2 / \epsilon)^{1/2}\), where \(m\) is the mass of the effective monomers. In the following, we choose \(k_B = 1\), and \(m = 1\) as well.

Furthermore, nearest-neighbor effective monomers along the backbone of a chain are bonded to each other by a finitely extensible nonlinear elastic (FENE) potential,\(^{39}\)
\[ U_F(r) = \frac{1}{2} k R_0^2 \ln\left[1 - \left(r / R_0\right)^2\right], \quad R_0 = 1.5, \quad k = 30. \]

With the parameters chosen, the superposition of the FENE and LJ potentials leads to a steep effective bond potential with a minimum at about \(r = 0.96\) (Fig. 2).\(^{40}\)

The length scale, which is energetically preferred by the effective bond potential, thus clearly is incompatible with the length scale preferred by the LJ potential \((r_{\text{min}} \approx 1.13)\), as far as simple crystal structures of the effective monomers (face-
centered cubic, body-centered cubic, etc.) are concerned. Of course, the polymer melt should still be able to crystallize, if the chains all stretch out linearly (forming straight lines or a kind of zig-zag arrangement) and then are all packed together in a parallel stacking that minimizes the interchain Lennard-Jones energies. However, a liquid–solid transition from the melt to such a crystal structure is kinetically very difficult, the polymer melt should still be able to crystallize, if there is no energetic tendency in favor of local chain stretching in this model. Thus, the incompatibility between the two types of short-range forces in the model renders formation of a regular crystalline structure unlikely.

The simulation technique used in the present work is molecular dynamics in the constant temperature–constant pressure ensemble, using Nosé–Hoover thermostats and Anderson–Hoover barostats. The microcanonical Newtonian equations of motion are extended by additional variables describing the coupling to a thermostat of ''mass'' \( Q \) and \( \eta \) describing the coupling to a barostat of ''mass'' \( M_\eta \).

\[
\begin{align*}
\dot{r}_i &= p_i/m_i + \eta (r_i - R_{CM}) \\
\dot{R}_{CM} &= \sum_j m_j r_j / \sum m_j, \\
\dot{p}_i &= -\partial U(r_i)/\partial r_i - (\eta + \xi) p_i, \\
\dot{\xi} &= \sum_j p_j^2 m_j / (3N + 1) k_B T / Q.
\end{align*}
\]

(9) \hspace{10cm} (10) \hspace{10cm} (11)

Here, \( U \) is the total potential energy and \( V \) the volume of the system, \( p(t) \) the actual pressure, and \( P_{ext} \) the given external pressure. Note that the volume is scaled isotropically so that we are always working with a cubic simulation cell. For the present size of the system (120 chains of length \( N = 10 \)), a total number \( N_{tot} = 1200 \) monomers) a choice of \( Q \) on the order of \( Q_{opt} = 6Nk_B T/\omega_{intrinsic}^2 \) is advantageous, as shown by extensive tests, where \( \omega_{intrinsic} \) is of the scale of the Einstein frequency of the system. We choose to work at \( Q = 1 \) in reduced units. However, it turns out that the proper choice of the barostat ''mass'' \( M_\eta \) is more problematic. Rewriting \( M_\eta \) as follows:

\[
M_\eta = (3N_{tot} V^{2/3})/(\pi q_\omega^2),
\]

(14) \hspace{10cm}

\( M_\eta \) is related to a dimensionless parameter \( q_\omega \) (roughly speaking, \( q_\omega \) can be interpreted as the ratio of the frequency of simulation box volume oscillations and the frequency of sound waves at the corresponding wavelength \( V^{1/3} \)), which was also set equal to \( q_\omega = 1 \). While this choice gave good results for temperatures \( T \geq 0.3 \), it turned out that for \( T < 0.3 \) huge volume oscillations did occur. When one takes much smaller values of \( q_\omega \) (e.g., \( q_\omega = 0.1 \)), these oscillations are reduced in amplitude, but become particularly regular and long lived; therefore, there is a great danger of systematic errors in data for \( T < 0.3 \), and we have decided not to include them in our analysis for this reason. While Eqs. (9)–(13) are formally valid, leading in principle to the desired \( (NpT) \) ensemble, the choice of optimal values for \( M_\eta \) is an unsolved problem. Note that for \( T < 0.3 \) for the time scales of interest for MD the model system is a nonrelaxing amorphous solid, which carries out vibrations that are at best weakly anharmonic. However, the restriction that only the range \( T > 0.3 \) is accessible should not be taken as a serious restriction, since previous work has yielded \( T_0 \approx 0.34 \) as an estimate for the Vogel–Fulcher–Tammann temperature, which is a lower bound for \( T_e(\Gamma) \), while the critical temperature \( T_c \) of mode coupling theory, \( T_c \approx 0.45 \), is an upper bound. Thus, one expects that the studied temperature range \( 0.3 \leq T \leq 0.6 \) brackets the temperature \( T_e(\Gamma) \), where \( V(T) \) shows a rounded kink [Fig. 1(c)], and the numerical results confirm this expectation (see the next section).

As to the cooling rate dependence, a stepwise cooling in steps of \( \Delta T = 0.02 \) starting from \( T_i = 0.6 \) downward was carried out, using nine cooling rates \( \Gamma = \Delta T/\Delta t \) defined from \( \Delta t = 8000 \), 16 000, . . . , 204 800 MD time steps [one MD time step corresponds to \( 3 \times 10^{-3} \tau_0 \)] with \( \tau_0 = (m v^2 / e)^{1/2} \). Faster cooling rates with \( \Delta t = 2000 \) and \( \Delta t = 4000 \) were also tried, but discarded since the data showed insufficient equilibration, already in the temperature region \( 0.46 \leq T \leq 0.56 \). It is of interest to estimate which cooling rates of a real polymer melt these computer experiments would correspond to. Estimating very roughly that \( T = 1 \) corresponds to 500 K, \( \Delta T = 10 \) K, and \( \tau_0 \approx 10^{-11} \) s, so the slowest cooling rate would correspond to \( \Delta t = 6000 \tau_0 \approx 10^{-7} \) s, i.e., \( \Gamma \approx 10^8 \) K/s.

Thus, this cooling procedure is about four orders of magni-

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**FIG. 2.** Effective bond potential (broken curve) and LJ potential (full curve) plotted vs distance between effective monomers. The bond potential results from a superposition of the LJ and FENE potentials [Eqs. (7), (8)] and was shifted by \( -20 \) to put it on the same scale as the LJ potential. The minimum position of the bond potential \( \approx 0.96 \) is smaller than that of the LJ potential \( \approx 1.13 \). This incompatibility prevents the formation of a regular crystalline structure (see Ref. 40).
still many orders of magnitude faster than real experiments.

IV. NUMERICAL RESULTS FOR THE COOLING RATE DEPENDENCE

In order to obtain data with a reasonable statistical accuracy, one needs to average for each cooling rate a large number of equivalent, statistically independent, runs. We have employed 55 runs for each of the different choices for $\Gamma$ is a set of parallel lines, the error resulting for $T_g(\Gamma)$ is greatly reduced by preventing any statistical scatter of the slopes $a_{G}(\Gamma)$ by the above assumption of a $\Gamma$-independent expansion coefficient $\sigma_{G}$. The resulting estimates for $a_{G}(\Gamma)$, $T_g(\Gamma)$, and the standard deviations $\sigma$ of $a_{G}(\Gamma)$ and of $T_g(\Gamma)$ are collected in Table I, together with corresponding data for the Lennard-Jones part of the potential energy.

![Figure 3](https://example.com/figure3.png)

**TABLE I.** Results of straight line fits for volume and Lennard-Jones energy $E^{(1J)}(T)$.

<table>
<thead>
<tr>
<th>$\Delta t$ (in MD time steps)</th>
<th>$a_{G}(\Gamma)$</th>
<th>$\sigma_{\sigma}$</th>
<th>$T_g(\Gamma)$</th>
<th>$\sigma_{\sigma_T}$</th>
<th>$b_{G}(\Gamma)$</th>
<th>$\sigma_{\sigma}$</th>
<th>$T_g(\Gamma)$</th>
<th>$\sigma_{T_g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8000</td>
<td>6.984 27</td>
<td>0.000 24</td>
<td>0.4684</td>
<td>0.0021</td>
<td>-24.394.6</td>
<td>3.8</td>
<td>0.467</td>
<td>0.0003</td>
</tr>
<tr>
<td>16000</td>
<td>6.984 19</td>
<td>0.000 24</td>
<td>0.4676</td>
<td>0.0021</td>
<td>-24.409.0</td>
<td>3.5</td>
<td>0.454</td>
<td>0.0005</td>
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<tr>
<td>32000</td>
<td>6.983 55</td>
<td>0.000 25</td>
<td>0.4619</td>
<td>0.0022</td>
<td>-24.417.8</td>
<td>3.5</td>
<td>0.446</td>
<td>0.0005</td>
</tr>
<tr>
<td>64000</td>
<td>6.983 10</td>
<td>0.000 24</td>
<td>0.4579</td>
<td>0.0021</td>
<td>-24.426.0</td>
<td>3.7</td>
<td>0.438</td>
<td>0.0005</td>
</tr>
<tr>
<td>128000</td>
<td>6.982 51</td>
<td>0.000 25</td>
<td>0.4527</td>
<td>0.0023</td>
<td>-24.433.9</td>
<td>3.5</td>
<td>0.431</td>
<td>0.0005</td>
</tr>
<tr>
<td>256000</td>
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<td>0.433</td>
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</tr>
<tr>
<td>512000</td>
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<td>0.0023</td>
<td>-24.431.5</td>
<td>4.0</td>
<td>0.433</td>
<td>0.0004</td>
</tr>
<tr>
<td>1024000</td>
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<td>0.000 28</td>
<td>0.4364</td>
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<td>-24.435.6</td>
<td>4.0</td>
<td>0.429</td>
<td>0.0004</td>
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<tr>
<td>2048000</td>
<td>6.980 27</td>
<td>0.000 28</td>
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<td>0.0025</td>
<td>-24.435.9</td>
<td>3.9</td>
<td>0.429</td>
<td>0.0004</td>
</tr>
</tbody>
</table>
E^{(LJ)}(T). Note that in the error of $T_g^{(LJ)}(\Gamma)$ we do not include systematic errors resulting from the error of the parameters $a_{\alpha}$, $a_{\beta}$, and $a_{\gamma}$, since these errors are the same for all values of $\Gamma$; they will, therefore, not influence the functional form of $T_g^{(LJ)}(\Gamma)$ although they add to the uncertainty in the determination of $T_g^{(LJ)}(\Gamma)$. Only the errors of $a_{\alpha}(\Gamma)$ are considered as a source of the errors for $T_g^{(LJ)}(\Gamma)$, as shown in Fig. 4. For $E^{(LJ)}(T)$, the parameters $b_{\alpha}$, $c_{\alpha}$, $b_{\beta}(\Gamma)$, and $c_{\beta}$ are defined from [note that $E^{(LJ)}(T)$ is a total energy, not normalized per monomer]

$$E_{\alpha}^{(LJ)}(T) = b_{\alpha} + c_{\alpha}T, \quad b_{\alpha} = -24910.5 \pm 25.4, $$

$$c_{\alpha} = 2232.9 \pm 46.5, $$

$$E_{\beta}^{(LJ)}(T) = b_{\beta}(\Gamma) + c_{\beta}T, \quad c_{\beta} = 1127.1 \pm 43.4. $$

From Table I and Fig. 4 it is obvious that the estimates for $T_g^{(LJ)}(\Gamma)$ obtained from $\ln V(T)$ and from $E^{(LJ)}(T)$ are only roughly in agreement with each other, but not strictly identical. However, such differences are expected: the relaxation times of volume fluctuations, and of energy fluctuations are not identical, of course, and thus it is no surprise that the process of falling out of equilibrium is felt somewhat differently in these quantities. More disturbing, however, is the fact that the plots in Fig. 4 are not very well describable by the straight lines [expected from Eq. (5)]. If one plots $T_g^{(LJ)}(\Gamma)$ vs $\ln \Gamma$, motivated by Eq. (6), one does not find very good straight lines either. It is clear that data at significantly smaller values of $\Gamma$ are indispensable to reach a clear distinction between Eqs. (5) and (6), but due to the enormous computational effort (the present study needed two years CPU time on a single Pentium III 800 MHz processor) such data will not become available in the near future. If, we nevertheless, try to fit a relation $T_g^{(LJ)}(\Gamma) = T_0 - E_A^{(LJ)}/\ln(\Gamma/T_0)$ to the data of Fig. 4, the quality of the data does not allow a meaningful fit of three parameters $T_0$, $E_A^{(LJ)}$, and $\Gamma_0$. Similarly, a unique fit to the alternative relation $T_g^{(LJ)}(\Gamma) = T_0' - E_A^{(LJ)}/\ln(\Gamma/T_0')$ also is not possible. If one makes the (somewhat arbitrary) assumption $\Gamma_0 = 1$, however, one does obtain a result for $T_0$ consistent with expectation, namely, $T_0 = 0.35$ (remember that $T_0 \approx 0.34$ was estimated from the Vogel–Fulcher–Tammann fit to the diffusion constant of silica, but the quality of this fit is rather low, as expected from the lack of straight line behavior seen in Fig. 4). These results also imply that a reliable extrapolation of $T_g^{(LJ)}(\Gamma)$ to cooling rates $\Gamma$ of interest in real experiments also still is premature. In any case, the data in Fig. 4 do give clear evidence that pronounced cooling-rate dependences of $T_g^{(LJ)}(\Gamma)$ in the simulation of the glass transition of polymer models are present, and it would be wrong to ignore them.

V. SEARCH FOR THE MELTING TRANSITION TEMPERATURE

In the simulation of SiO$_2$, it was found that the critical temperature of mode coupling theory occurs for $T_c \approx 3330$ K, while the melting transition of SiO$_2$ occurs (in the experiment) at about $T_m \approx 2000$ K. The simulations of silica melts clearly have not reached the region where the melt is supercooled for $T < T_m$. Thus, it is of interest to test how the present model behaves in this respect.

For this purpose, we tried to construct a suitable crystalline configuration as an initial state of a simulation where the system is heated up from low temperatures until it melts. Several choices for a crystalline structure were tested. Requiring that the density in the crystalline structure is higher than in the glass, while the energy should be lower and correspond to an energy minimum, a crystalline structure, where all chains are perfectly stretched out as straight lines in the $z$ direction and form a tetragonal Bravais lattice with a basis of two chains per cell was used. The basis vectors of the cell were

$$a = (1.37343314, 0, 0), \quad b = (0, 1.37343314, 0), \quad c = (0, 0, 9.81622145).$$

If the first chain of the basis starts at the coordinate origin, the second chain starts at a point $r_1 = (\frac{1}{2}a, \frac{1}{2}a, \frac{1}{2}b_{\min})$, where $b_{\min}$ is the minimum of the bond potential (see Fig. 2). Thus, the crystal consists of layers of polymer chains that are stretched out parallel to the $z$ axis, the monomers forming a body-centered tetragonal lattice, slightly distorted by larger distances between the chain ends of different polymer layers. Figure 5(a) illustrates the resulting structure. Note that for the starting structure every inner monomer of a chain was in the minimum of the Lennard–Jones potential from its eight nonbonded nearest neighbors, and the minimum of the bond potential due to its two nearest neighbors along the chain. Then, the potential energy of this.
structure was minimized, which led to a slight distortion of the originally chosen structure. The result of this energy minimization is quoted in Eq. (20).

The total size of the crystal was chosen such that 784 chains in two crystalline layers fit a box, which according to the above lattice parameters would have the length \( L_x = L_y = 19.273 \pm 0.067 \), \( L_z = 19.357 \pm 0.046 \). Since these linear dimensions are very close to cubic and since a systematic determination of the ground-state crystalline shape as a function of temperature was outside the scope of this work anyhow, it was decided that the finite temperature MD runs were carried out with an \( NpT \) algorithm using strictly cubic boxes (trying lengths \( L = 19.2730676 \) up to \( L = 19.3570676 \), for simplicity.\(^{33}\) With this cubic shape of the box (which is not strictly adequate, of course) the resulting crystal is not fully stable but only metastable, as evidenced by the negative value of the \( z \) component of the pressure tensor (Fig. 6). Of course, when the crystal melts the diagonal components of the pressure tensor coincide, and in this isotropic phase the cubic simulation box shape again is adequate. The melting is also very clearly evidenced form the behavior of the mean-square displacements, defined by \((N_{\text{tot}} = 7840 = \text{total number of monomers})\):

\[
\begin{align*}
g_{xx}(t) &= \frac{1}{N_{\text{tot}}} \sum_{i=1}^{N_{\text{tot}}} [x_i(t) - x_i(0)]^2, \\
g_{yy}(t) &= \frac{1}{N_{\text{tot}}} \sum_{i=1}^{N_{\text{tot}}} [y_i(t) - y_i(0)]^2, \\
g_{zz}(t) &= \frac{1}{N_{\text{tot}}} \sum_{i=1}^{N_{\text{tot}}} [z_i(t) - z_i(0)]^2.
\end{align*}
\]

One can see from Fig. 6 that at \( T = 0.75 \) the monomers only carry out localized oscillations around their positions, while at \( T = 0.77 \) diffusive motion clearly has set in. From this we would estimate that \( T_m = 0.76 \pm 0.01 \). However, since our simulation uses periodic boundary conditions and the simulation time is rather short, a substantial superheating is not really ruled out. On the other hand, the negative \( z \) component of the pressure tensor indicates some lack of stability of the crystal, which might lead to a lowering of the observed melting temperature. In any case, we can conclude that \( T_m \) is much higher than \( T_g(\Gamma) \) for the present model.

From Fig. 6(a) it is also evident that \( g_{xx}(t) \neq g_{yy}(t) \), contrary to what one would expect for a tetragonal crystal signature. As a matter of fact, this is a consequence of the distortion of the crystal into a monoclinic structure [Fig. 5(b)]. This structure has the following basis vectors:

\[
a = (L/7, 0, 0), \quad b = (L/14, L/14, 0), \quad c = (0, 0, L/2),
\]

where \( L = 19.47 \) for \( T = 0.75 \). In the basis there are four chains, starting at the sites \( r_0 = (0, 0, 0) \), \( r_1 = (L/28, L/28, \frac{L}{2p_{\text{min}}}) \), \( r_2 = (5L/56, L/56, \frac{L}{2p_{\text{min}}}) \), and \( r_3 = (3L/56, -L/56, 0) \). Of course, the cubic box requires that two domains (separated by two grain boundaries) must occur, which also may affect the precise location of the melting temperature. Finally, we point towards the possible existence of finite-size effects, since only two layers of polymers occur along the \( z \) direction. Taking into account all these caveats we estimate that our uncertainty for \( T_m \) is of the order 10%–15%.

VI. DISCUSSION

In this investigation the cooling-rate dependence observed in simulations of models of glass-forming polymer melts was considered. It was shown that with substantial effort (55 independent runs of systems containing 1200 effective monomers each), indeed, clear evidence for such a cooling-rate dependence could be detected. Of course, given
the experimental evidence for cooling-rate dependence of glass transition temperatures of real polymer melts this finding is not a surprise, but in view of the widespread desire to compare MD results quantitatively with experimental data it is important to quantify how large these cooling rate effects are for MD simulations, since the cooling rates employed in the latter are many orders of magnitude larger than in the experiments. In the present study a coarse-grained model was used, temperature being measured in units of the Lennard-Jones energy scale $\epsilon$ (assuming that effective monomers interact with simple Lennard-Jones forces), and times are measured in units of $\tau_{\text{MD}}=\left(\frac{m\sigma^2}{\epsilon}\right)^{1/2}$, $m$ being the mass of the effective monomers and $\sigma$ the range of the Lennard-Jones potential. Very roughly, one may estimate that $\epsilon \sim 500$ K and $\tau_{\text{MD}}\sim 10^{-11}$ s. Cooling rates in our simulation, ranging from about $3.25 \times 10^{-6}$ to $8.33 \times 10^{-4}$ in MD units then correspond to about $1.5 \times 10^3$–$4.10^5$ K/s. For this range of cooling rates, we have observed a shift of $T_g(\Gamma)$ from about $T_g(\Gamma) \sim 0.468$ (for the fastest rate) to about $T_g(\Gamma) \sim 0.432$ (for the slowest rate), if we use the data analysis of the temperature dependence of the volume $V(T)$. This means the relative decrease of $T_g(\Gamma)$ in this regime is almost 10%. Note, also that an analysis of various dynamic quantities in well-equilibrated melts at temperatures $T \geq 0.46$ (using diffusion constants, mean-square displacements, dynamic structure factors, etc.) has yielded the estimates $T_c \sim 0.45 \pm 0.01$ and $T_g \sim 0.34 \pm 0.01$ for the critical temperature of mode coupling theory $T_c$ and the Vogel–Fulcher–Tamann temperature $T_g$, respectively. This means that for (ultrafast) cooling in MD simulations one obtains glass transition temperatures $T_g(\Gamma)$ around $T_c$ [although $T_0$ lies within our error bars for $T_g(\Gamma)$ when we perform a complete error estimate including the uncertainties in $\alpha_{\text{II}}$, $\alpha_{\text{III}}$, and $\alpha_{\text{IV}}$], while the experimental values for $T_g(\Gamma)$ often are closer to $T_0$ than to $T_c$, if the experiments permit an identification of $T_c$ at all. Of course, in view of our estimates for the translation of the MD time scale to the physical time scale this conclusion is perfectly reasonable.

We also have attempted to test two popular predictions for the cooling rate dependence of $T_g$, namely $T_g(\Gamma) \sim T_0 + \text{const}/\ln(\Gamma/T_0)$ [Eq. (5)] or $T_g(\Gamma) \sim T_0 + \text{const}/\ln(\Gamma/T_0)^{\nu}$ [Eq. (6)], but unfortunately it appears that neither formula provides a very good fit of our data; in the range of available cooling rates $\Gamma$, we cannot establish which of these formulas is better. Of course, both approaches are highly phenomenological, and it is clearly possible that a more-refined treatment of glassy dynamics is needed before one can find a really useful expression for $T_g(\Gamma)$. It is also possible that Eqs. (5) and (6) only make sense if $T_g(\Gamma) < T_c$, which is not the case for part of our data. Note also, that the results for $T_g(\Gamma)$ extracted from $\ln V(T)$ and from $E^{(\text{LJ})}(T)$ are not in perfect mutual agreement either. This, again, is no surprise—the crossover from the behavior of a fluid in (metastable) equilibrium to a glass is a gradual one, in the actual data for $\ln V(T)$ or $E^{(\text{LJ})}$ there is no sharp kink but only a rounded transition region, and in this region various quantities are affected differently when the system gradually falls out of equilibrium. Finally, we have also presented a (preliminary) rough estimate of the melting temperature of our model as $T_m \approx 0.76$. If this estimate is maintained; it implies that the ratio between $T_0/T_m = 0.49$ in our model is somewhat smaller than in many real systems [where, as a rule of thumb, one finds $1/2 \approx T_0/T_m \leq 2/3$ (Refs. 4–6)].

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