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Intramolecular caging in polybutadiene due to rotational barriers

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We present molecular dynamics simulations of a chemically realistic model of 1,4-polybutadiene and a freely rotating chain model derived from the first model by neglecting all dihedral potentials. We show that the presence of energy barriers hindering dihedral rotation leads to an intermediate plateau regime in the tagged particle mean-squared displacement reminiscent of the cage effect underlying the mode-coupling description of the liquid-glass transition. This intramolecular caging, however, occurs already at temperatures well above the glass transition regime. Because of its different physical origin, it also does not comply with the theoretical predictions of the mode-coupling theory. Consequences for the applicability of the mode-coupling theory to the glass transition in polymer melts are discussed.

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I. INTRODUCTION

Research on the structural glass transition in the past 15 years [1] was strongly influenced by the mode-coupling theory (MCT) [2]. This theory singles out density fluctuations as the relevant slow variables and describes the onset of glassy slowing down in the slightly supercooled liquid. In its idealized form, it predicts a complete arrest of the structural relaxation at a dynamical critical temperature $T_c > T_g$, where T_g is phenomenologically defined as the temperature where the viscosity reaches 10^{13} P. The relevant length scale of the theory is the mean interparticle distance or, equivalently, the inverse of the position of the amorphous halo in the static structure factor of the liquid.

The physical picture is that in a dense liquid, every particle is in a cage formed by its next neighbors. At high temperatures and low densities, this cage is short lived due to the high mobility of all particles. The particle motion displays a crossover from a ballistic regime at short times to a diffusive regime at long times when it has moved about the next neighbor distance. Upon lowering the temperature or increasing the density, the packing constraints increase the lifetime of the cage and the particles become temporarily arrested until the cage breakes up.

In its original form, the theory has been set up for simple liquids and it has been numerically solved in closed form for hard spheres [3], soft spheres [4], and a binary Lennard-Jones mixture [5]. Furthermore, it has been extended to simple aspherical molecules with an intramolecular orientational degree of freedom [6,7]. The only experimental systems conforming to the theoretical assumptions and forming a structural glass are sterically stabilized colloids [8]. Many structural glass formers are organic molecules or even macromolecules and a large amount of the experimental tests of the MCT have been performed on these systems [1]. *A priori*, however, it was not clear whether and to what extent the theory would be applicable to the glass transition of, for instance, a polymer melt. Computer simulations of a bead-spring-type coarse-grained polymer model [9–12] could be consistently analyzed in terms of the predictions of the MCT. For this model system, this could be explained by the fact that caging sets in on a scale of monomer displacements where the connectivity of the chains is not yet felt. The connectivity could be shown to alter the late stage of the caging process (the MCT β-relaxation regime). These findings motivated an extension of the MCT to such model polymers, which is able to reproduce these results [13]. In a molecular dynamics (MD) simulation of a chemically realistic model of 1,4-polybutadiene (PBD) [14], van Zon and de Leeuw studied the scaling behavior of the structural relaxation in terms of mode-coupling predictions. Their data conformed to the α-scaling predictions of the MCT, however, with a critical temperature of 162 K, whereas the experimental T_c is 220 K. It is not clear whether this discrepancy is caused by deficiencies in the model they employed or by the fact that they were not able to equilibrate their simulation in the temperature range they studied. Using the same approach, these authors also studied the glass transition in a polyethylenelike chemically realistic model [15]. For this model, they found that the structural relaxation and the late part of the β-relaxation regime for the tagged particle motion in the supercooled liquid could be consistently described by the MCT. They showed that the exponent parameter for their model differs from the one for the bead-spring model of Bennemann *et al.* and is in better agreement with typical values found in experiments on polymers. From this, one can conclude that the form of the intramolecular potential, especially the presence of a dihedral angle potential, has an influence on the properties of the relaxation in the MCT regime.

Experimentally, the glass transition in polybutadiene has been extensively studied by a wide range of techniques, ranging from neutron scattering [16–22] to light scattering [23,24], x-ray scattering [25], nuclear magnetic resonance [26–28], dielectric spectroscopy [29–32], and dynamic mechanical response [33–35]. For PBD as well as for other glass-forming polymers, some features of the glassy slowing down could be well described by the MCT, but it was concluded that the caging regime could not be described consistently with the MCT [36–38] in the way it was possible for the bead-spring polymer model. The discrepancies were occurring especially in the short time behavior and it was argued that the lack of time scale separation between the vibrational motion and the relaxational motion treated within

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the MCT lies at the origin of the observed deviations.

In this work, we will present MD simulations of a chemically realistic model of PBD that can resolve the effect of intramolecular rotational barriers on the particle motion on length and time scales corresponding to the MCT β-relaxation regime. We will try to understand the effect of the torsional potential on the tagged particle motion and chain relaxation in polymer melts by comparing this model to a model with the same chemical backbone structure but without torsional potentials. Working at temperatures well above the mode-coupling T_c of PBD, we are able to well equilibrate our model and study the dynamics in thermodynamic equilibrium. The following section will give some details on our model and simulation technique. Section III will then present the necessary background on the MCT and Sec. IV will detail our results. Finally, we will offer our conclusions in Sec. V.

II. MODEL AND SIMULATION TECHNIQUE

We will present MD simulations of a chemically realistic united atom model for PBD employing a carefully validated quantum chemistry based force field [39]. It was shown that MD simulations employing this force field are able to quantitatively reproduce experimental results on the structure and dynamics of polybutadiene melts at elevated temperatures [40–43]. We will study a random copolymer of 55% *trans*-1,4-PBD and 45% *cis*-1,4-PBD. We have 40 chains of 29 repeat units (115 backbone carbons) and we will be using a united atom model for the CH, CH_2, and CH_3 groups. The simulations are performed in the NVT ensemble using the Nosé-Hoover thermostat [44,45] after determining the correct density at ambient pressure for each temperature. We will focus mainly on results obtained for $T=273$ K and $T=240$ K. To bring out the effects of the torsional barriers on the local dynamics of the atoms, we also study a freely rotating chain (FRC) version of this chemically realistic chain (CRC) model, where we switch off all torsion potentials.

We will show in Sec. IV that this has no influence on the mesoscale to large-scale chain structure and on the local packing in the melt. At low temperatures, we can therefore use the FRC model to equilibrate the large-scale structure of our systems and do a local postequilibration for the conformational properties of the CRC system switching on the torsion potentials starting from an equilibrated FRC configuration. However, even for the FRC model the longest relaxation time (Rouse time) in this temperature range is already of the order of 100 ns, requiring a substantial computational effort.

III. MODE-COUPLING THEORY

This section will present a short summary of the pertaining ideas and results of the MCT. Starting from the Liouville equation and using the Mori-Zwanzig projection operator formalism, one arrives at the following formally exact equation [2]:

$$\ddot{\phi}_q(t)+\Omega_q^2\phi_q(t)+\Omega_q^2\int_{-\infty}^{t}dt'\,m_q(t-t')\,\dot{\phi}_q(t')=0, \quad (1)$$

where

$$\phi_q(t)=\langle \delta\rho_q(t)\,\delta\rho_q^*(0)\rangle \quad (2)$$

is the correlator for density fluctuations or intermediate scattering function. Ω_q is a microscopic frequency scale and $m_q(t)$ is a memory kernel containing the essential physics of the problem. In the idealized version of the MCT, this kernel is again expressed in terms of coupled density fluctuations and the coupling constants are completely determined by the static structure of the melt. Upon lowering the temperature towards the glass transition or increasing the density, this coupling induces a qualitative change in the dynamics. In the supercooled liquid regime, a two-step relaxation develops consisting of the final α or structural relaxation and a plateau or the MCT β-relaxation regime intervening between the microscopic dynamics and the structural relaxation. This β regime is the time regime of caging. Upon lowering the temperature, the lifetime of the plateau (cage) increases until it is infinite at T_c and all correlation functions only decay onto their plateau value. For the incoherent density correlations, this plateau value is the Debye-Waller factor of the glass. For the glass transition in the bead-spring model of Bennemann *et al.* [10,12], this picture was essentially confirmed.

A central result of the MCT for the behavior of correlation functions in the β regime is the factorization theorem. It states that close to T_c and in this time regime, all correlation functions can be written in the following way:

$$f_A(t)=f_A^c+h_A G(t), \quad (3)$$

where A is some physical observable, f_A^c is its plateau value, h_A is an amplitude, and $G(t)$ is the universal β correlator. A necessary consequence of this theorem is the following prediction. When we pick two times, t',t'', in the β regime, then the function

$$R(t)=\frac{f_A(t)-f_A(t'')}{f_A(t')-f_A(t'')}=\frac{G(t)-G(t'')}{G(t')-G(t'')} \quad (4)$$

for t in the β regime is the same for all correlation functions. This prediction has been successfully tested, for instance, on simulations of a chemically realistic model of SiO_2 [46] and for the bead-spring polymer model [12]. This theorem, therefore, furnishes a criterion to check for the applicability of the MCT, which works directly with the observed correlation functions and involves no fitting procedures.

IV. RESULTS

We will discuss our simulation results in two steps. In the first part, we will show that the two models we studied agree in essential structural properties. In the second part, we will then analyze their dynamic behavior for short length and time scales.

A. Static properties

In a previous publication [47] where we studied the influence of the presence or absence of torsional barriers on the chain dynamics, we have already presented a comparison of some of the structural properties for the two models we are discussing here and a third one with a different chain microstructure. These comparisons were done in a temperature range where the chemically realistic models as well as the freely rotating model can both be equilibrated in a simulation time below 100 ns. The slowest relaxation in the amorphous melts occurs for the large-scale conformational structure of the chains, i.e., the distributions of the radius of gyration. It was shown that these are identical in equilibrium for the three models (neither the omission of the torsional potentials nor the small change in chain microstructure for the third model had any influence on the large-scale structure) and that the distribution of the radius of gyration of these chains shows no temperature dependence. We, furthermore, presented an analysis of the chain structure on smaller scales in terms of the Rouse modes

$$\vec{X}_p(t)=\frac{1}{N}\sum_{n=1}^{N}\cos\left(\frac{\pi p(n-1/2)}{N}\right)\vec{r}_n(t) \tag{5}$$

and showed that the Rouse mode amplitudes are identical between the CRC and FRC models for all mode indices and temperatures. From this we can conclude that within a simulation time window where we can reach the free diffusion limit for the FRC chains, we can equilibrate the large-scale structure of the chains, also for further simulation with the CRC potentials. Also, the simulations with the freely rotating chains are performed at the zero-pressure densities for the CRC model, so that we will not have to equilibrate small-wavelength density fluctuations when switching from one model to the other. The time scale of simulation of the CRC model then only needs to be long enough to equilibrate the dihedral distributions and chain structure on the scale of a statistical segment. The simulation time window of 100 ns we analyzed for the CRC model is more than enough to perform this equilibration, since the torsional transitions which equilibrate the local structure occur on a time scale of less than 100 ps at all temperatures we studied.

To exemplify the difference in rotational behavior between the FRC and the CRC model, we present in Fig. 1 the probability distribution for the alkyl bond in PBD, i.e., the bond joining adjacent repeat units. For the CRC model, we can identify the rotational isomers *trans* (at $0°$) and *gauche* (at $\pm 120°$). The distribution for the FRC model shows that the nonbonded Lennard-Jones interaction along the chain slightly prefers locally stretched conformations so that the distribution is not completely flat. At the temperatures of our simulations, however, this angle can rotate without much hindrance so that we can speak of a freely rotating chain.

Another way to present the behavior of the chain structure is to look at the single-chain structure factor

$$S(q)=\left\langle \frac{1}{N}\sum_{i=1}^{N} e^{i\vec{q}\cdot\vec{r}_n}\right\rangle, \tag{6}$$

where the average is meant to include a spherical and a thermal average. This function is shown in Fig. 2 for $T=240,273$, and, 353 K for the CRC model and for 273 K for the FRC model. The behavior for small momentum transfers agrees well with the Debye function $f_D(x)=(2/x^4)(e^{-x^2}+x^2-1)$ where $x=qR_g$, which describes the scattering of a Gaussian coil. The obtained value for the radius of gyration agrees well with the directly measured value. The single-chain structure factor shows no temperature dependence in the depicted temperature range and agrees perfectly between the FRC and CRC models.

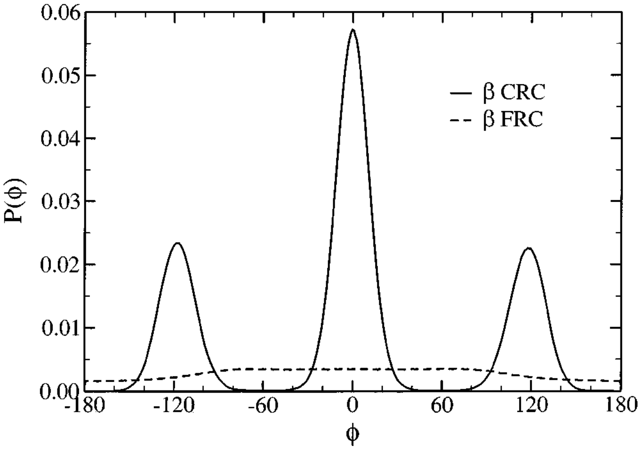

FIG. 1. Histograms of the occurrence of different dihedral angles for the β torsion in PBD melt simulations at 273 K. The full line is for the CRC model and dashed line for the FRC model.

The central structural property of the polymer melt governing its glass transition according to the MCT is its liquid structure factor. This is shown over a wide momentum transfer range in Fig. 3 at 273 K. For the calculation we have used the united atoms as scattering centers of equal scattering strength, calculating in this way the structure of the actual simulated systems. A quantitative comparison to the structure factor of PBD would be improved by reinserting the hydrogen atoms into their mechanical equilibrium positions [48] and explicitly using the scattering lengths of the carbon and hydrogen atoms in the system. It is gratifying that even so the position of the amorphous halo at $q=1.47$ Å^{-1} agrees nicely with the experimental results [16] and also the behav-

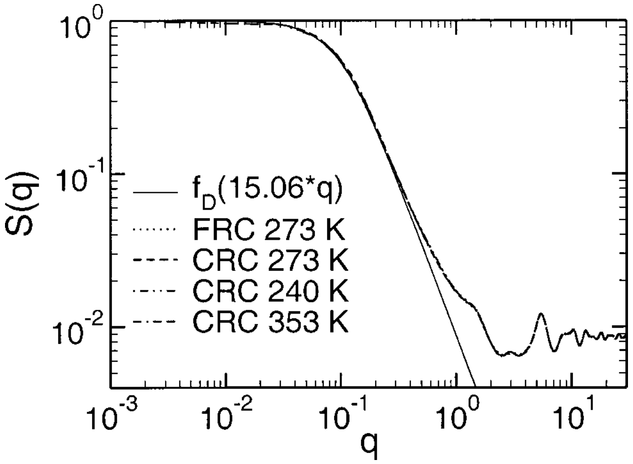

FIG. 2. Single-chain static structure factor obtained for the FRC model at 273 K and at different indicated temperatures for the CRC model.

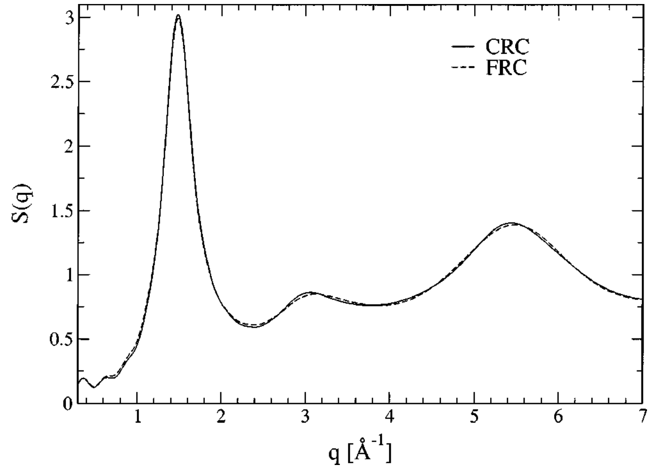

FIG. 3. Single-chain static structure factor obtained for the FRC model at 273 K and at different indicated temperatures for the CRC model.

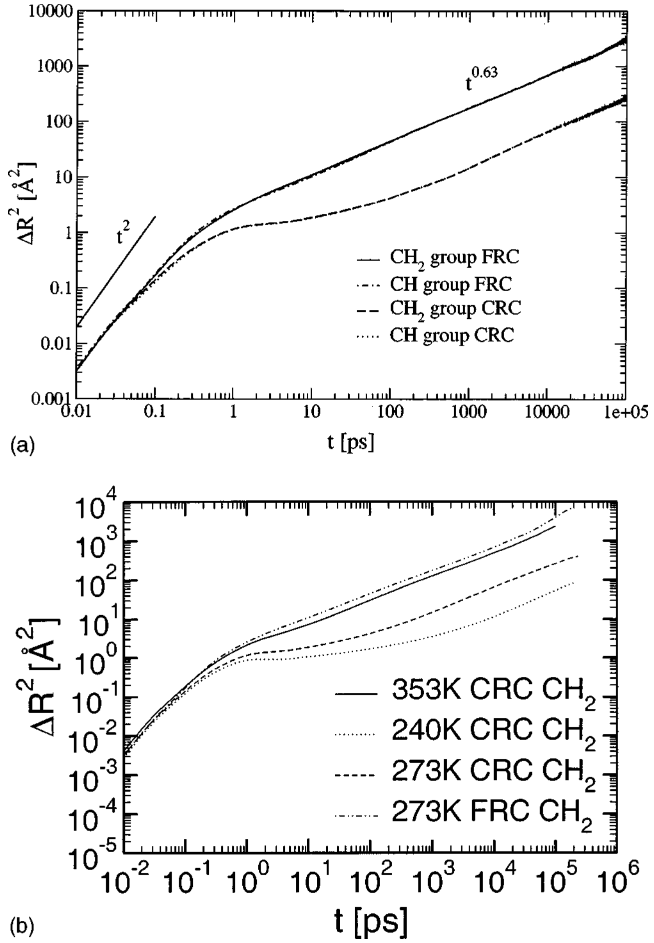

FIG. 4. Double-logarithmic plot of monomer mean-square displacements vs time. Panel (a) compares the FRC model to the CRC model at 273 K and also shows that the displacements of different chemcial groups along the backbone are identical. The short time behavior is ballistic and for the FRC model the Rouse-like motion at late times is indicated with the $t^{0.63}$ power law. Panel (b) shows the temperature dependence of the plateau for the mean-square displacements in the CRC model.

ior at higher momentum transfers is comparable (to as large q as there are experimental data available).

From these two results, we can conclude that the chain structure of our two models is identical and, even more important, that the local packing in the melt is the same.

B. Local dynamics

When we follow the basic approximation underlying the MCT that the equilibrium liquid structure as measured by the static structure factor determines the dynamics on the scale of the next neighbor distance, the local translational dynamics of our two models should be the same. When we look at the mean-square displacements of the united atoms, however, we find striking differences between the two models. Figure 4 shows the mean-square displacement of the different united atom types in the chain comparing the behavior in the CRC and FRC models. Panel (a) shows the behavior of inner monomers for $T=273$ K and both models. Panel (b) shows the displacement of inner monomers for a wide temperature range. The displacement curves of the CH and CH$_2$ groups are identical, as would be expected. For the FRC model we see the crossover from the short time ballistic motion to the long time diffusion via an intermediate Rouse regime where ideally we should see a behavior $\Delta r^2 \propto t^{0.5}$ [49] due to the connectivity of the chains. The observed exponent in this regime differs from the ideal prediction as was found for coarse-grained models [11,50] as well as for a chemically realistic model of polyethylene [51]. For the CRC model, however, there is a well-developed plateau region interspersed between the short time ballistic motion and the Rouse-like regime.

In panel (b) of Fig. 4, we see the development of this plateau as a function of temperature. At high temperatures (353 K), there is only a slight indication of it and the mean-square displacement curve for the CRC model at that temperature looks similar to the one for the FRC model at 273 K. With decreasing temperature, the temporal extent of the plateau increases and the plateau value decreases. On first glance, this looks exactly like the caging behavior observed for the glass transition of the bead-spring model polymer melt and predicted by the MCT. So let us give three reasons why this behavior is not the caging process described by the MCT. First of all, the two temperatures we are studying here are still high above the mode-coupling T_c that experimentally is 220 K for this polymer. Since our chains are shorter than the experimental ones for which this temperature was established, we would expect T_c for our CRC model to lie below this value. By all experience, the onset of caging starts to be observable around 10% above T_c and the process should not be as well developed as we observe it here. Second, for the glass transition, the value of the plateau in the mean-square displacement curves generally is equal to about the square of one-tenth of the next neighbor distance in the liquid. This puts the expected plateau value at $\Delta r_p^2 \approx 0.2$ Å^2 and not at 1.5 Å^2, as we are observing it for 273 K. For 240 K, the plateau value has decreased to about 0.9 Å^2 but is still

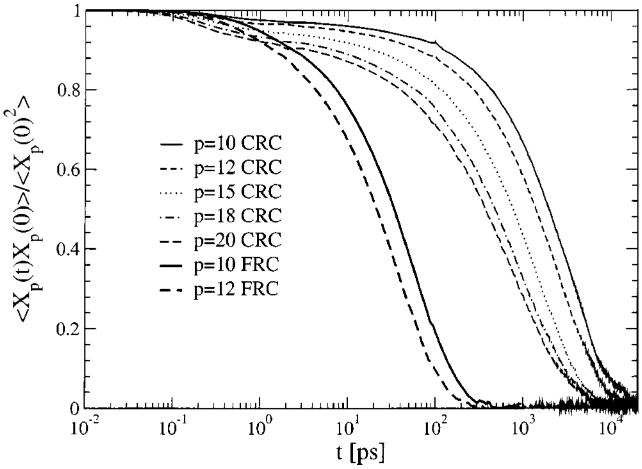

FIG. 5. Comparison of the Rouse mode autocorrelation functions for large-p modes in the FRC model (thick curves) and the CRC model (light curves).

a factor of 4 larger than the expected value for the cage effect.

As we discussed earlier, the factorization theorem offers a parameter-free prescription to test for the applicability of the MCT in the plateau regime, i.e., the MCT β regime. We choose to perform this test with the dynamic behavior of the Rouse modes, defined in Eq. (5). In the Rouse theory, their autocorrelation function is predicted to decay exponentially,

$$\Phi_p(t)=\frac{\langle \vec{X}_p(t)\cdot\vec{X}_p(0)\rangle}{\langle \vec{X}_p(0)\cdot\vec{X}_p(0)\rangle}=e^{-t/\tau_p} \qquad (7)$$

with autocorrelation times $\tau_p=\tau_R/p^2$ where τ_R is the longest relaxation time, the so-called Rouse time. In a previous publication [47], we have shown that the small-p modes (which measure the large-scale relaxation of the chain structure) for our models are well described by stretched exponential functions, with a stretching exponent that decreases with decrease of p. In Fig. 5, we show the relaxation functions of several large-p modes. For the FRC model, these are again stretched exponential decays with a stretching exponent of around 0.75, whereas for the CRC model the modes show a two-step relaxation. The long time behavior can also be fitted with a stretched exponential with an exponent that decreases from 0.85 for $p=10$ to 0.63 for $p=20$. The well-developed plateau regime at short times corresponds to the plateau in the mean-square displacements. It is worth noting from the start that an applicability of the MCT to this two-step decay would require it to be present in the small-p modes also [12]. However, the effect may be difficult to resolve in the simulation due to a plateau value close to 1. So let us ask whether at least the large-p modes for which we can clearly resolve the plateau follow the factorization theorem.

Using the correlation functions Φ_p for the correlator A in Eq. (4), we arrive at Fig. 6. Here we used the times $t'=0.8$ ps and $t''=3$ ps as the fixed times in the plateau regime. The inflection point of the mode autocorrelation functions, which serves as an estimate for the center of the β regime, is around 2 ps. The factorization theorem is clearly violated and the curves only intersect at $t=t'$ and $t=t''$. The figure is plotted on the same scale as the respective figure in Ref. [12] where a successful test of the theorem for a glass-forming polymer model close to its mode-coupling T_c showed the modes as one superimposed line in the β regime. It will be interesting to test for range and limits of the applicability of the MCT to the glass transition in this chemically realistic polymer model at lower temperatures in future work.

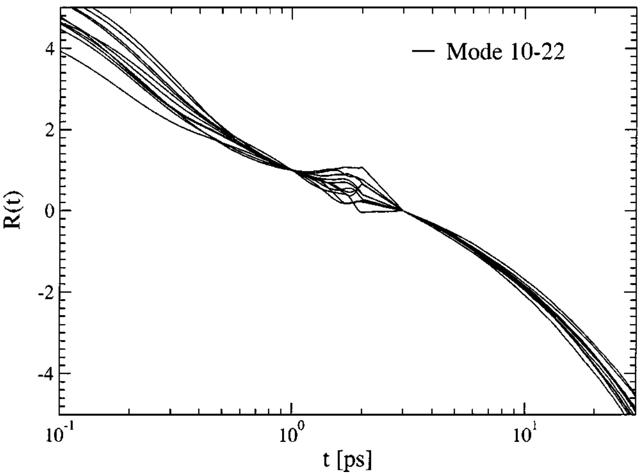

FIG. 6. Test of the factorization theorem of the MCT using the Rouse mode autocorrelation functions for modes 10–22 for the CRC model. The fixed time points in the plateau regime are $t'=0.8$ ps and $t''=3$ ps (see text).

V. CONCLUSIONS

We have clearly seen that the dynamics of the FRC and CRC models for polybutadiene in the picosecond time regime are very different, although their static properties as revealed by the single-chain and liquid structure factors are identical. The CRC model displays a well-developed plateau regime in the particle mean-square displacement, which is reminiscent of the cage effect discussed in the mode-coupling theory of the structural glass transition. However, using the factorization theorem of the MCT we could prove that this slowing down is not caused by intermolecular caging as treated in the MCT. A first indication of this was the value of the mean-square displacement at the plateau which at 273 K is an order of magnitude larger than the expected value for intermolecular caging.

The physical origin of this slowing down lies in the presence of intramolecular rotational barriers for the dihedral degrees of freedom and we therefore choose to call this effect intramolecular caging. For typical polymeric systems, there occurs a vibration-relaxation crossover in the dynamics at around 1 ps [52]. That is, all bond length, bond angle, and torsional vibrations are damped on this time scale. For the FRC model, local conformational relaxation (rotation) sets in on the same time scale and we see a crossover to Rouse-like behavior. For the CRC model, the local torsional degrees of freedom are stuck in their respective isomeric states and can only cross over the rotational barriers to adjacent minima, i.e., contribute to local conformational relaxation, after a waiting time that can be understood using transition state arguments. In Ref. [43], it was shown that the mean times between torsional transitions for the different dihedral degrees of freedom in the CRC model of PBD increase in an Arrhenius fashion with an activation energy given by the typical barrier for that degree of freedom. The typical waiting time between these transitions is around 33 ps at 273 K and this defines the time scale of the cage breakup.

From our findings, we can draw two conclusions for the understanding of the thermal glass transition in polymer melts. First, we have shown that the structure of the MCT implying the factorization theorem is able to distinguish between a slowing down due to intermolecular caging (packing effects) or due to intramolecular caging (rotation barriers). Not all plateau regimes in relaxation functions can be described by the MCT. Second, our results show that the scenario for the glass transition in polymer melts is different from the standard MCT scenario as derived for simple liquids and experimentally verified, for instance, for hard sphere colloids [8]. One such difference was already observed in simulations of a coarse-grained bead-spring-type polymer model [10] where it was seen that the late-stage β regime (von Schweidler regime) for polymers crosses over to a subdiffusive behavior with an even smaller exponent (Rouse-like regime) and not to the diffusion regime as in simple liquids. This effect has recently been incorporated into the MCT [13]. More basically, however, according to our results, for fragile polymers we should see a crossover from intramolecularly dominated activated relaxation at high temperatures to intermolecularly dominated activated relaxation at low temperatures, whereas the MCT incorporates a crossover from ‘‘barrierless’’ flow into intermolecularly dominated activated processes. This can be expected to at least reduce the temperature range above the MCT critical temperature (crossover temperature) where the theory can be consistently applied to the relaxation behavior in polymer melts, but it may also give rise to a qualitatively different behavior in the crossover region. We think that our result can provide an explanation for the difficulties encountered in the application of the mode-coupling predictions to experimental results for the glass transition in polymer melts.

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