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Dynamic arrest in a liquid of symmetric dumbbells: Reorientational hopping for small molecular elongations

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We present extensive equilibrium and out-of-equilibrium molecular-dynamics simulations of a liquid of symmetric dumbbell molecules, for constant packing fraction, as a function of temperature and molecular elongation. We compute diffusion constants as well as odd and even orientational correlators. The notations *odd* and *even* refer to the parity of the order l of the corresponding Legendre l polynomial, evaluated for the orientation of the molecular axis relative to its initial position. Rotational degrees of freedom of order l are arrested if, in the long-time limit, the corresponding orientational l correlator does not decay to zero. It is found that for large elongations translational and rotational degrees of freedom freeze at the same temperature. For small elongations only the even rotational degrees of freedom remain coupled to translational motions and arrest at a finite common temperature. On the contrary, the odd rotational degrees of freedom remain ergodic at all investigated temperatures. Hence, in the translationally arrested state, each molecule remains trapped in the cage formed by its neighboring molecules, but is able to perform 180° rotations, which lead to relaxation only for the odd orientational correlators. The temperature dependence of the characteristic time of these residual rotations is well described by an Arrhenius law. Finally, we discuss the evidence in favor of the presence of the type-A transition for the odd rotational degrees of freedom, as predicted by mode-coupling theory for small molecular elongations. This transition is distinct from the type-B transition, associated with the arrest of the translational and even rotational degrees of freedom for small elongations, and with all degrees of freedom for large elongations. Odd orientational correlators are computed for small elongations at very low temperatures in the translationally arrested state. The obtained results suggest that hopping events restore the ergodicity of the odd rotational degrees of freedom at temperatures far below the A transition. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2085030]

I. INTRODUCTION

Mode-coupling theory[1–3] (MCT) is, at present, the only first-principle theory of the glass transition. Initially introduced for systems of hard spheres, it has been developed in recent years to account for the arrest mechanism of more complex molecules with orientational degrees of freedom, as linear probes in systems of hard spheres,[4] liquids of dipolar hard spheres,[5] dumbbells,[6–10] or ellipsoids,[11,12] polymer melts,[13] and models of water[14] or orthoterphenyl.[15]

The ideal MCT equations have been recently solved in the site-site representation for a system of symmetric hard dumbbell molecules,[9,10] as a function of the packing fraction φ and the elongation ζ. Interestingly enough, the theory predicts two different dynamic arrest scenarios, on varing φ and ζ (see Fig. 1 in Ref. 9). For large elongations, it is predicted that all rotational correlation functions are strongly coupled to the translational degrees of freedom and dynamic arrest takes place at a common φ value, $\varphi_c^B(\zeta)$. According to MCT, the transition is of type B, i.e., the nonergodicity parameter, defined as the long-time limit of translational and rotational correlation functions, jumps *discontinuously* from zero to a finite value at the ideal glass transition line. The ideal glass transition line (the B line) has a nonmonotonic shape in the φ-ζ plane, with a maximum at $\zeta=0.43$. The B line continues

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for small elongations until the hard-sphere limit at $\zeta=0$ is reached.

However, for small elongations $\zeta<\zeta_c=0.345$, the theory predicts a novel different scenario: Only the translational and the *even* rotational degrees of freedom freeze at the B line. Here even and *odd* refer to the parity of the order l of the rotational correlator $C_l(t)=\langle P_l(\cos\theta(t))\rangle$, where P_l is the Legendre polynomial of order l, $\cos\theta(t)=\hat{e}(t)\cdot\hat{e}(0)$, and $\hat{e}(t)$ is a unit vector along the molecular axis at time t. The freezing of rotational degrees of freedom of order l means that C_l does not decay to zero in the long-time limit. For $\zeta<\zeta_c$, the *odd-l* rotational degrees of freedom freeze at higher values of the packing fraction, namely, at a so-called A line $\varphi_c^A(\zeta)>\varphi_c^B(\zeta)$, that merges with the B line at $\zeta=\zeta_c$. The glass transition of the odd degrees is of type A, i.e., the nonergodicity parameter of the odd rotational correlation functions increases *continuously* from zero on crossing the A line.

The A and B lines separate the φ-ζ plane in three regions with different dynamic behaviors: an ergodic fluid, a completely arrested state, and an intermediate *translationally* arrested state (located between the A and B lines) which is the amorphous analog of a plastic crystal. In such a state, each molecule remains trapped in the cage formed by the neighboring molecules, but is able to perform 180° rotations within the cage, which lead to relaxation for the odd l but not for the even-l rotational correlators. An analogous scenario is predicted by molecular MCT for the case of hard ellipsoids of aspect ratio close to one.[11]

Several computational investigations have tested predictions of the molecular MCT for liquids of dumbbells.[7,16,17] However, simulations were restricted to a single elongation value in the region $\zeta>\zeta_c$, where odd and even rotational degrees of freedom freeze at the common B line. In order to test the predictions of Refs. 9 and 10 and, in particular, to provide evidence of the existence of the type-A transition for small ζ, we have recently carried out molecular-dynamics simulations[18] in a binary mixture of the Lennard-Jones (LJ) dumbbell molecules at fixed packing fraction, as a function of the elongation using the temperature T as control parameter (instead of φ used in the theoretical work). For a comparison with the theory at a *qualitative* level, there are several reasons for preferring a LJ potential instead of hardcore interactions. First, decreasing T plays qualitatively the same role as increasing φ. Second, temperature is the usual control parameter in investigations of real glass-forming liquids. Third, event-driven simulations of systems of nonspherical hard objects are technically involved, as compared with simulations of systems with soft interactions as the LJ potential. Finally, even if we had simulated a *binary mixture* of hard dumbbells, a direct quantitative comparison with Refs. 9 and 10 would not be possible, since the theoretical results reported there correspond to a system of *identical* dumbbells. The reason for choosing a binary mixture is well known: A system of identical dumbbells would crystallize, a fact not accounted for by MCT.

The simulations in Ref. 18 report a nonmonotonic dependence on the elongation for the isodiffusivity curves, in qualitative agreement with MCT predictions, with a minimum at a value of ζ close to the maximum of $\varphi_c^B(\zeta)$.[9] For small elongations $\zeta\leqslant 0.3$ at low temperature, the coherent intermediate scattering function evaluated at the maximum of the static structure factor, as well as the rotational correlator $C_2(t)$, decays to zero at times several orders of magnitude longer than those for $C_1(t)$. An analysis of the plateau height for the $C_1(t)$ correlator shows a sharp drop of the former in the range of $0.3<\zeta<0.5$, consistent with the theoretical ζ_c value predicted for the hard dumbbell fluid. These features suggest the presence of a nearby type-A transition in the investigated LJ dumbbell system.

The simulations in Ref. 18 were carried out in *equilibrium* liquid states, for state points above the B transition, i.e., at T such that translational and both the odd and even rotational degrees of freedom are ergodic. In this article we present new results focused on the reorientational dynamics *below* the B transition, i.e., in *out-of-equilibrium* states, where the translational and even rotational degrees of freedom are arrested. We aim to shed light on the dynamic features of amorphous analogs to plastic crystals. We also provide a *direct* evidence of the existence of the type-A transition, which in Ref. 18 was inferred from precursor effects. We show that hopping events dominate rotational dynamics for small molecular elongations, and restore ergodicity for reorientations at temperatures far below the A transition.

II. SIMULATION DETAILS

We investigate a binary mixture of 410:102 dumbbell molecules[19] in a box of side L with periodic boundary conditions. Each molecule consists of two identical atoms, denoted by A and B, respectively, for the most and the less abundant components of the mixture. The interaction between atoms of different molecules is given by a Lennard-Jones potential plus a linear term:

$$V_{\alpha\beta}(r)=4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12}-(\sigma_{\alpha\beta}/r)^{6}+A_0+A_1 r/\sigma_{\alpha\beta}], \quad (1)$$

where α and $\beta\in\{A,B\}$. The interaction parameters are the same of the monoatomic binary mixture of Ref. 20, i.e., $\epsilon_{AA}=1.0$, $\epsilon_{AB}=1.5$, $\epsilon_{BB}=0.5$, $\sigma_{AA}=1.0$, $\sigma_{AB}=0.8$, and $\sigma_{BB}=0.88$. The values of A_0 and A_1 are selected to guarantee the continuity of the potential and forces at the cutoff distance $c\sigma_{\alpha\beta}$, with $c=2.5$. The resulting values are $A_0=c^{-6}(7-13c^{-6})$ and $A_1=6c^{-7}(2c^{-6}-1)$. The same atomic mass $m=1$ is used for both A and B particles. Hence, each dumbbell has a mass equal to two.

Simulations have been carried out for elongations $\zeta=0.125$, 0.20, 0.30, 0.40, 0.55, 0.70, and 0.85 at different values of T and constant packing fraction $\varphi=0.708$. The packing fraction is defined by

$$\varphi=\frac{\pi}{6L^3}(N_{AA}\sigma_{AA}^3+N_{BB}\sigma_{BB}^3)\left[1+\frac{3}{2}\zeta-\frac{1}{2}\zeta^3\right], \quad (2)$$

where $N_{AA}=410$ and $N_{BB}=102$ are the numbers of AA and BB molecules. Temperature, time, and the diffusion coefficient D are, respectively, calculated in units of ϵ_{AA}/k_B, $(m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$, and $(\sigma_{AA}^2\epsilon_{AA}/m)^{1/2}$. Equations of motion are integrated, with a time step ranging from 2×10^{-4} to 5×10^{-3} according to T and/or ζ, using the velocity Verlet scheme combined with the SHAKE algorithm (see, e.g., Ref. 21) for keeping the molecular elongation constant.

At each state point, the system is thermalized at the requested T by periodic velocity rescaling. A microcanonical run is performed after suitable equilibration to generate a representative trajectory in phase space. Statistical averages are performed over 20 independently generated equilibrium trajectories. At high T, the thermalization process is started from a distorted crystalline configuration that melts quickly. At low T, it is started from equilibrated high T configurations. After reaching equilibrium, energy and pressure show no drift. Also, translational and rotational mean-squared displacements, as well as dynamic correlation functions, show no aging, i.e., there is no systematic dependence of the dynamical properties from the selected time origin. In practice equilibration requires that each dumbbell has on average moved several diameters and performed several full rotations from its initial position.

At very low T and small ζ, the relaxation times for translational and even rotational degrees of freedom become exceedingly long for the time scale of the simulation. In these conditions only the odd orientational correlators decay to zero. We perform long runs of $\approx 10^7$ steps until neither significant drift in T and pressure nor aging in the translational and even rotational correlation functions are observed, to ensure that the residual rotational motion of the dumbbells takes place in an essentially frozen structure.[22] After this preliminary simulation, trajectories are calculated.

III. RESULTS AND DISCUSSION

Figure 1 shows the data for D and for the relaxation times τ_1 and τ_2 of the rotational correlators $C_1(t) = \langle \cos\theta(t)\rangle$ and $C_2(t) = (1/2)\langle 3\cos^2\theta(t) - 1\rangle$. The diffusion coefficient was evaluated from the long-time limit of $\langle r^2(t)\rangle/6t$, where $\langle r^2(t)\rangle$ is the mean-squared displacement. The brackets denote ensemble average over all particles. The relaxation times τ_1 and τ_2 are defined as the times at which the corresponding correlation functions decay to 3% of their initial value. As previously done in the analysis of other systems characterized by slow dynamics,[18,23,24] we report isochrones (constant τ_1) and isodiffusivity (constant D) curves, to provide an indication of the shape of the glass line in the (T-ζ) plane. The isodiffusivity curves are consistent with the same quantities calculated in Ref. 18 and, as previously noted, show a minimum around $\zeta = 0.55$, close to the MCT prediction for hard dumbbells.[9] Figure 1 shows that, especially at low T, the iso-τ_2 curves follow the same trend as the isodiffusivity curves, tending to collapse in a common curve, as expected on approaching a type-B transition. The iso-τ_1 curves show a similar trend only at large ζ. In contrast with this, for small elongations the iso-τ_1 curves depart from the iso-D and iso-τ_2 curves. Differently from the τ_2 isochrones, the τ_1 isochrones are, within the resolution in ζ of our calculations, monotonic in the T-ζ plane. The fact that the iso-τ_1 curves lay significantly below the iso-τ_2 curves shows very clearly that, for small ζ, fast relaxation of the odd degrees of freedom takes place even when the even degrees are arrested.

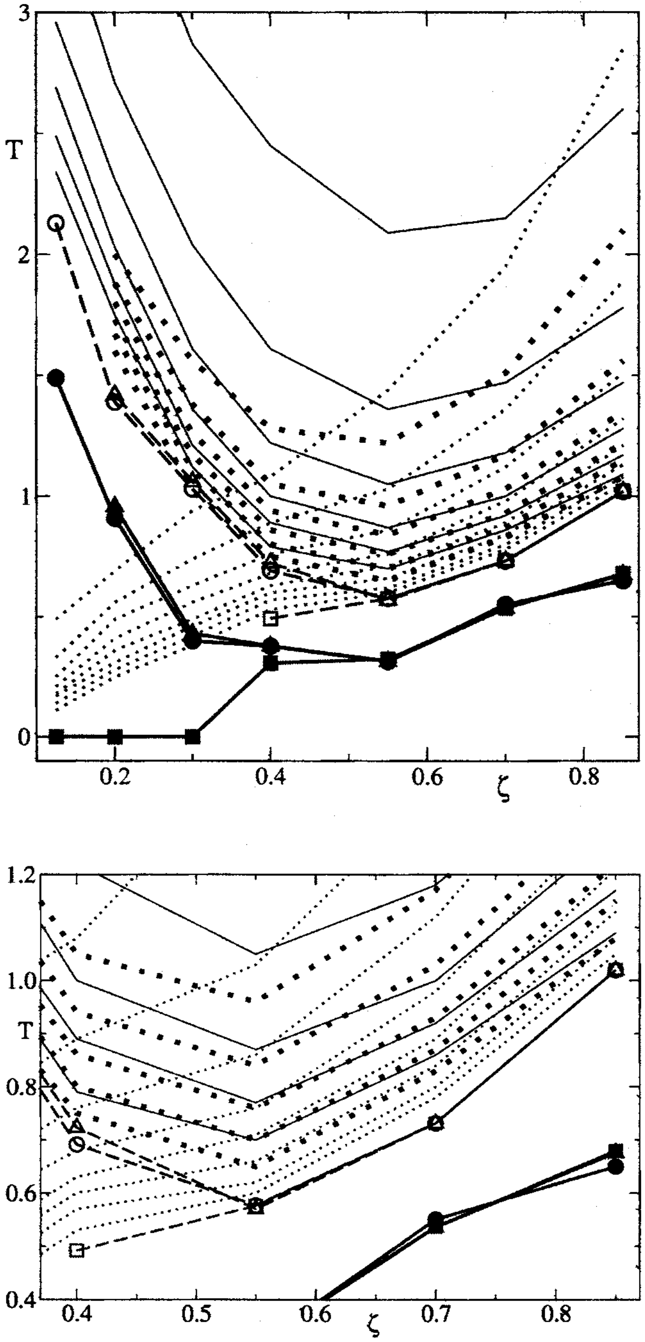

FIG. 1. Top panel: Isodiffusivity lines (thin continuous lines) and τ_1 (thin dotted lines) and τ_2 (thick dotted lines) isochrones in the T-ζ plane. These quantities are averaged over all the particles in the system. Line segments join the numerical data (symbols are not included for clarity). The corresponding values are, from top to bottom, $D = 1\times10^{-2}$, 3×10^{-3}, 1×10^{-3}, 3×10^{-4}, 1×10^{-4} and 3×10^{-5}, $\tau_1 = 3\times10^{1}$, 1×10^{2}, 3×10^{2}, 1×10^{3}, 3×10^{3}, 1×10^{4}, 3×10^{4}, and 1×10^{5}, and $\tau_2 = 3\times10^{1}$, 1×10^{2}, 3×10^{2}, 1×10^{3}, 3×10^{3}, and 1×10^{4}. The empty and filled symbols are, respectively, the estimated MCT and VFT temperatures (see text) for D (circles), τ_1 (squares), and τ_2 (triangles). The thick dashed and thick continuous lines are corresponding guides for the eyes. The lower panel shows a magnification, for $\zeta > 0.4$, of the results in the neighborhood of the estimated MCT transition temperatures.

A detailed quantitative comparison of the presented results with the MCT predictions for dynamic exponents and scaling laws cannot be simply performed, except for large ζ. Indeed, it has been shown that the range of validity of the asymptotic MCT laws—for the small ζ hard dumbbell fluid case[10]—is limited to unusually small values of the separation parameter $\epsilon=(\varphi_c^B-\varphi)/\varphi_c^B$. In particular, Ref. 10 shows that the exponent γ for the well-known power law $D,1/\tau\propto(\varphi_c^B-\varphi)^\gamma$, can only be correctly estimated by exploring the range $\epsilon<10^{-2}$. For small ζ, a fit of the data in the range of $10^{-2}<\epsilon<10^{-1}$ shows an apparent power-law behavior, but the corresponding fit yields an "effective" exponent, which, contrary with the asymptotic limit, does not take a universal value, but instead depends on the chosen observable.[10] A similar phenomenon is expected to be present in the studied system at small ζ, preventing the possibility of an accurate determination of the asymptotic laws close to the MCT critical temperature T_c^B. In addition, we recall that the ideal MCT neglects activated processes which are known to be present in reality around and below T_c^B.[25–30] Only when the hopping phenomena can be neglected, a MCT study very close to T_c^B can be feasible.

Figure 2 shows the T dependence of D, τ_1, and τ_2 for several ζ values. If a fit (not shown) of the T dependence of D and $1/\tau_2$ according to the functional form $(T-T_c^B)^\gamma$ is performed, we obtain very similar values of T_c^B for both quantities in the whole ζ range (see Fig. 1). For the case of $1/\tau_1$, reasonable power-law fits can be performed only for $\zeta\gtrsim 0.4$. For $\zeta=0.55$ the fits provide values of T_c^B consistent with those obtained for D and $1/\tau_2$ but with different γ values. Only for $\zeta\geqslant 0.70$ a simultaneous consistent description for D, $1/\tau_1$, and $1/\tau_2$ is achieved, with identical T_c^B and γ values. Specifically $T_c^B=0.732$ and $\gamma=2.50$ for $\zeta=0.70$ and $T_c^B=1.02$ and $\gamma=2.06$ for $\zeta=0.85$.

To provide a lower bound to T_c^B at small ζ, we also fit the data in terms of the well-known phenomenological Vogel-Fulcher-Tammann (VFT) law $D,1/\tau_{1,2}\propto\exp[-A/(T-T_{\mathrm{VFT}})]$,[31] which predicts a dynamic arrest of the corresponding degree of freedom at a finite temperature $T_{\mathrm{VFT}}<T_c^B$.[20,27,28] In all cases, the VFT law provides a consistent effective representation of the dynamics, with a fit quality comparable to the MCT power-law fit. The resulting $T_{\mathrm{VFT}}(\zeta)$ for D, τ_1, and τ_2 are reported in Fig. 1. Interestingly, the T_{VFT} for D, τ_1, and τ_2 coincide for large elongations, indicating strong coupling between the translational and all the rotational degrees of freedom. However, for $\zeta\lesssim 0.4$ the T_{VFT} for τ_1 is much smaller than the T_{VFT} for D and τ_2, confirming that around this value of ζ the odd degrees of freedom completely decouple from the even and from the translational ones. This latter value of ζ is consistent with the merging point of the A and B transitions for the hard dumbbell fluid[9] and with the estimates of Ref. 18. At smaller elongations $\zeta\leqslant 0.3$, for τ_1 we find $T_{\mathrm{VFT}}\approx 0$. This implies that a good description of the data is provided by an Arrhenius law $\tau_1\propto\exp(E/k_BT)$ [see Fig. 2(b)]. The activation energies $E/\epsilon_{AA}=1.8$, 3.3, and 5.0, respectively, for $\zeta=0.125$, 0.20, and 0.30 roughly follow a linear dependence on ζ.

The presence of an activated Arrhenius T dependence in $\tau_1(T)$ for small molecular elongations strongly suggests that the residual reorientational dynamics at very low temperatures, in the T region where the translational dynamics is already arrested, is characterized by 180° rotations which do not lead to the relaxation of the even rotational degrees of freedom. The Arrhenius functional form also suggests that the hopping phenomena are extremely relevant, so much to completely mask the presence of a finite type-A glass transition temperature, if the analysis is limited only to the T dependence of τ_1 (or any other odd τ).

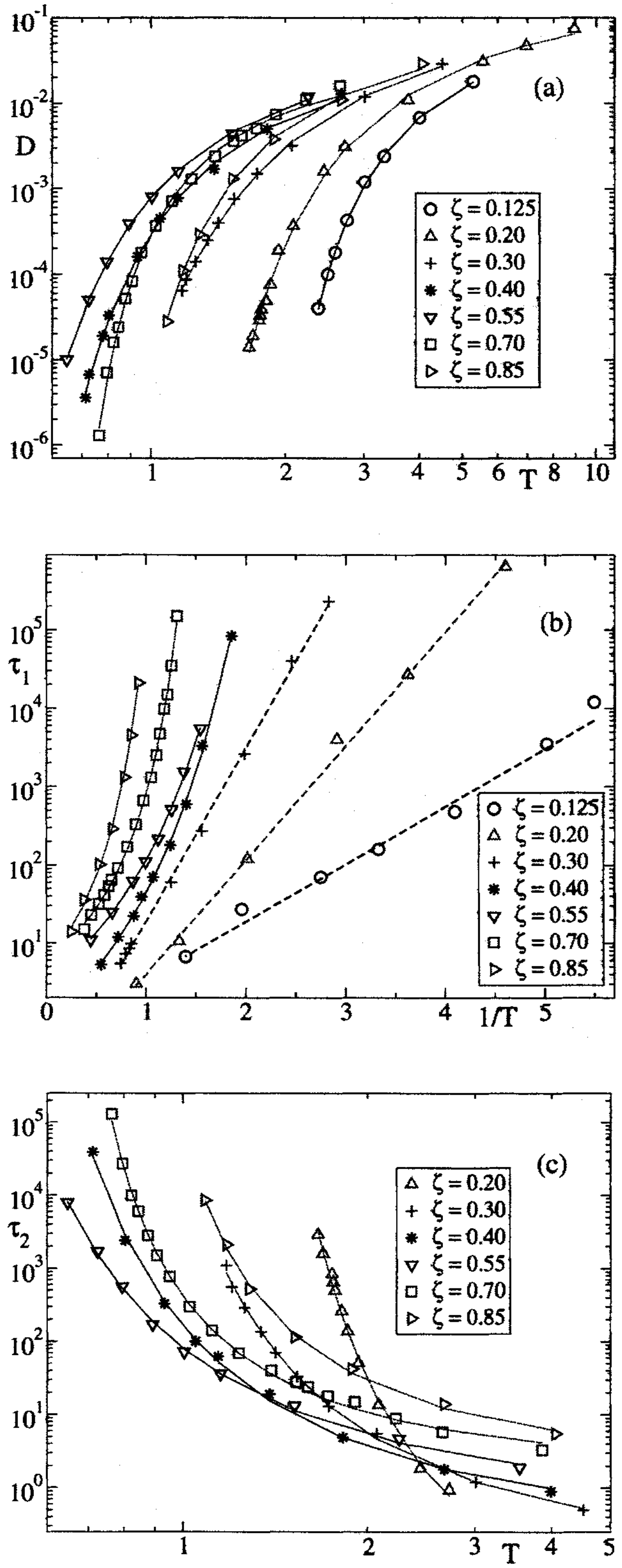

FIG. 2. Symbols: Temperature dependence of D (a), τ_1 (b), and τ_2 (c). The continuous lines are fits to the VFT functions (see text). The dashed lines in panel (b) are Arrhenius fits. The data for τ_1 have been represented vs $1/T$ in order to show the Arrhenius behavior at small ζ.

While we cannot expect, due to this strong hopping decorrelation, to observe any critical law, an indication of a

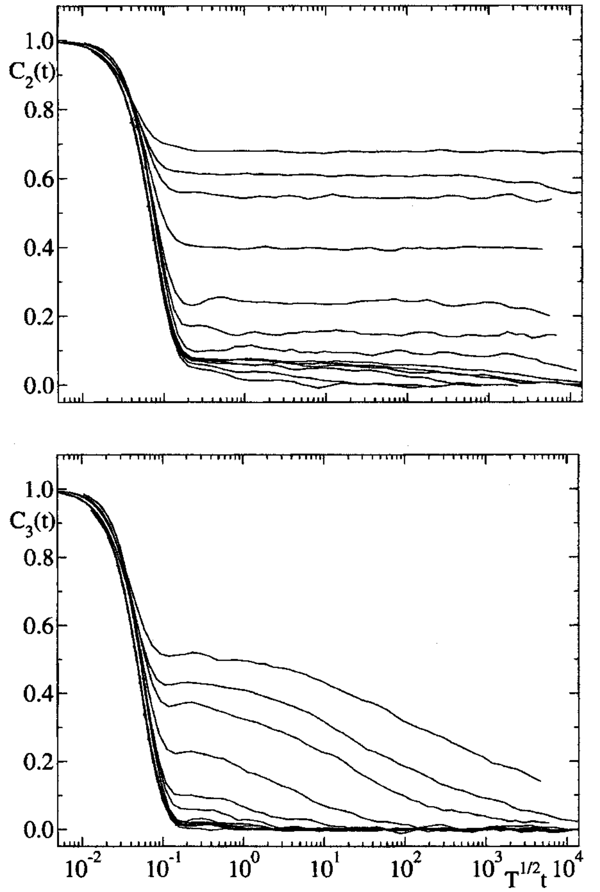

FIG. 3. Temperature dependence of the rotational correlators $C_2(t)$ and $C_3(t)$ vs time rescaled by $T^{1/2}$, for elongation $\zeta=0.2$. From top to bottom $T=0.217$, 0.276, 0.343, 0.496, 0.750, 1.110, 1.396, 1.693, 1.770, 1.815, 1.933, 2.443, and 3.776.

residual crossover finite temperature can still be observed in the full dependence of the correlation functions, and in particular, in the strength of the long-time α relaxation process. The main effect of hopping is indeed manifested in the long-time decay from the plateau value. Hence, in the absence of these additional relaxation channels, the correlation function would decay only down to the plateau value (i.e., the nonergodicity parameter). Figure 3 shows, for $\zeta=0.2$, the T dependence of $C_2(t)$ and $C_3(t)=(1/2)\langle 5\cos^3\theta(t)-3\cos\theta(t)\rangle$, in a wide range of T (across $T_{\mathrm{VTF}}=0.96$ for τ_2). Though the correlator $C_1(t)$ has more experimental relevance, $C_3(t)$ is more adequate to discuss the behavior of the nonergodicity parameter, since it shows a more pronounced plateau. A representation of $C_i(t)$ vs $tT^{1/2}$, i.e., rescaling the time by the thermal velocity, yields a clearer visualization of the decay of the correlation function. The data reported in Fig. 3 show two important features:

(i) At low T the plateau height for both C_2 and C_3 progressively grows, signaling a crossing of the critical MCT temperatures. However, while in case of $C_2(t)$, the increase of the plateau value is connected to a nonergodic long-time behavior (i.e., C_2 does not decay to zero within the simulation time window); $C_3(t)$ always relaxes toward zero. This fact evidences that hopping processes restore ergodicity for reorientations at T far below the temperature at which the plateau value starts to increase.

(ii) The decay of the C_2 correlation function is characterized by a finite T interval in which the plateau value is essentially constant (within the present numerical error). For smaller T, the height of the plateau starts to increase, as discussed above. Instead, the decay of the C_3 correlation function is not characterized by any plateau at high T, and the increase of the plateau starts from zero, consistently with the presence of a type-A transition which, due to the hopping effects, is significantly weakened. Moreover, the first T at which the C_3 plateau value is different from zero is lower than the T at which the C_2 plateau starts to increase. This suggests that the type-A transition temperature is different and lower than the type-B T_c^B. We also note that the α-relaxation process for odd C_i is highly stretched, which is likely to be due to the local cage heterogeneity.

IV. CONCLUSIONS

In summary, we have provided direct evidence for the existence of the type-A transition predicted by the mode-coupling theory for the reorientational dynamics of glass-forming liquids of small molecular elongation. Our numerical results at $T<T_c^B$ confirm those recently reported for $T>T_c^B$ in Ref. 18, where the existence of the A transition was inferred from precursor effects. Moreover, by computing relaxation times and plateau heights of odd rotational dynamic correlators—in the arrested state for the even rotational and the translational degrees of freedom—we show that reorientational hopping dominates the dynamics for small elongations and restores ergodicity down to temperatures far below the type-A transition. Though these results have been specifically obtained for a liquid of symmetric dumbbells, experimental techniques probing $C_1(t)$ and $C_2(t)$, at very low temperatures, will yield qualitatively similar results for small elongated molecules with a weak asymmetry which disfavors rotations different from ≈180°. Finally, the present model can become a test case for developing theories of the glass transition in which activated processes, which become relevant around and below T_c^B, can be studied.

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