Dynamics in a supercooled liquid of symmetric dumbbells: Reorientational hopping for small molecular elongations

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We present extensive molecular dynamics simulations of a liquid of symmetric dumbbells, for constant packing fraction, as a function of temperature and molecular elongation. 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. The odd rotational degrees of freedom remain ergodic at all investigated temperature and the temperature dependence of the corresponding characteristic time is well described by an Arrhenius law. Finally, we discuss the evidence in favor of the presence of a type-A transition temperature for the odd rotational degrees of freedom, distinct from the type-B transition associated with the arrest of the translational and even rotational ones, as predicted by the mode-coupling theory for the glass transition.

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The ideal mode-coupling theory (MCT) equations have been recently solved in the site-site representation for a system of symmetric hard dumbbell molecules, as a function of the packing fraction and the elongation $\zeta$. Interestingly enough, the theory predicts two different dynamic arrest scenarios, on varying $\varphi$ and $\zeta$ (see Fig. 1 in Ref). 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 $\varphi$ value, $\varphi_c^B(\zeta)$. According to MCT, the transition is of type-B, i.e. 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 non-monotonic shape in the $\varphi$-$\zeta$ plane, with a maximum at $\zeta = 0.43$. The $B$-line continues for small elongations until the hard sphere limit at $\zeta = 0$ is reached. However, for small elongations $\zeta < \zeta_c = 0.345$, 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 of the rotational correlator $C_l(t) = \langle \hat{P}_l(\hat{e}(t) - \hat{e}(0)) \rangle$, where $\hat{P}_l$ is the Legendre $l$-polynomial and $\hat{e}(t)$ is a unitary vector along the molecular axis at time $t$. The odd rotational degrees of freedom freeze at higher values of the packing fraction, namely at an $A$-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 long time limit of the odd rotational correlation functions increases continuously from zero on crossing the $A$-line.

The $A$- and $B$-lines separate the $\varphi$-$\zeta$ plane in three dynamic regions: an ergodic fluid, a completely arrested state, and an intermediate 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 neighbouring molecules, but is able to perform $180^\circ$ 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 in the limit of small aspect ratio.

In order to test these predictions, we have recently carried out molecular dynamics simulations in a binary mixture of Lennard-Jones (LJ) dumbbell molecules at fixed packing fraction, as a function of the elongation using the temperature $T$ as control parameter (instead of $\varphi$ used in the theoretical work). In agreement with MCT predictions, a non-monotonic dependence on the elongation has been observed for the isodiffusivity curves, with a minimum at a value of $\zeta$ close to the maximum of $\varphi_c^A(\zeta)$. For small elongations $\zeta < 0.3$, in deep supercooled states, 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 $0.3 < \zeta < 0.5$, consistent with the theoretical $\zeta_c$ value predicted for the hard dumbbell fluid. These features suggest the presence of a nearby type-A transition in the investigated LJ dumbbell system.

Simulations in Ref. have been 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 manuscript we complement equilibrium simulations and we also investigate 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 at providing evidence of the type-A transition, and to shed light on the dynamic features of amorphous analogs to plastic crystals.
We investigate a binary mixture of 410:102 dumbbell molecules 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 component of the mixture. The interaction between atoms of different groups is given by a Lennard-Jones potential plus a linear term: $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}(\sigma_{\alpha\beta}/r)^{12} - 2\epsilon_{\alpha\beta}(\sigma_{\alpha\beta}/r)^{6} + A_0 + A_1(r/\sigma_{\alpha\beta})$, where $\alpha, \beta \in (A,B)$. The interaction parameters are the same of the monoatomic binary mixture of Kob and Andersen, i.e., $\epsilon_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\epsilon_{BB} = 0.5$, $\sigma_{AA} = 1.0$, $\sigma_{AB} = 0.8$, $\sigma_{BB} = 0.88$. The values of $A_0$ and $A_1$ are selected to guarantee continuity of potential and forces at the cutoff distance $\sigma_{\alpha\beta}$, 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 (each dumbbell has 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 $\varphi = (\pi/6)(N_{AA}\sigma_{AA}^3 + N_{BB}\sigma_{BB}^3) L^{-3}[1 + (3/2)\zeta - (1/2)\zeta^2]$, where $N_{AA} = 410$, $N_{BB} = 102$ are the number of AA and BB molecules. Temperature, time and diffusion coefficient $D$ are respectively calculated in units of $k_B / (m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$ and $(\sigma_{AA}^2 \epsilon_{AA}/m)^{1/2}$. Equations of motion are integrated, with a time step ranging from $2 \times 10^{-4}$ to $5 \times 10^{-3}$ according to $T$ and/or $\zeta$, using the velocity Verlet scheme combined with the SHAKE algorithm 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 quickly melts. At low $T$, it is started from equilibrated high $T$ configurations. After reaching equilibrium, energy or 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, in average, has moved several diameters and performed several full rotations from its initial position.

At very low $T$ and small $\zeta$, relaxation times for translational an even rotational degrees of freedom become exceedingly long for the time scale of the simulation. In these conditions only the odd rotational degrees of freedom 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 is observed, to ensure that the residual rotational motion of the dumbbells takes place in an essentially frozen structure. After this preliminary simulation, trajectories are calculated.

Fig. 1 shows data for $D$ and for the relaxation times $\tau_1, \tau_2$ of the rotational correlators $C_1(t)$ and $C_2(t)$. The diffusion coefficient is evaluated from the long time limit of the mean square displacement, while $\tau_1$ and $\tau_2$ are defined as the time 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, we report isochrones (constant $\tau_1$) and isodiffusivity (constant $D$) curves, to provide an indication of the shape of the glass line in the $(T - \zeta)$ plane. The isodiffusivity curves are consistent with the same quantities calculated in Ref. and, as previously noted, show a minimum around $\zeta = 0.55$, close to the MCT prediction for hard dumbbells. Fig. 1 shows that, especially at low $T$, the iso-$\tau_2$ 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-$\tau_1$ curves show a similar trend only at large $\zeta$. On the contrary, for small elongations the iso-$\tau_1$ curves depart from the iso-$D$ and iso-$\tau_2$ curves. Differently from $\tau_2$, within the resolution in $\zeta$ of our calculations, the $\tau_1$ isochrones are monotonic in the $T - \zeta$ plane. The fact that the iso-$\tau_1$ curves lay significantly below the iso-$\tau_2$ curves shows very clearly that fast relaxation of the odd degrees of freedom takes place even when the even degrees are arrested.

A detailed quantitative comparison of the presented re-
MCT neglects activated processes which are known to be present in reality around and below $T_c^B$. Only when hopping phenomena can be neglected, an MCT study can be feasible very close to $T_c^B$.

Fig. 2 shows the $T$ dependence of $D$, $\tau_1$ and $\tau_2$ for several $\zeta$ 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 all the $\zeta$ 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 $\zeta = 0.55$ fits provide values of $T_c^B$ consistent with those obtained for $D$ and $1/\tau_2$ but with different $\gamma$ values. Only for $\zeta \gtrsim 0.70$ a simultaneous consistent description for $D$, $1/\tau_1$ and $1/\tau_2$ is achieved, with identical $T_c^B$ and $\gamma$ values. Specifically $T_c^B = 0.732$, $\gamma = 2.50$ for $\zeta = 0.70$ and $T_c^B = 1.02$, $\gamma = 2.06$ for $\zeta = 0.85$.

To provide a lower bound to $T_c^B$ at small $\zeta$, we also fit the data in terms of the well-known phenomenological Vogel-Fulcher-Tammann (VFT) law $D/\tau \propto \exp[-A/(T-T_{VFT})]$, which predicts a dynamic arrest of the corresponding degree of freedom at a finite temperature $T_{VFT} < T_c^B$. 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 $T_{VFT}(\zeta)$ for $D$, $\tau_1$ and $\tau_2$ are reported in Fig. 1. Interestingly, $T_{VFT}$ for $D$, $\tau_1$ and $\tau_2$ coincide for large elongations, indicating strong couplings between the translational and all the rotational degrees of freedom. However, for $\zeta \lesssim 0.4$ the $T_{VFT}$ for $\tau_1$ is much smaller than the $T_{VFT}$ for $D$ and $\tau_2$, confirming that around this value of $\zeta$ the odd degrees of freedom completely decouple from the even and from the translational ones. This latter value of $\zeta$ is consistent with the merging point of the $A$- and $B$-transitions for the hard dumbbell fluid and with estimates of Ref. 4. At smaller elongations $\zeta \leq 0.3$, for $\tau_1$ we find $T_{VFT} \approx 0$. This implies that a good description of the data is provided by an Arrhenius law $\tau_1 \propto \exp[E/k_B T]$ (see Fig. 2). The activation energies $E/k_B = 1.8$, 3.3 and 5.0, respectively for $\zeta = 0.125$, 0.20 and 0.30, roughly follow a linear dependence on $\zeta$. 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 $180^\circ$ rotations which do not lead to relaxation of the even rotational degrees of freedom. The Arrhenius functional form also suggests that 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 $\tau_1$ (or any other odd $\tau$).

While we can not expect, due to this intense hopping decorrelation, to observe any critical law, indication of a residual cross-over finite temperature can still be observed in the full dependence of the correlation functions, and in particular in the strength of the long time $\alpha$ relax-
important features: velocity, yields a clearer visualization of the decay of the factor) for both $C_i$ of it shows a more pronounced plateau. A representation of it is to be published.

In summary, we have provided evidence for the existence of the type-A transition predicted by MCT for the reorientational dynamics of glass-forming liquids of small molecular elongation. Our numerical results complement those recently reported for $T > T_c^B$ in Ref. [4]. 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 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 disfavours rotations different from $\approx 180^\circ$. 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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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 $T = 0.217, 0.276, 0.343, 0.496, 0.750, 1.110, 1.396, 1.770, 1.815, 1.933, 2.443$ and 3.776.

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