

## Evidence for the Weak Steric Hindrance Scenario in the Supercooled-State Reorientational Dynamics

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We use molecular-dynamics computer simulations to study the translational and reorientational dynamics of a glass-forming liquid of dumbbells. For sufficiently elongated molecules the standard strong steric hindrance scenario for the rotational dynamics is found. However, for small elongations we find a different scenario—the weak steric hindrance scenario—caused by a new type of glass transition in which the orientational dynamics of the molecule’s axis undergoes a dynamical transition with a continuous increase of the nonergodicity parameter. These results are in agreement with the theoretical predictions by the mode-coupling theory for the glass transition.

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Systems of particles interacting only via hard core potentials show, in spite of their apparent simplicity, a variety of phases: fluids, crystals, and glasses. Several investigations have focused on the transition between these phases upon a change of the packing fraction  $\varphi$ . Recent experimental and computational studies on systems with *elongated* particles, such as ellipsoids [1] and spherocylinders [2], have revealed interesting features concerning their random (amorphous) jammed packing. For example, it has been found that for the latter systems the maximum attainable packing fraction  $\varphi_{\max}$  is a nonmonotonic function of the elongation parameter  $\zeta$  [3] which characterizes the shape of the particles [1,2]. Starting, for  $\zeta = 0$ , at  $\varphi_{\max} \approx 0.64$ , the value for random close packing of hard spheres,  $\varphi_{\max}$  reaches a maximum  $\approx 0.70$  at  $\zeta \approx 0.5$  and then decreases again for larger  $\zeta$ . For hard core particles the quantity  $\Delta\varphi = \varphi_{\max} - \varphi$  is the relevant parameter that governs the relaxation dynamics of the system. Hence it can be expected that the nonmonotonic behavior of  $\varphi_{\max}$  has an important implication on the  $\varphi$  and  $\zeta$  dependence of the dynamics, i.e., on the diffusion constant or the  $\alpha$ -relaxation time. For instance, it implies that, if the shape of the particle is changed at fixed  $\varphi$ , the dynamics can accelerate or decelerate. Since for small  $\Delta\varphi$  the dynamics depends very strongly on this difference, the relaxation times of the system can change by orders of magnitude upon a change of  $\zeta$  of just a few percent, which thus can have important consequences for the mechanical properties of the jammed packing or the crystallization dynamics.

From the theoretical side it is possible to understand the observed nonmonotonic behavior of  $\varphi_{\max}(\zeta)$  at least qualitatively within the framework of mode-coupling theory (MCT). For the case of ellipsoids or dumbbells the theory predicts that the critical packing fraction  $\varphi_c(\zeta)$ , at which the system undergoes a dynamical arrest, shows a maxi-

mum at intermediate values of  $\zeta$  [4,5]. Although MCT predictions concern the line  $\varphi_c(\zeta)$  and not  $\varphi_{\max}(\zeta)$ , it can be expected that these two curves track each other closely and that therefore the theory does indeed provide an explanation for the experimental findings.

MCT also predicts that features of the *reorientational* dynamics strongly depend on  $\zeta$ . It is predicted, if  $\zeta$  exceeds a certain threshold,  $\zeta > \zeta_c$  ( $\zeta_c = 0.345$  for hard dumbbells [5]), that a dynamic arrest takes place at  $\varphi_c(\zeta)$  which is usually denoted as “type-B transition” [6]. In supercooled states near  $\varphi_c(\zeta)$ , orientational correlation functions for angular-momentum index  $\ell$ ,  $C_\ell^{(s)}(t) = \langle P_\ell[\vec{e}(t) \cdot \vec{e}(0)] \rangle$ , show a two-step decay with a *finite* plateau height (here  $P_\ell$  is the Legendre polynomial of order  $\ell$ , and  $\vec{e}(t)$  is the orientation of a molecule at time  $t$ ). When  $\zeta$  is significantly larger than  $\zeta_c$ , the height of this plateau is predicted to be larger, the relaxation time to be longer, and the final  $\alpha$  decay to be less stretched for  $\ell = 1$  than for  $\ell = 2$ . Such a scenario is called “strong steric hindrance scenario,” and all these features are in qualitative agreement with the experimental results found by dielectric loss ( $\ell = 1$ ) and depolarized-light-scattering ( $\ell = 2$ ) spectroscopy for propylene carbonate [7] and glycerol [8], and also with simulation results for water [9] and *ortho*-terphenyl (OTP) [10].

When particles are more spherical, i.e.,  $\zeta < \zeta_c$ , MCT predicts a different type of dynamical transition for odd- $\ell$  reorientational correlators [4,5,11]. Translational and even- $\ell$  reorientational dynamics are predicted to undergo a dynamical arrest at a packing fraction  $\varphi_c(\zeta)$ , whereas odd- $\ell$  correlators remain ergodic. Only at a higher packing fraction  $\varphi_A(\zeta) > \varphi_c(\zeta)$  are the latter predicted to undergo a dynamical arrest; i.e., the orientation of the molecule’s axis ( $\ell = 1$ ) freezes into a random direction. Most remarkably it is predicted that this second transition is of “type A”; i.e., the height of the plateau in the odd- $\ell$

reorientational correlator is a smooth function of  $\varphi$ , zero for  $\varphi < \varphi_A(\zeta)$ , and increases linearly for  $\varphi > \varphi_A(\zeta)$ . This is in contrast to the translational and even- $\ell$  rotational correlators which exhibit a type-B transition at  $\varphi_c(\zeta)$ ; i.e., the height of the plateau already takes a finite value at  $\varphi_c(\zeta)$ . The scenario for the reorientational dynamics of small elongations which is caused by the nearby type-A singularity has been termed “weak steric hindrance scenario” since, in the range  $\varphi_c(\zeta) < \varphi < \varphi_A(\zeta)$ , the odd- $\ell$  correlators relax even if the translational and even- $\ell$  reorientational dynamics are frozen [11]. In this case, the  $\alpha$ -relaxation dynamics is predicted to be strongly modified for the  $\ell = 1$  reorientational dynamics, whereas no such modification is predicted for  $\ell = 2$ . So far the predicted existence of this type-A transition has not been investigated either by experiments or computer simulations. The goal of the present Letter is to explore whether this novel transition really exists and whether its features are in agreement with the theoretical predictions.

Since one component systems are very prone to crystallization, we have simulated a binary system of dumbbells. For the sake of computational efficiency, these dumbbells are not hard core particles but instead interact with a Lennard-Jones (LJ) potential. Thus the system we consider is a binary mixture of rigid, symmetric dumbbell molecules, to be denoted by  $AA$  and  $BB$  dumbbells. Each molecule consists of two identical fused LJ particles of type  $A$  or type  $B$  having the same mass  $m$ , and their bond lengths are denoted by  $l_{AA}$  and  $l_{BB}$ . The interaction between two molecules is given by the sum of the LJ interactions between the four constituent sites,  $V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\{(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6\} + C_{\alpha\beta} + D_{\alpha\beta}r$ , where  $\alpha, \beta \in \{A, B\}$ , with the LJ parameters  $\epsilon_{AA} = 1.0$ ,  $\sigma_{AA} = 1.0$ ,  $\epsilon_{AB} = 1.5$ ,  $\sigma_{AB} = 0.8$ ,  $\epsilon_{BB} = 0.5$ , and  $\sigma_{BB} = 0.88$ , taken from Ref. [12].  $C_{\alpha\beta}$  and  $D_{\alpha\beta}$  are chosen so that  $V_{\alpha\beta}(r)$  and  $V'_{\alpha\beta}(r)$  are zero at the cutoff  $r_{\text{cut}} = 2.5\sigma_{\alpha\beta}$ , and the LJ parameters are simultaneously renormalized to ensure that the minimum of the potential is  $-\epsilon_{\alpha\beta}$  at  $r = 2^{1/6}\sigma_{\alpha\beta}$ . Bond lengths are specified by a single elongation parameter  $\zeta$ , defined such that  $\zeta = l_{AA}/\sigma_{AA} = l_{BB}/\sigma_{BB}$ . The number of  $AA$  and  $BB$  dumbbells is 800 and 200, respectively, giving the number densities  $\rho_{AA} = 800/L^3$  and  $\rho_{BB} = 200/L^3$ , where  $L$  denotes the length of the cubic box used in the simulation. The “packing fraction” is then defined by  $\varphi_{\text{tot}} = \varphi_{AA} + \varphi_{BB}$ , where  $\varphi_{\alpha\alpha} = (\pi/6)\rho_{\alpha\alpha}\sigma_{\alpha\alpha}^3(1 + \frac{3}{2}\zeta - \frac{1}{2}\zeta^3)$  for  $0 \leq \zeta \leq 1$ . Fixing  $\varphi_{\text{tot}}$  thus specifies  $L$  for each  $\zeta$ . In this study, we have used the value  $\varphi_{\text{tot}} = 0.708$ . We note that, when specialized to  $\zeta = 0$ , our system reduces to the spherical system studied in Ref. [12], apart from a factor of 2 in temperature  $T$  and mass. In the following, all quantities are expressed in reduced units with the unit of length  $\sigma_{AA}$ , the unit of energy  $\epsilon_{AA}$  (setting  $k_B = 1$ ), and the unit of time  $(m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$ . Standard molecular-dynamics simulations have been performed as in Ref. [12]. The longest runs were  $10^8$  time steps, and in order to improve the statistics of the results,

we have averaged over 16 independent runs. More details will be presented elsewhere [13].

It is necessary to make a comment on the notion of packing fraction. Since LJ interactions are finite, the LJ dumbbells can penetrate each other, thus making the concept of packing fraction somewhat ill defined. However, it is reasonable to assume that, at fixed  $T$ , this penetration is only a very weak function of the elongation  $\zeta$ . Therefore it does make sense to study the relaxation dynamics of the system at given  $T$  and  $\varphi_{\text{tot}}$  as a function of  $\zeta$  and hence to check for the presence of a nonmonotonic  $\zeta$  dependence of the diffusion constant and the predicted type-A transition.

To characterize the  $\zeta$  dependence of the translational dynamics, we have calculated the mean-squared displacement of the center of mass of the molecules, from which the diffusion constant  $D$  is determined. In Fig. 1 we show isodiffusivity loci, at fixed  $\varphi_{\text{tot}}$ , as a function of  $\zeta$ . Since, for  $D \rightarrow 0$ , the isodiffusivity lines approach the glass transition locus, they provide a numerical estimate of the shape and location of the glass line, which can be compared with theoretical predictions.

From Fig. 1 we recognize that at fixed  $T$  the diffusion constant increases with increasing  $\zeta$ , reaches a maximum at around  $\zeta = 0.5$ , and then decreases again. Since this behavior is observed for all values of  $D$ , we can conclude that the temperature of dynamic arrest does indeed show a minimum as a function of  $\zeta$ , in agreement with the experimental findings [1,2] and the theoretical calculations for a system of hard dumbbells (HDS) [5]. In Ref. [5] it has been argued that such a  $\zeta$  dependence can be understood from the  $\zeta$  dependence of the first sharp diffraction peak in the static structure factor, and in Ref. [13] we will demonstrate that the proposed mechanism seems indeed relevant for the present system.

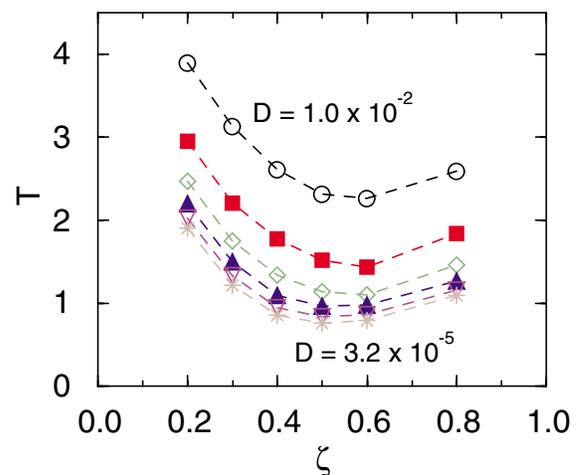


FIG. 1 (color online). Symbols, connected by lines, show the center of mass isodiffusivity curves for the  $AA$  dumbbells. The diffusion constants  $D$  are  $D = 1.0 \times 10^{-2}$ ,  $3.2 \times 10^{-3}$ ,  $1.0 \times 10^{-3}$ ,  $3.2 \times 10^{-4}$ ,  $1.0 \times 10^{-4}$ , and  $3.2 \times 10^{-5}$ , from top to bottom.

We now turn our attention to the  $\zeta$  dependence of the rotational dynamics that we will characterize in terms of the above defined reorientational correlators  $C_\ell^{(s)}(t)$ . The time dependence of these correlators is shown in Fig. 2 for the case  $\ell = 1, \dots, 4$ . Different panels correspond to four representative values of  $\zeta$ , and the temperatures are close to those given by the  $D = 3.2 \times 10^{-5}$  isodiffusivity locus. At this  $D$  value, the lowest curve reported in Fig. 1, the system is strongly supercooled [14]. For the sake of comparison, we have also included, as circles, the normalized site-site coherent intermediate scattering function  $F(q, t)$  for the wave vector  $q$  that corresponds to the first maximum in the static structure factor [13].

Most of these correlators show a two-step relaxation: They decay on intermediate times to a plateau, a motion that corresponds to the relaxation of the molecule inside the cage formed by its neighbors, followed by a final  $\alpha$  decay in which the molecules leave their cage [or reorient in the case of  $C_\ell^{(s)}(t)$ ]. In the following, we will denote the

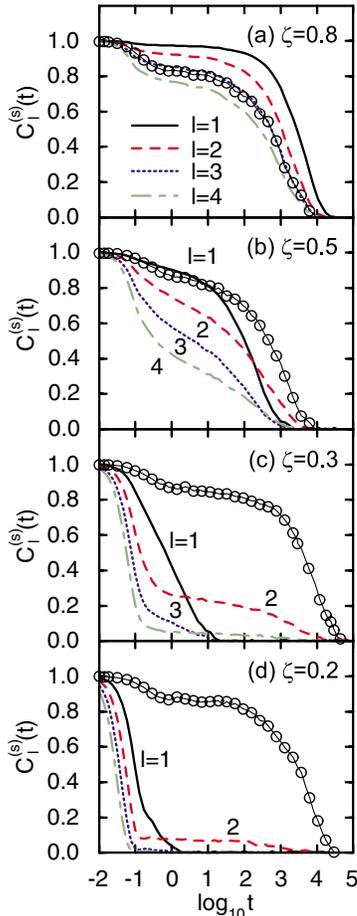


FIG. 2 (color online). The coherent intermediate scattering function (circles) and the reorientational correlators  $C_\ell^{(s)}(t)$  for the AA dumbbells in supercooled states for  $\ell = 1$  (solid line), 2 (dashed line), 3 (dotted line), and 4 (dash-dotted line) for (a)  $\zeta = 0.8$  and  $T = 1.06$ , (b)  $\zeta = 0.5$  and  $T = 0.75$ , (c)  $\zeta = 0.3$  and  $T = 1.13$ , and (d)  $\zeta = 0.2$  and  $T = 1.85$ .

plateau height by  $f_\ell^c$  and estimate its value via appropriate fits of  $C_\ell^{(s)}(t)$  with von Schweidler's law [6,13]. The  $\alpha$ -relaxation time  $\tau_\ell$  will be defined as  $C_\ell^{(s)}(\tau_\ell) = f_\ell^c/10$ .

For sufficiently large elongation [ $\zeta = 0.8$ , Fig. 2(a)], steric hindrance for reorientations is substantial, and thus  $C_\ell^{(s)}(t)$  exhibit the dynamics of the strong steric hindrance scenario [5,11]: The plateau height  $f_\ell^c$  and the  $\alpha$ -relaxation time  $\tau_\ell$  decrease monotonously with increasing  $\ell$ . In particular,  $f_1^c > f_2^c$  and  $\tau_1 > \tau_2$ . These features are in qualitative agreement with previous findings for various glass-forming systems [7–10]. Upon a decrease of the elongation, the steric hindrance effects for reorientations weaken, leading to smaller  $f_\ell^c$  compared to those for larger elongation. The relations  $f_1^c > f_2^c$  and  $\tau_1 > \tau_2$  hold until  $\zeta \approx 0.6$ . For intermediate elongations, e.g.,  $\zeta = 0.5$  shown in Fig. 2(b), the condition  $f_1^c > f_2^c$  still holds, but now  $\tau_1 < \tau_2$ . Thus for intermediate elongations one expects that the strength of the  $\alpha$  peak in dielectric spectroscopy—a technique sensitive to the  $\ell = 1$  decorrelation—is more pronounced than the one in dynamic light scattering ( $\ell = 2$ ), but that the location of the former is at higher frequencies than the latter.

If the elongation is decreased even further [Figs. 2(c) and 2(d)], the  $\alpha$ -relaxation process for  $\ell = 1$  basically vanishes, although the one for  $\ell = 2$  is still clearly visible. In this case,  $f_1^c = 0$ . A closer inspection of the curves shows that this result holds for all odd values of  $\ell$ . Thus, for small  $\zeta$ , a dielectric spectroscopy experiment would not show an  $\alpha$  peak anymore, although such a peak would still be visible in a dynamic light scattering experiment or an inelastic neutron scattering experiment [which probes  $F(q, t)$ ]. Results reported in Fig. 2 provide evidence that, for nearly the same value of  $D$ , the relaxation dynamics of the molecules depends strongly on their shape: For elongated molecules all correlators decay on a similar time scale, whereas for more spherical molecules the translational and even- $\ell$  reorientational dynamics relax much slower than the reorientational ones for odd values of  $\ell$ .

The observed peculiar behavior of the odd- $\ell$  reorientational correlators at small values of  $\zeta$  can be interpreted as being caused by the nearby type-A transition, predicted by MCT for hard dumbbells [5]. Evidence for the existence of this transition can be obtained by investigating the  $\zeta$  dependence of the height of the plateaus in the orientational correlation functions, i.e.,  $f_\ell^c(\zeta)$ . MCT predicts that, moving along the ideal glass line, for even- $\ell$  this height decreases smoothly with decreasing  $\zeta$  and becomes zero at  $\zeta = 0$ , reflecting the weakened steric hindrance effects. In contrast to this, the  $\zeta$  dependence of  $f_\ell^c(\zeta)$  for odd- $\ell$  is predicted to show a smooth dependence on  $\zeta$  down to the critical value  $\zeta_c$  discussed above, to vanish at  $\zeta = \zeta_c$ , and then to stay zero for  $\zeta < \zeta_c$ .

These predictions are indeed compatible with the results from our simulations, as demonstrated in Fig. 3 where we plot the  $\zeta$  dependence of  $f_1^c$  and  $f_2^c$ . Starting from large  $\zeta$ , the plateau height  $f_2^c$  decreases smoothly toward the limit

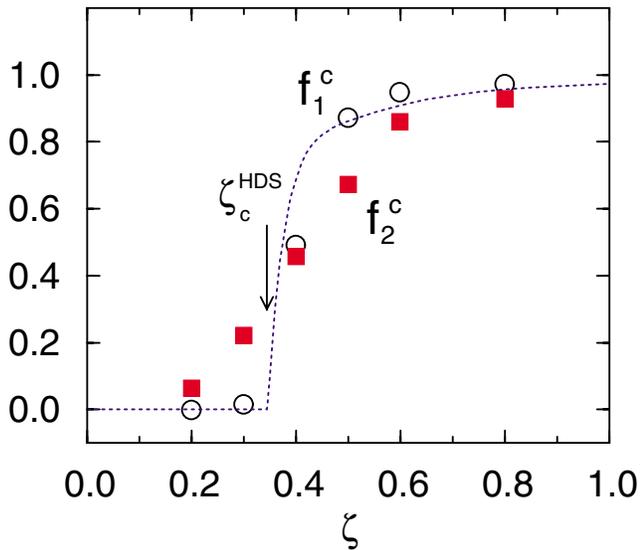


FIG. 3 (color online). Plateau heights  $f_1^c$  (circles) and  $f_2^c$  (solid squares) for AA-dumbbell's correlators  $C_\ell^{(s)}(t)$  for  $\ell = 1$  and  $2$ , respectively. The dotted line represents  $f_1^c$  for the HDS taken from Ref. [5] with the arrow indicating the critical elongation  $\zeta_c^{\text{HDS}}$ .

$f_2^c = 0$  for a spherical system ( $\zeta = 0$ ). Instead, the height  $f_1^c$  decreases smoothly with decreasing  $\zeta$  at large and intermediate  $\zeta$ , but it shows, around  $\zeta = 0.4$ , a sudden drop and becomes zero within the statistical accuracy around  $\zeta = 0.3$ . This behavior suggests the existence of a critical elongation  $\zeta_c$ , which is located between  $\zeta = 0.3$  and  $0.4$ . For the sake of comparison, we have added to Fig. 3 also the theoretical curve  $f_1^c$  for the HDS (dotted line) as well as the location of its critical elongation  $\zeta_c^{\text{HDS}}$  [5]. Note that  $f_1^c(\zeta)$  shows nearly the same  $\zeta$  dependence as the theoretical quantity for HDS, which corroborates the existence of  $\zeta_c$  between  $\zeta = 0.3$  and  $0.4$ , and hence the presence of the type-A transition in molecular systems of small elongations.

Since the appearance of the plateau regime for the even- $\ell$  correlators is due to the cage effect, the results from the simulation for  $\zeta = 0.2$  and  $0.3$  [Figs. 2(c) and 2(d)] imply that (i) the relaxation of the odd- $\ell$  correlators occurs via large-angle flips between the energetically identical orientations  $\vec{e}$  and  $-\vec{e}$ , which do not alter the even- $\ell$  correlators, and (ii) these flips occur before the molecule has left the cage. Such a behavior for the reorientational dynamics is in striking contrast to the strong steric hindrance scenario for large elongations for which the reorientation occurs continuously and on the time scale of the molecule's escape from the cage.

Even for elongations exceeding  $\zeta_c$ , precursor effects of the type-A transition do influence seriously the results for the odd- $\ell$  reorientational dynamics, the most noticeable one being the speeding up of their  $\alpha$  processes [11]. For instance, one concludes from Fig. 2(b) that the steric

hindrance effect is still considerable for  $\zeta = 0.5$  since  $f_1^c$  remains close to 1. However, the canonical order  $\tau_1 > \tau_2$  expected for the strong steric hindrance scenario is violated for  $\zeta = 0.5$ , as can be seen from Fig. 2(b), which is evidence for the nearby type-A transition.

Although strictly speaking the type-A transition discussed here exists only for symmetric molecules in which two ends are identical, most of the mentioned features can be expected to be observable, in the form of precursor effects, also for molecules in which this symmetry is slightly broken. For example, Kammerer *et al.* [15] have studied a system with slightly *asymmetric* dumbbells with  $\zeta = 0.5$ . These authors found  $\tau_1 < \tau_2$  in spite of the large plateau  $f_1^c$ , in full agreement with the present results and the theoretical expectation, indicating that the scenario caused by a nearby type-A transition can indeed be found in a class of molecular systems which are weakly elongated.

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