A Letters Journal Exploring the Frontiers of Physics

October 2008

EPL, **84** (2008) 16003
doi: `10.1209/0295-5075/84/16003`

`www.epljournal.org`

Glassy dynamics in monodisperse hard ellipsoids

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received 1 August 2008; accepted 22 August 2008

PACS `64.70.pv` – Colloids
PACS `61.20.Ja` – Computer simulation of liquid structure
PACS `61.25.Em` – Molecular liquids

Abstract – We present evidence from computer simulations for glassy dynamics in suspensions of monodisperse hard ellipsoids. In equilibrium, almost spherical ellipsoids show a first-order transition from an isotropic phase to a rotator phase. When overcompressing the isotropic phase into the rotator regime, we observe super-Arrhenius slowing-down of diffusion and relaxation, accompanied by two-step relaxation in positional and orientational correlators. The effects are strong enough for asymptotic laws of mode-coupling theory to apply. Glassy dynamics are unusual in monodisperse systems. Typically, polydispersity in size, a mixture of particle species or network-forming covalent bonds are prerequisite to prevent crystallization. Here, we show that a slight particle anisometry acts as a sufficient source of disorder. This sheds new light on the question of which ingredients are required for glass formation.

Hard-particle models play a key role in statistical mechanics. They are conceptually and computationally simple, and they offer insight into systems in which particle shape is important, including atomic, molecular, colloidal, and granular systems. Ellipsoids are a classic model of non-spherical particles. We report here that this simple anisometry can hinder crystallization and facilitate glassy dynamics —a phenomenon which does usually not occur in monodisperse systems. Typically, polydispersity, additional particle species, or other sources of disorder, such as tetra-valency, are needed for the development of glass-like behavior (*i.e.* drastic slowing-down of the dynamics without a change in structure).

In recent years, there have been two studies closely related to our topic, which we briefly summarize here: Letz and coworkers [1] have applied idealized molecular mode-coupling theory (MMCT [2,3]) to the hard-ellipsoid fluid. In addition to conventional mode-coupling theory (MCT) [4], MMCT takes orientational degrees of freedom into account. For nearly spherical ellipsoids, they predicted a discontinuous glass transition in positional and orientational degrees of freedom. MMCT locates the transition inside the coexistence region between the isotropic fluid and the positionally ordered phases. In addition, a continuous transition was predicted upon further compression into the rotator regime. This transition affects only the odd-parity orientational correlators, *e.g.* 180° flips.

However, MCT cannot make statements about crystal nucleation. Hence, the MCT prediction of a glass transition is not sufficient to conclude that the transition will occur in a simulation or experiment. A prominent example is the overcompression of monodisperse hard spheres. Here, the nucleation barrier can be easily crossed, and crystallization always prevents glass formation.

De Michele *et al.* [5] have recently studied the dynamics of hard ellipsoids by molecular dynamics simulations. The states which they simulated were mostly located in the isotropic region. They computed isodiffusivity lines, which showed that the dynamics of the positional and orientational degrees of freedom were decoupled, since the positional isodiffusivity lines crossed the orientational ones at nearly 90°. This decoupling also appeared in correlation functions. The self-part of the intermediate scattering function displayed slight stretching only when overcompressing nearly spherical ellipsoids, while the second-order orientational correlator showed such stretching only for sufficiently elongated particles, *i.e.* near the isotropic-nematic transition. Clear indicators of glassy dynamics, however, would include a strong increase of relaxation times with volume fraction, even pointing towards dynamical arrest. Typically, correlators then develop a two-step decay, whose second step is affected by

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this slowing-down. Such phenomena were not seen in [5] as overcompression was not significant.

We have performed Monte Carlo (MC) and molecular dynamics (MD) simulations for hard symmetrical ellipsoids of length-to-width ratios $l/w = 1.25$ (prolate) and $l/w = 0.8$ (oblate). We overcompressed these systems into the rotator regime (*i.e.* beyond volume fraction $\phi \approx 0.55$ [6]). We found two-step relaxation both in positional and even-parity orientational correlators. Positional and orientational relaxation slow down more strongly than an Arrhenius law. Odd-parity orientational correlators indicate that flipping is not affected. The observed glassy dynamics are strong enough to compare with MMCT. Also, we compare the MC and MD results.

The systems were equilibrated using MC at constant particle number N, pressure P and temperature T [7,8] in a cubic box with periodic boundaries. Each system contained more than 3000 particles. Random isotropic configurations were used as starting configurations. Towards the end of each run, a configuration with a volume fraction close to the average volume fraction was chosen and scaled to the average volume fraction exactly. The systems were considered equilibrated[1] when the volume fraction had settled and all positional and the orientational correlators were independent of absolute simulation time. For production, we used MC and MD. In the MC simulations (now at constant volume) the step sizes were fixed to small values, so that unphysical grazing moves were negligible. The particles then mimic Brownian motion, similar to colloidal ellipsoids suspended in a liquid. The step sizes were the same for all runs, hence a unique time scale could be established. The MD simulations implemented free flight and elastic collisions [9].

The systems had a slight tendency to crystallize to the rotator phase at high volume fractions. To monitor crystallinity, we computed the local positional order using the bond-orientational order parameter q_6 [10]. The fraction of particles which were part of crystalline clusters never exceeded 2.6% and was typically below 0.5%.

To demonstrate the slowing-down of the positional degrees of freedom, we consider the self-part of the intermediate scattering function, $F_\mathrm{s}(q,t) = \langle \exp[i\mathbf{q}\cdot\Delta\mathbf{r}(t)]\rangle$, where $\mathbf{q}$ is the wave vector, $\Delta\mathbf{r}(t)$ the displacement of an ellipsoid after time t, and the angle brackets denote average over particles and ensemble average. In isotropic systems, F_s is a function of the absolute value q only. Decay of $F_\mathrm{s}(q,t)$ indicates that structural relaxation has occured on the length scale set by q. In fig. 1 we show $F_\mathrm{s}(q,t)$ for all simulations. The wavelength q_max was chosen close to the first maximum of the static structure factor (prolate: $6.85/w$, oblate: $7.85/w$), *i.e.* it corresponds to the neighbor spacing. One can clearly see the development of a plateau with increasing volume fraction. This means that there are two distinct stages of relaxation, and the latter slows down dramatically upon increase of volume fraction (note the logarithmic time scale). This two-step decay is a typical phenomenon in glass formers [4]. It is interpreted in terms of particles being trapped in cages formed by their nearest neighbors. The initial decay corresponds to motion within the traps, and the final decay to escape. At high volume fractions, exceedingly cooperative rearrangements are required for escape, making such events rare. Indicators of caging have not been seen in hard ellipsoids before (unless the moment of inertia was strongly increased [11]).

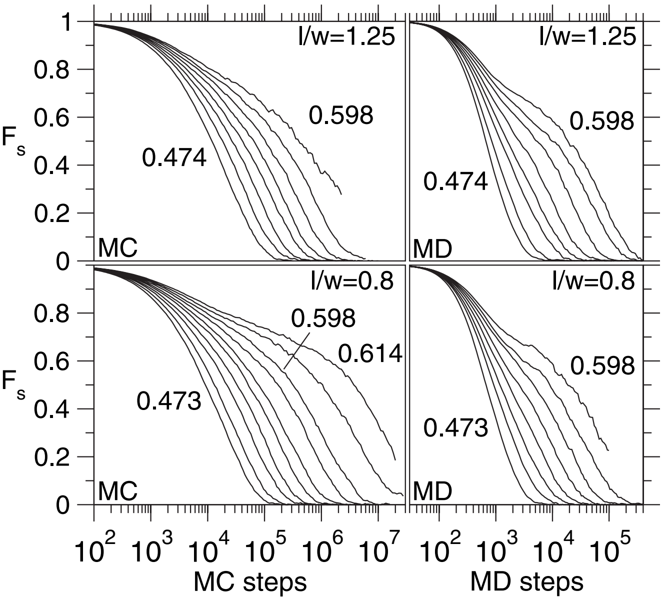

Fig. 1: Self-intermediate scattering functions at several volume fractions ϕ (prolate: 0.474, 0.511, 0.533, 0.551, 0.565, 0.578, 0.588, 0.598; oblate: 0.473, 0.504, 0.533, 0.550, 0.565, 0.578, 0.589, 0.598, 0.606, 0.614). At high volume fractions there is a plateau on intermediate time scales. The final relaxation is slowed down strongly with increasing volume fraction, indicative of glassy dynamics.

Dynamics in the orientational degrees of freedom is observed in terms of the second-order orientational correlator $L_2(t) = (1/2)\langle 3\cos^2\theta(t) - 1\rangle$, where $\theta(t)$ is the angle between the orientation at time t and the original orientation of an ellipsoid. Decay of this function indicates that relaxation of orientational degrees of freedom has taken place. Since $L_2(t)$ is an even function in $\cos\theta(t)$, the head-to-tail symmetry of the particles is taken into account. Figure 2 shows the orientational correlation functions. As in the intermediate scattering functions, plateaus develop at high volume fractions. Evidently, the cages hinder rotations of the ellipsoids. As a consequence, orientational and positional degrees of freedom are coupled. This is in contrast with the decoupling found at lower volume fractions [5].

The shape of both positional and orientational correlators differs between MC and MD on short time scales,

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[1] For the case of overcompression, "equilibrated" here means within the metastable isotropic basin.

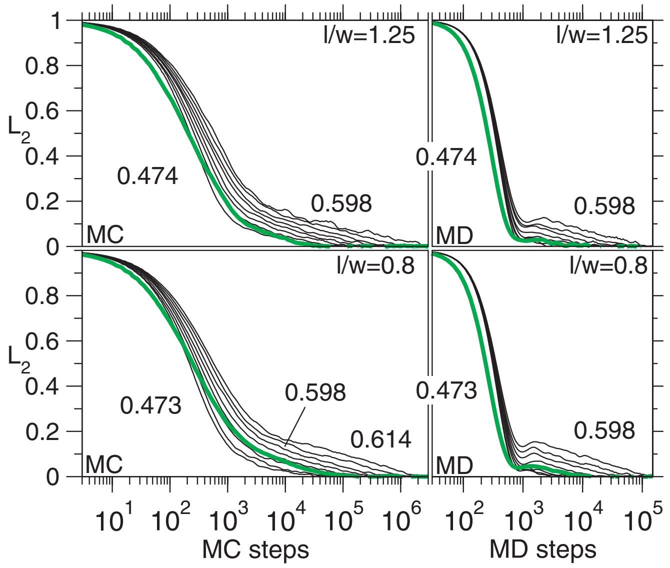

Fig. 2: (Color online) Second-order orientational correlators at several volume fractions ϕ as in fig. 1. Again a plateau develops with increasing ϕ. Hence, orientational degrees of freedom are coupled to the positional ones. Also shown are the third-order correlators at the highest density (bold green lines). They do not slow down, indicating that flipping modes are not affected.

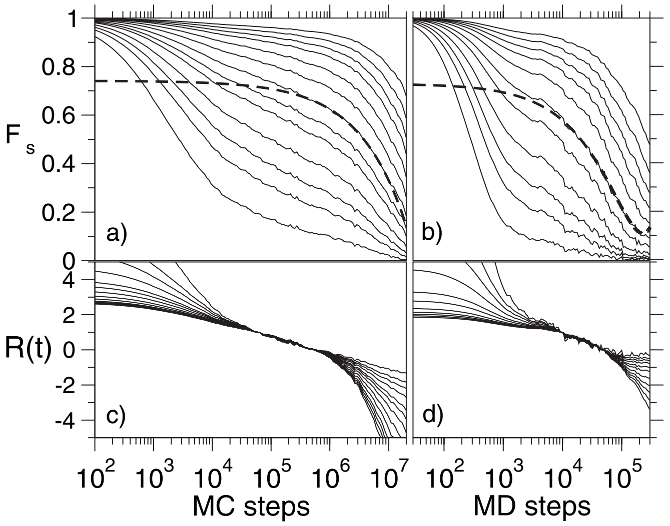

Fig. 3: Self-intermediate scattering functions $F_\mathrm{s}(q,t)$ of a) the oblate system (MC data) and b) the prolate system (MD data) at the highest volume fraction, for the range $2.8 < qw < 20$. The dashed lines show fits to the von Schweidler law $F_\mathrm{s}(q,t) = f_\mathrm{q} - h_\mathrm{q}^{(1)} t^b + h_\mathrm{q}^{(2)} t^{2b}$ with $b = 0.65$. c) and d) show the same data transformed to $R(t) = [F_\mathrm{s}(q,t) - F_\mathrm{s}(q,t_1)]/[F_\mathrm{s}(q,t_2) - F_\mathrm{s}(q,t_1)]$. The collapse of the functions onto master curves demonstrates the factorization property.

reflecting the individual microscopic dynamics. On intermediate and long time scales, they do not differ significantly. Furthermore, when the correlators of the highest few volume fractions are rescaled by their decay time, their long time parts fall onto a master curve. These properties confirm predictions of MCT [12].

Unlike $L_2(t)$, the third-order orientational correlation function $L_3(t) = (1/2)\langle 5\cos^3\theta(t) - 3\cos\theta(t)\rangle$ does not show plateaus (bold green lines in fig. 2). Hence, while the overall reorientation slows down, flipping is barely hindered. This is in accord with the MMCT prediction of Letz *et al.* [1] and has also been found for the case of diatomic Lennard-Jones dumbbells [13], and symmetric Lennard-Jones dumbbells [14]. We note in passing that crystallization, if it occurs, releases the orientational degrees of freedom: The orientational correlators accelerate by three orders of magnitude and no longer have a plateau.

Next, we show that the slowing-down in our systems is strong enough to test MCT asymptotic laws. To this end, we first return to the intermediate scattering functions and focus on their q-dependence at high volume fractions. Figure 3 presents these functions for a) the oblate system (MC) and b) the prolate system (MD; in each case the other method shows similar results), with wavelengths in the range $2.8 < qw < 20$. We test two MCT predictions for the vicinity of the glass transition [4]. Firstly, for the late stages of the plateau and the early stages of the final decay, these functions should be well-fitted by the von Schweidler law (including the second-order correction), $F_\mathrm{s}(q,t) = f_\mathrm{q} - h_\mathrm{q}^{(1)} t^b + h_\mathrm{q}^{(2)} t^{2b}$, where f_q is the plateau height, $h_\mathrm{q}^{(i)}$ are amplitudes, and b is a system-universal exponent (also independent of the microscopic dynamics). Agreement is excellent, as shown for two examples in fig. 3 (dashed lines). MC and MD data of both systems are consistent with $b = 0.65 \pm 0.2$. Secondly, where the $F_\mathrm{s}(q,t)$ are near their plateaus, they should obey $F_\mathrm{s}(q,t) = f_\mathrm{q} + h_\mathrm{q} G(t)$, where h_q is an amplitude, and $G(t)$ is a system-universal function. This relation entails the "factorization property", *i.e.* that $F_\mathrm{s}(q,t)$ can be factorized into a q-dependent and a t-dependent part. To test this property for our systems, we transform $F_\mathrm{s}(q,t)$ to $R(t) = [F_\mathrm{s}(q,t) - F_\mathrm{s}(q,t_1)]/[F_\mathrm{s}(q,t_2) - F_\mathrm{s}(q,t_1)]$, as done in [15], where t_1 and t_2 are times in the regime where the property holds. Since $R(t)$ is not a function of q, all correlators should fall onto a single master curve. Moreover, the curves should remain ordered, *i.e.* a curve which is above another on the left-hand side remains above the other on the right-hand side. Panels c) and d) of fig. 3 demonstrate the validity of the factorization property, and indeed they remain ordered.

We finally demonstrate the applicability of an MCT scaling law for the slowing-down, which even allows us to extract the MCT glass transition volume fraction. Figure 4 shows relaxation times and diffusion constants as a function of volume fraction. The relaxation times are defined as the times at which the positional correlators have reached the value 0.1, and the orientational correlators have reached the value 0.02 (since the plateau is quite low). The diffusion constants were determined from the mean squared displacements via the Einstein relation $D = \lim_{t\to\infty} \frac{\mathrm{d}}{\mathrm{d}t}\langle(\Delta\mathbf{r}(t))^2\rangle/6$. The upper panels

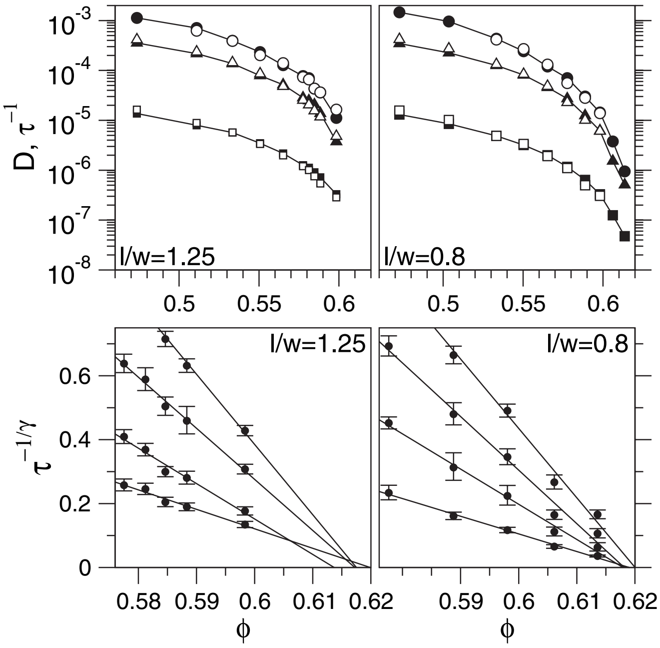

Fig. 4: Upper panels: inverse relaxation times τ^{-1} obtained from $F_{\mathrm{s}}(q_{\max}, t)$ (triangles) and from $L_2(t)$ (circles), and diffusion constants D (squares), as a function of volume fraction ϕ. MC data (filled symbols, lines to guide the eye, and rescaled to match MD time scale) and MD data (open symbols) show excellent agreement. Lower panels (MC data only): $\tau^{-1/\gamma}$ multiplied by arbitrary factors for clarity, from $F_{\mathrm{s}}(q,t)$ (several values of q) and $L_2(t)$, demonstrating the validity of the MCT scaling law $\tau^{-1} \propto (\phi_c - \phi)^\gamma$. $\gamma = 2.3$. The straight-line fits indicate a glass transition volume fraction of $\phi_c = 0.615 \pm 0.005$ (prolate system) and $\phi_c = 0.618 \pm 0.005$ (oblate system). MD data agree.

of fig. 4 show inverse relaxation times τ^{-1} obtained from $F_{\mathrm{s}}(q_{\max}, t)$ (triangles) and from $L_2(t)$ (circles), and diffusion constants D (squares). The MC values (filled symbols) have been multiplied by a factor of 24 (prolate) and 18 (oblate) to match the MD time scale (L_2: 19 and 16, respectively). The errors are of symbol size or less. Note that in each system, one common factor for the positional variables yields excellent agreement between MC and MD (open symbols), in agreement with MCT. The factor for the orientational relaxation times need not be the same since it depends on the choice of the orientational MC move size. The slowing-down of all variables is super-Arrhenius. According to MCT, it should approach a power law of the form $D \propto \tau^{-1} \propto (\phi_c - \phi)^\gamma$, where ϕ_c is the MCT glass-transition volume fraction, and γ is related to the von Schweidler exponent b. Both ϕ_c and γ should be system-universal. In the lower panels of fig. 4 we demonstrate the validity of this prediction for the MC results of $F_{\mathrm{s}}(q,t)$ (from top: prolate: $qw = 6.85$, 11, 16; oblate: $qw = 7.85$, 16, 20) and L_2 (bottom). The exponent $\gamma = 2.3$ was chosen in agreement with $b = 0.65$. The straight-line fits comply with a common $\phi_c = 0.615 \pm 0.005$ for the prolate system and with $\phi_c = 0.618 \pm 0.005$ for the oblate system. The fact that there is a common value for positional and orientational relaxation times further demonstrates the strong coupling of these degrees of freedom. We found agreement with the analogous analysis of the MD data. The values we found differ from the MMCT predictions of Letz *et al.* [1], *viz.* $\phi_c = 0.540$ and 0.536 ($l/w = 1.25$ and 0.80, respectively). The mismatch between the numerical MCT calculations based on static structure, and scaling law fits based on simulated dynamics is, however, not unusual [16,17] and has been attributed to activated ("hopping") processes for which MCT does not account. A similar mismatch is found in the hard-sphere system [18]. We note that the present study also displays the prolate-oblate symmetry seen in previous work on the equilibrium properties and dynamics of ellipsoids [1,5,6]. However, we observed that crystallization does not have this symmetry: the prolate system crystallizes more readily.

In summary, we have performed molecular dynamics and Monte Carlo simulations of the hard-ellipsoid fluid. In this very simple anisometric model we observe glassy dynamics sufficiently strong that MCT asymptotic scaling laws can be tested and are found to apply. We find strong coupling of positional and orientational degrees of freedom, leading to a common value for the glass-transition volume fraction ϕ_c for positional and orientational relaxation times ($l/w = 1.25$: $\phi_c = 0.615 \pm 0.005$, $l/w = 0.80$: $\phi_c = 0.618 \pm 0.005$). The presence of glassy dynamics has been predicted by MMCT. However, as MMCT cannot make a statement about crystallization, a test by simulation was required. We argue that particle anisometry acts as a sufficient source of disorder to prevent crystallization. This sheds new light on the question of which ingredients are required for glass formation. Experimental studies of glassy dynamics in the isotropic phase of liquid crystals have been conducted [19], but not in ellipsoids. It is possible to synthesize ellipsoids of colloidal size [20,21] and to study their dynamics with confocal microscopy [22]. In the light of the above, an experimental study of glassy dynamics in colloidal hard ellipsoids seems very promising.

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This work was supported by the Emmy Noether Program and SFB TR6 of the Deutsche Forschungsgemeinschaft (DFG), and the European Network of Excellence SoftComp. We are grateful to M. P. Allen for sharing his molecular dynamics code, to the NIC, Jülich for computing time, and to K. Binder, R. Schilling, M. P. Allen, J. Horbach, J. Baschnagel, W. Kob, M. Letz and W. A. Siebel for helpful suggestions.

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