Decoupling of translational and rotational diffusion in quasi-2D colloidal fluids

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We observe the translational and rotational diffusion of dimer tracer particles in quasi-2D colloidal samples. The dimers are in dense samples of two different sizes of spherical colloidal particles, with the area fraction $\phi$ of the particles varying from dilute to nearly glassy. At low $\phi$ rotational and translational diffusion have a ratio set by the dimer size, as expected. At higher $\phi$ dimers become caged by their neighboring particles, and both rotational and translational diffusion slow. For short dimers we observe rapid reorientations so that the rotational diffusion is faster than translational diffusion: the two modes of diffusion are decoupled and have different $\phi$ dependence. Longer dimers do not exhibit fast rotations, and we find translational and rotational diffusion stay coupled for all $\phi$. Our results bridge prior results that used spheres (very fast rotation) and long ellipsoids (very slow rotation).

I. INTRODUCTION

A comprehensive explanation for the dramatic increase in viscosity on approaching the glass transition is still lacking, although there are a variety of theories \cite{10}. What makes the matter more complicated is the inadequacy of the traditional concept of viscosity and its relation with microscopic diffusion in supercooled liquids. In liquids, the Stokes-Einstein-Sutherland equation \cite{4,5} relates microscopic translational diffusion ($D_T$) as inversely proportional to solvent viscosity $\eta$. Rotational diffusion ($D_R$) is also inversely proportional to $\eta$, known as the Stokes-Einstein-Debye relation. Further, the ratio of translational to rotational diffusion constants ($D_T/D_R$) should be independent of viscosity and temperature. However, many experiments and simulations \cite{6,7} have shown a violation of the Stokes-Einstein and Stokes-Einstein-Debye relations in supercooled liquids. These violations can manifest as $D_T$ and/or $D_R$ no longer being inversely related to $\eta$, and also $D_T/D_R$ no longer being a constant.

Pioneering experiments in the early 1990’s observed a violation of these relations on approaching the glass transition in ortho-terphenyl \cite{8,9}. Rotation and translational diffusion constants were measured indirectly through spin-relaxations. They observed an enhancement of translation relative to rotation approaching the glass transition. At the time, this strange difference was attributed to spatial distribution of rotational timescales $\rho(\tau)$, and measured rotation and translation measurements being sensitive to different moments of this distribution \cite{10}. But it was thought that on the single molecule scale, translation and rotation remain coupled.

However, recent simulations and colloidal experiments have found that decoupling occurs even at the single particle level \cite{11,12}. The current hypothesis is that decoupling occurs due to translation and rotation degrees encountering different dynamic length scales \cite{15}. Moreover, some studies found that translation was enhanced relative to rotation \cite{14,16,17}, whereas others found rotation was enhanced relative to translation \cite{11,13}. These different experiments had different probe shapes and conditions so direct comparison of the observations is challenging.

In this study we examine how the probe details influence translational-rotational decoupling in colloidal samples. Colloidal samples at high concentration have been established as model glass formers \cite{18,19}, and have the advantage that individual particles can be visualized. Here we use naturally occurring anisotropic silica dimers of different aspect ratio as tracers, and find that the dimer length determines translation-rotation decoupling.

These dimers are at a very low concentration, less than 5 percent and the experiments are the same as previously published (where we studied only the monomer particles\cite{20}). We find that for dimers of smaller lengths, rotations do not slow down as much as translations, on approaching the glass transition, similar to the case of spheres as probes \cite{13}. However we find that in our longest dimers, $D_T$ and $D_R$ remain coupled at all concentrations, i.e. $D_T/D_R \sim$ constant. Figure 1 shows an

FIG. 1: Left - short dimer ($l_1 = 3.92\mu m$) in concentrated sample. Right- long dimer ($l_1 = 5.37\mu m$) in concentrated sample $\phi = 0.79$. Rendering is adapted from particle positions. Dimers are in red, and neighbors in blue.

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example computer rendering of a long dimer and short dimer in one of our samples. Our key result is that the shorter dimer can rotate more easily as it is easier to relax the steric hindrance of the neighboring particles.

II. MATERIALS AND METHODS

A. Experimental methods

For this work we reanalyze movies corresponding to previously published data [20]. In the experiments we use gravity to confine bidisperse non-functionalized silica particles to a monolayer (diameters $\sigma_S = 2.53$ and $\sigma_L = 3.38$ $\mu$m, Bangs Laboratories, SS05N). The number ratio is $N_L/N_S = 1.3 \pm 0.5$, and varies from sample to sample. The control parameter is the area fraction $\phi$, with glassy samples found for $\phi > 0.79$; the data we present here are all with $\phi < 0.79$. The particles are sedimented to the microscope coverslip of our sample chamber prior to observation. The coverslip is made hydrophobic by treatment with Alfa Aesar Glassclad 18 to prevent particle adhesion, and indeed we do not observe any particles stuck to the glass. We do not add salt. We verify that in all experiments, only one layer of particles is present (ensured by keeping the overall particle concentration below the level that requires a second layer to form). We use brightfield microscopy and a CCD camera to record movies of particles diffusing.

The samples have naturally occurring dimers at dilute concentrations from $2 - 5\%$. The dimers are stable during our observations. Moreover, all dimers are made of identical particles (either two small particles or two large particles), indicating they are formed prior to the experiment; they seem to be present in the samples as received. Rather than being two spheres barely touching, they are somewhat fused together, as can be seen in Fig. 2(a). The aspect ratio (length/width) is always less than two, and varies from dimer to dimer.

B. Imaging and tracking dimers

We need to follow the translational and rotational motion of the dimers. We start by using standard particle tracking software [21] to track the two particles of a dimer, as shown in Fig. 2(b). Next we select the region of the image (ROI) that included dimers. Based on brightness, we threshold this ROI to get a black and white image (Fig. 2(c)). We identify connected regions in this thresholded image, and selected the largest such region as the dimer of interest. The length of the longest axis of this connected region is measured as $l_s$, and then we identify the length of the short axis $l_d$, as the longest distance across the connected region perpendicular to the long axis. The aspect ratio then is $l_s/l_d$.

Recent work has shown that two-dimensional glass-forming systems need to be analyzed slightly differently than 3D systems [22, 23]. The key concern is that 2D systems are subject to Mermin-Wagner fluctuations which move particles locally but do not lead to structural rearrangements [22, 28]. Particles are “caged” by their neighbors, but Mermin-Wagner fluctuations result in coherent motion of the cage. Analyzing the motion of particles relative to their cage neighbors removes the influence of these fluctuations, making apparent the motions that lead to structural relaxation [29].

Accordingly, to determine the relaxation time scale for our samples, we define the cage relative translational correlation function as: $F_{S-CR}(k, \Delta t) = \langle \exp(i \vec{k} \cdot \Delta \vec{r}_{CR}) \rangle_t$ where $\Delta \vec{r}_{CR} = \vec{r}(t + \Delta t) - \vec{r}(t) - \frac{1}{N} \sum_j [\vec{r}_j(t + \Delta t) - \vec{r}_j(t)]$, where $j$ denotes the nearest neighbors of the particle at the initial time $t$, and the sum is over all neighbors. The $\alpha$ relaxation timescale $\tau_\alpha$ is the timescale when $F_{S-CR}$ reaches 0.37, and defines the time scale over which the sample has significant structural rearrangements [20].

The cage relative mean square displacement (MSD) is defined using the same displacements $\Delta \vec{r}_{CR}$. We measure the long time translational diffusion coefficient $D_T$ from the cage relative MSD. For our tracers, we do not see a significant difference between the MSD and the cage-relative MSD in the observed area fraction range. However, softer samples are known to have larger differences [22, 23]. We are interested in the $\Delta t \to \infty$ behavior, so distinctions between motion along the dimer axis and perpendicular to that axis will not be important to us [30]. Rotational mean square displacements (MSD$_R$) do not require cage-relative analysis. For the MSD$_R$ we identify the instantaneous angle $\theta(t)$ of a dimer (in radians); unwrap this angle so that it can take values smaller than 0 or larger than $2\pi$; and then compute the MSD$_R$ from this unwrapped angle.
C. Hydrodynamic theory

The dimers we analyze have an aspect ratio $l_1/l_2 < 2$, whereas for perfect dumbbells have aspect ratio 2. Nonetheless, a reasonable starting approximation is to model our dimers as dumbbells. For dumbbells in a liquid the ratio of translational to rotational diffusion coefficients $\frac{D_T}{D_R}$ is given as

$$\frac{D_T}{D_R} = \frac{\sigma^2}{4}$$

where $\sigma$ is the diameter of particles in the dumbbell. This predicts a ratio of 1.60 $\mu$m$^2$ for a dimer composed of two small particles in our experiment and 2.86 $\mu$m$^2$ for a dimer composed of two large particles.

Figure 3 shows $D_T/D_R$ as a function of dimer length $l_1$ in a medium-concentration sample. The data are scattered with no systematic dependence on $l_1$. The dashed line shows Eqn. 1 and the data are within a factor of two of this prediction. This is reasonable, as (1) our dimers are not the perfect dumbbell shape as assumed by theory, and (2) Eqn. 1 does not take into account the hydrodynamic influence of the bottom wall $[32]$, which affects translational and rotational modes differently $[30, 33]$. It is also possible that the different values of $l_1$ for dimers ostensibly made from identical particles give rise to dimers of different shapes (different amounts of overlap of the two particles) which could account for the scatter in our data. In sum, we recognize an inherent uncertainty for the ratio of $D_T/D_R$ of about a factor of 2, and will look for this ratio to vary by more than a factor of two as we approach the glass transition.

III. RESULTS

Figure 4 shows translational and rotational MSDs in medium concentration (A,B) and high concentration (C,D) samples corresponding to different length dimers. For the medium concentration samples ($\phi = 0.55$) all MSDs rise diffusively, MSD $\sim \Delta t$, as can be seen by comparing the data to the straight black line which has slope 1. The long dimer diffuses a bit slower, as seen by the blue diamonds lying below the red circles in (A,B). Interestingly at large concentration ($\phi = 0.79$), in Fig. 4(C,D), we see that while the translational MSD is similar for the short and long dimers, the rotational MSD is much different (Fig. 4D). Comparing Fig. 4A and C, we see that both long and short dimers show a similar slow down in translation. However, Fig. 4B and D are very different. Here, long dimers (blue diamonds in this graph) show a much larger slowdown in rotation as compared with short dimers (red circles).

Figure 5 shows the trajectories of the dimers corresponding to Fig. 4. For the medium concentration sample (A), long and short dimers have similar trajectories. In contrast, the concentrated sample (C) shows that the long dimer (blue) spends more time localized (perhaps with a reversible cage rearrangement event in the middle $[34]$, and an irreversible jump at the end). The shorter dimer (red) moves more frequently.

Additionally, we track the angular motion of each
The translation diffusion coefficient $D_T$ (using cage-relative displacements) is measured as $\langle \Delta R^2_{\text{CR}}(\Delta t) \rangle = 4D_T \Delta t$. The average is over all particles and all initial times. The rotational diffusion coefficients are measured similarly, through $\langle \theta^2(\Delta t) \rangle = 2D_R \Delta t$, where $\Delta \theta$ is angular displacement in $\Delta t$. Figure 7(a) plots $D_T$ as a function of $\tau$ for all samples. Here we see that all dimers follow the black line, which is the bulk $D_T$ of the spherical particles in the sample. The black curve follows $D_T \sim \tau^{-0.73}$, which is in the range of exponents observed in other experiments [7, 14].

Rotational diffusion also slows for glassy samples as shown by the data for $D_R$ in Fig. 7(b). In contrast with $D_T$, these data become more scattered for the samples closer to the glass transition (larger $\tau$). It is apparent that the slowest rotational diffusion is seen for the longest dimers (blue diamonds) which slow by $\sim 10^2 - 10^3$ as $\tau$ grows by $10^3$. In contrast, the shortest dimers (red circles) decrease by only $\sim 10^1$ over the same range. The difference between $D_R$ of the long and short dimers is more than an order of magnitude at the largest $\tau$. The mild decrease in $D_R$ for the short dimers is similar to that seen with spherical colloids in a prior experiment [13]. Overall, this is what we expect based on the conceptual sketch of Fig. 4: long dimers require their neighbors to move out of the way to facilitate their rotation, whereas short dimers are constrained less by their neighbors. Likewise this is supported by Fig. 5(d) where the short dimer makes large jumps in angle.

We examine decoupling of rotational and translational diffusion by plotting $D_T/D_R$ in Fig. 7(c). The long dimers (blue diamonds) show a constant $D_T/D_R$ independent of $\tau$; here the two diffusion constants are coupled at all area fractions. In contrast, the short dimers (red circles) show a decrease in $D_T/D_R$ with increasing $\tau$. The colored lines show best fit lines for the three different dimer length regimes. At the largest $\tau$, the difference between $D_T/D_R$ of the long and short dimers...
FIG. 7: Diffusion coefficients as a function of \( \tau_\alpha \) for different dimer lengths. (a) Translational diffusion constants \( D_T \). The line denotes bulk sample \( D_T \), that is, the diffusion coefficient of the spherical bath particles. (b) Rotational diffusion constants \( D_R \). (c) The ratio \( D_T/D_R \). In all panels, the different colors denote different ranges of \( l_l \) as indicated in the legend in panel (a).

is more than an order of magnitude. We see decoupling: while both rotational and translational diffusion slow as the glass transition is approached, rotational diffusion slows less dramatically – at least for the short dimers.

Organizing the data based on dimer length shows a clear trend from long dimers (no decoupling) to short dimers (decoupling); another possible variable is the aspect ratio. Figure 8(a) shows \( D_T/D_R \) plotted as a function of \( \tau_\alpha \), equivalent to Fig. 7(c), but here different colors denote different ranges of \( l_l \) as indicated in the legend.

Fig. 7(c). Hence the longest axis seems to be the relevant parameter, rather than aspect ratio. A final way to think about the data is motivated by Fig. 5(d) showing that the short dimers can rotate by 180º; this is presumably because their cage of neighboring particles expands slightly, allowing the rotation. The expansion distance can be estimated as \( l_l - l_s \), arguing that the neighbors start \( \sim l_s \) away from the middle of the dimer and expand to \( \sim l_l \) to allow the long axis to rotate past them. This suggests that the \( l_l \) dependence [Fig. 7(c)] could be a dependence on \( l_l - l_s \). This seems plausible; Fig. 8(b) shows the data with color indicating different ranges of \( l_l - l_s \), which reasonably well separates the faster rotating dimers (red dimers, small \( l_l - l_s \)) from the slower rotating dimers (green squares, large \( l_l - l_s \)). The fact that \( l_l \) works slightly better [Fig. 7(c)] may be because the number of neighbors that need to move scales as \( l_l \), independent of \( l_s \). Previous simulations found that quantifying translation-rotation decoupling depends on the analysis method [12, 35]. The “Debye method” uses dot products of the initial and final orientation of a tracer; using this method to measure \( D_R \) changed the nature of decoupling [12, 35]. We also measured \( D_R \) from this formalism, in the same way as by Edmond et al [14]. We find that both methods to measure \( D_R \) give the same
result within error, as also found by Edmond et al.

Our results indicate that the longest dimension controls how the particle rotation is sterically constrained by the neighbors on approaching the glass transition. Figure 1 suggests this may be because the longest dimension determines how many neighboring particles can restrict rotational motion.

IV. DISCUSSION

Prior groups have studied glass transitions in colloidal glasses composed of anisotropic particles [13, 14, 17]. Kim et al. [13] studied rotation and translation of optically anisotropic spheres (aspect ratio 1). Here, $D_T/D_R$ in the concentrated regime was almost 2 orders of magnitude smaller than the dilute limit [13]. As spheres rotate without any steric hindrance from neighboring spheres, in this experiment, translation slows down more than approaching the glass transition [15, 19].

Other experiments by Zheng et al. looked at ellipsoids of aspect ratios varying from 2.5 to 6 [16, 17]. For the small aspect ratio of 2.3, $D_T/D_R$ did not change approaching the glass transition, similar to what we see with our long dimers. For the large aspect ratio 6, however, $D_T/D_R$ was a magnitude higher than the dilute limit, indicating that rotation slows down more than translation. This study concluded that the decoupling with enhanced translational motion occurs for situations with aspect ratio $\geq 2.5$ [17]. A similar observation of enhanced diffusion was seen by Edmond et al. who studied tetrahedral cluster tracers in a 3D sample of spherical particles [14]. There, the ratio between the longest dimension of the tracer to the mean particle size was 2.9. While a direct comparison between 2D ellipsoids and 3D tetrahedra seems dubious, nonetheless the observations of Edmond et al. [14] is in conceptual agreement with the observation of Zheng et al. [17].

Our dimer experiments bridge the gap between aspect ratio $\sim 1.3 - 2$. We see that close to the glass transition, small changes in dimer length cause significant changes in rotational diffusion. Smaller dimers show a weaker slowdown in rotation on approaching the glass transition. This is because smaller dimers rotate more freely even in a dense sample. Figure 5(d) shows that this easier rotation is likely due to slight motions of neighboring particles which momentarily allow a rotation of 180° for the short dimers. The results of Kim et al. with spheres [13] are the logical limit of our results, where a particle can rotate freely with only hydrodynamic interactions with neighbors, but no steric hindrance to rotation.

In our experiments, translational diffusion is not affected as much by the dimer length. This is in marked contrast to previous experiments in polymer glasses, where translational diffusion was found to be affected by shape, and not rotational diffusion [36]; in polymer experiments, translational diffusion slowed down more than rotational diffusion as the glass transition was approached. These results are different from what we see, but more like the long ellipsoid experiments [16, 17].

In summary, our results span the prior colloidal observations, and collectively these observations show that steric interactions affecting rotational diffusion depend in an important way on the longest dimension of the tracer particles. This highlights the importance of steric interactions for understanding decoupling of translational and rotational diffusion near the glass transition.

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