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LETTER TO THE EDITOR

Ageing dynamics of translational and rotational diffusion in a colloidal glass

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Abstract

We study the dynamics of translational and rotational diffusion during the ageing of a colloidal glass of Laponite using polarized and depolarized dynamic light scattering. The dynamics are qualitatively similar between the two degrees of freedom. The short-time diffusion is independent of the time elapsed since the sample preparation. The intermediate- and long-time diffusion, on the other hand, slows down by several orders of magnitude during the ageing. The slowing down of the rotational diffusion is found to be much faster than that of the translational diffusion.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Colloidal glasses are good experimental models to study glassy dynamics. Indeed, perhaps the most convincing evidence for the applicability of the classical mode-coupling theory (MCT) for glasses comes from studies on hard-sphere colloidal systems [1]. Significant progress on the understanding of the glassy dynamics was made recently by extending the MCT below T_g [2]. The most fundamental difference is that below T_g the system is not in equilibrium, and evolves indefinitely: the system is said to age. Here, we study the ageing of a colloidal system made of charged anisotropic particles that is approaching a non-ergodic glassy state. The evolution of translational diffusion and rheological properties of this system have been

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well studied [3–8]. The translational motion of the particles slows down concomitant with the growth of complex viscosity of the system. Despite these various studies of the ageing dynamics of translational diffusion and viscoelastic response of this system, no information is available on the ageing dynamics of the particles' rotational coordinate. In addition to the slowing down of the translational diffusion during the ageing, the ageing dynamics of the rotational motion of the particles can also be investigated using depolarized dynamic light scattering. We ask whether the rotational degree of freedom also slows down and, if it does so, whether that happens at the same rate as the translational degree of freedom. This allows us to study whether translational–rotational decoupling can be observed in colloidal glasses. Such decoupling is characteristic of supercooled liquids or glasses with dynamic heterogeneity [9, 10]. Recent studies on (hard-sphere) colloidal glasses reveal the presence of such dynamical heterogeneities for these systems [11]; it would be interesting to see whether this has repercussions for the rotational dynamics. Hence we report here, for the first time, the evolution of the rotational diffusion during the ageing of the system.

2. Experimental details

We study charged colloidal discs of Laponite, with radius of 15 nm and 1 nm thickness. We focus on the concentration region where the suspension is known to form a glass (2–3.5 wt%, ionic strength 10^{-4} mol l^{-1}) [4]. Since Laponite can absorb water up to 20% of its weight, it was first dried in an oven at 100 °C for one week and was subsequently stored in a desiccator.

Laponite solutions are prepared in ultra-pure Millipore water (18.2 MΩ cm^{-1}) with NaOH to obtain a pH = 10 and are stirred vigorously for 1:45 h to make sure that the Laponite particles are fully dispersed. The dispersions are filtered using Millipore Millex AA 0.8 μm filter units to obtain a reproducible initial state [4]. This instant defines the zero of waiting time, $t_w = 0$.

A standard dynamic light scattering set-up (He–Ne laser, ALV-60X0 correlator), equipped with a polarizer and an analyser, allowed us to measure the VV and VH intensity correlation functions. Correlation functions were measured every 10 min for a concentration of 2.5 wt% and every 5 min for 3 wt%.

Due to their intrinsic optical and geometrical anisotropy, the Laponite particles provide us with the possibility of measuring the rotational diffusion coefficient using depolarized dynamic light scattering.

The total electric field scattered by particles with axially symmetric optical anisotropy (when the incident electric field is linearly polarized in the vertical direction) has two components; the first is the vertically *polarized* component E_{VV} with an amplitude proportional to the average polarizability. The second one is the horizontal *depolarized* component E_{VH}. Its amplitude is proportional to the intrinsic anisotropy of particle β, which is the difference between the polarizabilities parallel and perpendicular to the optical axis. Polarized and depolarized dynamic light scattering (DLS and DDLS) experiments measure the time correlations of VV and VH scattered intensities ($I = EE^\star$), respectively. Assuming that orientations of different particles are uncorrelated and decoupled from the translation, the measured correlations at scattering vector $\vec{q}$ (with modulus $q = \frac{4\pi n}{\lambda}\sin(\frac{\Theta}{2})$, Θ being the scattering angle, λ the wavelength and n the refractive index of the solvent) are

$$g^{(2)}_{VV}(q,t) = \frac{\langle I_{VV}(q,t)I_{VV}(q,0)\rangle}{\langle I_{VV}(q)\rangle^2} = 1 + \left[\frac{\alpha^2 F_c(q,t) + \frac{4}{45}\beta^2 F_r(t)F_s(q,t)}{\alpha^2 + \frac{4}{45}\beta^2}\right]^2 \tag{1}$$

$$g^{(2)}_{VH}(q,t) = \frac{\langle I_{VH}(q,t)I_{VH}(q,0)\rangle}{\langle I_{VH}(q)\rangle^2} = 1 + [F_s(q,t)F_r(t)]^2 \tag{2}$$

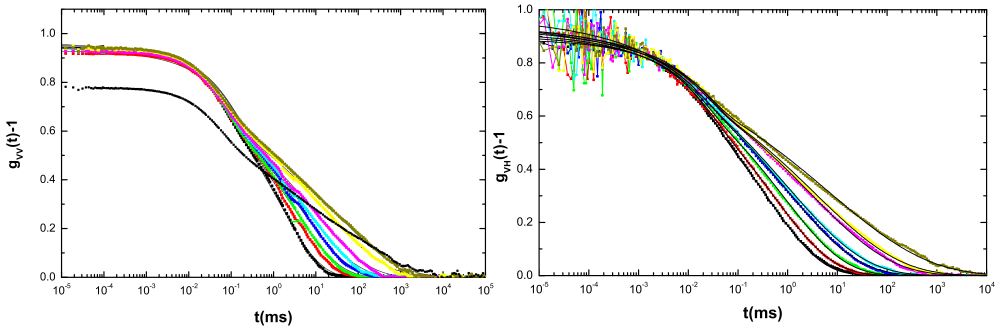

Figure 1. Evolution of polarized (VV) and depolarized (VH) intensity correlation functions (symbols) and their corresponding fits (solid curves) according to equation (3) for Laponite 3 wt% (pH $= 10$) water, at scattering angle 90°. The curves are measured at increasing waiting times (from left to right) that are ($t_{\mathrm{w}} = 19, 42, 64, 86, 108, 130, 152, 174, 213$ min) for VV correlations and ($t_{\mathrm{w}} = 25, 48, 70, 92, 102, 136, 158, 179$ min) for VH correlations.

where α is the average polarizability of the particles; $F_{\mathrm{c}}(q,t) = \frac{1}{N}\sum_{i,j}^{N}\langle \exp(\mathrm{i}\vec{q}\cdot[\vec{r}_i(0) - \vec{r}_j(t)])\rangle$ is the dynamic structure factor. It is related to the collective diffusion. $F_{\mathrm{s}}(q,t) = \langle \exp(\mathrm{i}\vec{q}\cdot[\vec{r}_i(0) - \vec{r}_i(t)])\rangle$ is the translational self-correlation function and $F_{\mathrm{r}}(t) = \langle Y^{*}_{2,-1}(\hat{u}(0))Y_{2,-1}(\hat{u}(t))\rangle$ is the rotational self-correlation function in which $\hat{u}(t)$ is the unit vector determining the orientation of a particle at time t. The contribution of the rotational motion to the VV correlation is proportional to $\frac{4}{3}\frac{I_{\mathrm{VH}}}{I_{\mathrm{VV}}}$. From measuring the relative values of VV and VH photon count rates, this ratio turns out to be around 0.02. Hence the dynamics of $g^{(2)}_{\mathrm{VV}}$ reflects mainly the translational diffusion of the particles, while $g^{(2)}_{\mathrm{VH}}$ is determined by both translational and rotational motion. Note that due to the particles' anisotropy the diffusion coefficients in the direction parallel $D_{\parallel}$ and perpendicular $D_{\perp}$ to the axis of the disc are not equal. In DLS experiments one measures a sort of average diffusion $D^{\mathrm{t}}_0 = 1/3(D_{\parallel} + 2D_{\perp}) = \frac{kT}{12\eta R}$ for translational diffusion. Here η is the solvent viscosity. The rotational degree of freedom around the symmetry axis cannot be detected by DDLS, hence we only consider the rotation of the symmetry axis for the rotational diffusion $D^{\mathrm{r}}_0 = \frac{3kT}{32\eta R^3}$.

3. Results

Aqueous Laponite dispersions are initially fluid, but undergo ageing [3, 6]. This means that relevant physical observables of the system change with waiting time. Here we measure the intensity correlations of scattered light from Laponite dispersions in VV and VH modes. One observes two regimes of ageing in the evolution of the intensity correlations: in the first regime the system is ergodic and the slowing down of dynamics is very fast, whereas the second one corresponds to a non-ergodic (arrested) state. The cross-over from the former to the latter is visible because the normalized correlation function no longer varies between one and zero: some of the degrees of freedom are frozen in on the timescale of the measurement. Here we mainly focus our study on the evolution of the system in the first ageing regime.

Figure 1 shows the evolution of VV and VH correlation functions for a 3 wt% sample measured at a fixed scattering angle of $\Theta = 90°$. The acquisition time for each measurement is set to 5 min allowing for sufficient statistics considering the low count rate in VH mode, and assuming that no significant ageing of the system occurs during the measurement. For the VH measurements, similarly to what has already been found for the VV correlation functions [5], a two-step relaxation can be observed. The first one observed for short delay times $t < 10^{-2}$ ms

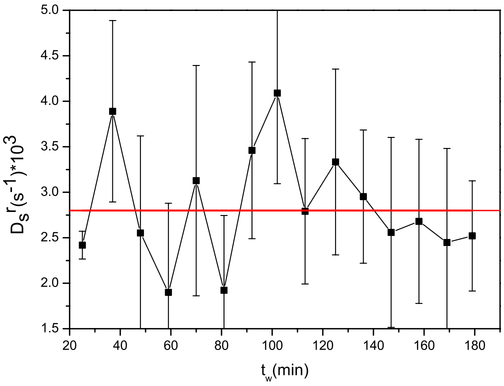

Figure 2. Short-time rotational diffusion versus waiting time (note the large error bars are due to noisy data at short times).

is fast and appears to be practically independent of the waiting time (figure 2). The second relaxation time, observed for longer delay times, depends strongly on the waiting time. For waiting times longer than 3 h the system becomes non-ergodic. This shows up in the correlation function: it no longer goes from approximately one to zero.

In order to describe the two processes quantitatively, we fit the normalized correlation functions, both VV and VH, by a sum of an exponential and a stretched exponential as

$$g^{(2)}(q,t) - 1 = B[A\exp(-t/\tau_1) + (1-A)\exp(-(t/\tau_2)^a)]. \tag{3}$$

The stretched exponential is used since it has been found empirically that it provides a good description of the slow relaxation processes encountered in glassy systems [5, 13]. To ensure the accuracy of the extracted value for short-time diffusion and constrain the fitting procedure, we first determined τ_1 independently using a linear fit for $\ln(g_{\mathrm{VH}}^{(2)}(q,t) - 1)$ for short times $t < 0.003$ ms, corresponding to the short-time diffusion.

From the VH data, we find $D_{\mathrm{s}}^{\mathrm{r}} = 2.8 \times 10^3\ \mathrm{s}^{-1}$ after subtracting the contribution of translational diffusion. This value is roughly two orders of magnitude smaller than the one calculated for dilute solution of hard discs (i.e., colloids without charges) ($1.1 \times 10^5\ \mathrm{s}^{-1}$). This probably results from both hydrodynamic and electrostatic interactions [14, 15], which restrict the rotational motion of the particles. This result is in contrast to the short-time translational diffusion, which is half that of the hard discs. For Laponite 3 (2.5) wt% we have $\frac{D_0^{\mathrm{t}}}{D_{\mathrm{s}}^{\mathrm{t}}} = 2.3\ (1.4)$, $\frac{D_0^{\mathrm{r}}}{D_{\mathrm{s}}^{\mathrm{r}}} = 36.6\ (22)$. Since Laponite particles have an aspect ratio of 30, we have used the diffusion coefficients of infinitely thin discs for them, not so different from the one calculated for the oblate ellipsoids of an aspect ratio 30 [12]. For hard discs of radius $R = 15$ nm the translational and rotational diffusion coefficients are $D_0^{\mathrm{t}} = 2.59 \times 10^{-11}\ \mathrm{m}^2\ \mathrm{s}^{-1}$ and $D_0^{\mathrm{r}} = 1.1 \times 10^5\ \mathrm{s}^{-1}$, respectively.

The slow relaxation time τ_2 is found to grow exponentially as a function of waiting time (t_{w}) $\tau_2 = \tau_0 \exp(t_{\mathrm{w}}/t_0)$, where $\tau_0 = 0.3$ ms and $t_0 = 62$ min for the VH data. Performing the same fits for the VV correlations, we find that the two results are comparable; $\tau_0 = 1.5$ ms and $t_0 = 59$ min for VV (figure 3(a)). Also it is observed that the stretching exponent a decreases linearly with waiting time (figure 3(b)), at almost the same rate ($0.001\ \mathrm{min}^{-1}$) as the corresponding one from VV correlation.

We conclude from the similar behaviour of the VV and VH correlations that both the translational and the rotational dynamics slow down as the system ages. Notably, the average relaxation time (the time that it takes for the particles to 'forget' their initial orientation)

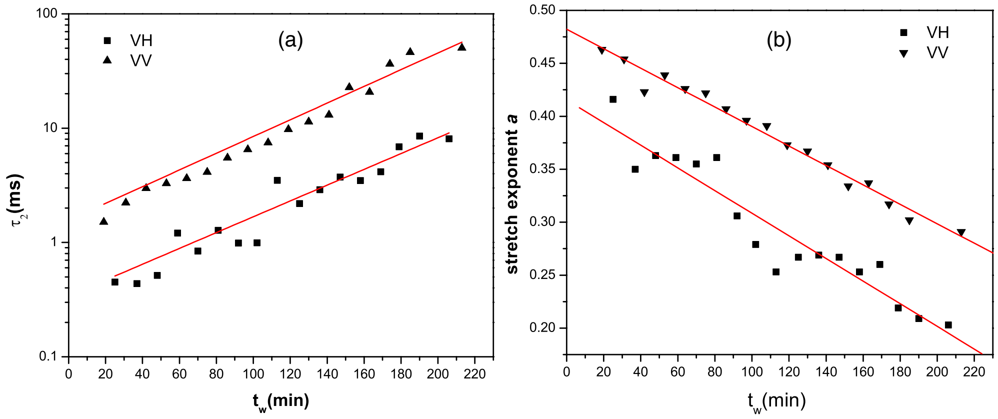

Figure 3. (a) Characteristic time τ_2 of the slow relaxation as a function of waiting time. The relaxation time grows exponentially. (b) Stretching exponent a as a function of waiting time and its linear fit for 3 wt% Laponite suspensions from depolarized VH and polarized VV auto-correlation functions taken at scattering angle $\Theta = 90°$.

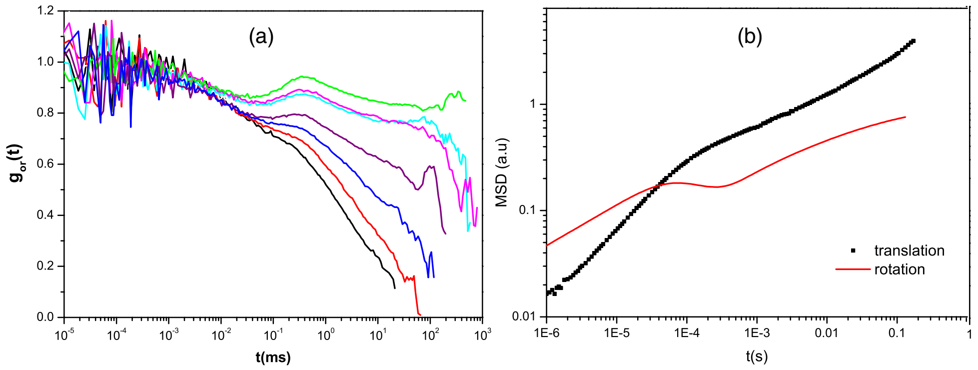

Figure 4. (a) The orientational time correlation for Laponite 3%, pH = 10 at different waiting times. The rotational degree of freedom freezes at shorter ageing times, comparing to translational motion. The curves are measured at increasing waiting times (from left to right) $t_{\mathrm{w}} = 25, 48, 70, 102, 125, 158$ and 179 min. (b) Rotational and translational MSD (arbitrary units) at $t_{\mathrm{w}} \approx 90$ min; the wiggling motion appears at the same timescale as the cage rearrangements.

increases exponentially with waiting time and the good fit with a stretched exponential suggests that rotational degrees of freedom of different particles relax with different rates. Furthermore, the decrease of the stretching exponent with waiting time expresses the fact that the distribution of these relaxation times becomes wider as the system ages, again in line with earlier observations for the translational dynamics [5]. In order to gain more insight into the rotational dynamics, we extract the orientational correlation function from the ratio $g_{\mathrm{or}} = |\frac{f_{\mathrm{VH}}}{f_{\mathrm{VV}}}|^2$, assuming that to a first approximation the rotational and translational motions are uncorrelated. The orientational correlations are depicted in figure 4(a) for different waiting times. As can be noticed for waiting times larger than 70 min, the orientational correlation develops a peak at the characteristic timescale of cross-over from short-time to intermediate-time diffusion and the peaks becomes more pronounced as the waiting time progresses. The peak suggests that the rotation can become oscillatory through the interactions with the cage formed by the surrounding particles (figure 4(b)). In figure 4(b) we have plotted the translational and rotational mean square displacements (MSDs) defined as $\langle \Delta r^2(t) \rangle = -\frac{6\ln(g^{(2)}_{\mathrm{VV}}(q,t)-1)}{2q^2}$, $\langle \Delta\theta^2(t) \rangle = -\frac{1}{12}\ln\left(\frac{g^{(2)}_{\mathrm{VH}}(t)-1}{g^{(2)}_{\mathrm{VV}}(t)-1}\right)$, respectively for a fixed waiting time $t_{\mathrm{w}} \approx 90$ min. A second remarkable feature is that the rotational diffusion slows down much faster than the translational diffusion. As can be observed, the orientational correlation becomes non-ergodic after only 1 h, compared to 3 h for the translation. Hence the orientational degree of freedom freezes out already before the translational degree of freedom enters the ergodicity breaking regime. This points to the issue of translational–rotational decoupling, also observed in molecular glasses [10]. These two qualitative features are not affected by the assumption that self- and collective diffusion behave similarly, that is used in the calculation of the orientational correlation function. In addition, in [5] it has been shown that both τ_1 and τ_2 relaxation times for the VV correlation scale as q^{-2}, hence the non-Gaussian corrections are small and the collective diffusion should not be very different from self-diffusion.

4. Discussion

We have measured both the translational and rotational dynamics in an ageing colloidal glass. The dynamics are qualitatively very similar between the two degrees of freedom. The short-time diffusion is independent of the time elapsed since the sample preparation. The intermediate- and long-time diffusion, on the other hand, slows down over several orders of magnitude during the ageing. The slowing down of the rotational diffusion is much faster than that of the translational diffusion. It was suggested previously [4, 5] that the translational diffusion dynamics in this (and many other glassy systems) can be described by a cage-diffusion process: for short times or small displacements ‘normal’ Brownian motion is observed; however, for larger times or excursions, the particles are confined in effective cages formed by their neighbours. The slow mode then corresponds to the escape of the particles from their respective cages, which becomes more and more difficult when the system ages: this shows up in the experiments as an increase of the relaxation time of the slow mode. The rotational degree of freedom that we look at here is the rotation of the disc around an axis parallel to the faces of the disc; our measurements thus indicate that this motion, too, is hindered more and more for longer waiting times and is not purely diffusive at the timescale on which the cage rearrangements happen.

Another issue that deserves to be discussed is the non-exponential relaxation dynamics. As shown before, both VV and VH correlations could be fitted with a stretched exponential. Also the orientational correlations are obviously non-exponential, meaning that we have a broad distribution of relaxation times for both translational and rotational degrees of freedom. It seems likely that this distribution of relaxation times is at least partially due to the spatially heterogeneous dynamics, i.e., rotational and translational motions of particles are faster in some parts of the sample than the other parts and particles in the slow domains are responsible for the long tail of correlations. These heterogeneities must exist over a broad range of length scales (comparable to the probing length scale $\frac{2\pi}{q} \approx 335$ nm) to be observable by dynamic light scattering measurements. We are planning confocal microscopy imaging to see whether these heterogeneities are observable in real space.

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References

[1] Pusey P N and van Megen W 1987 *Phys. Rev. Lett.* **59** 2083
van Megen W, Underwood S M and Pusey P N 1991 *Phys. Rev. Lett.* **67** 1586
Pham K N, Egelhaaf S U, Pusey P N and Poon W C K 2004 *Phys. Rev.* E **69** 011503
[2] Cugliandolo L and Kurchan G 1997 *Prog. Theor. Phys. Suppl.* **126** 407
[3] Kroon M, Wegdam G H and Sprik R 1996 *Phys. Rev.* E **54** 6541
[4] Bonn D, Kellay H, Tanaka H, Wegdam G and Meunier J 1999 *Langmuir* **15** 7534
Bonn D, Tanaka H, Kellay H, Wegdam G and Meunier J 1998 *Europhys. Lett.* **45** 52
[5] Abou B, Bonn D and Meunier J 2001 *Phys. Rev.* E **64** 021510
[6] Bonn D, Coussot P, Huynh H T, Bertrand F and Debregeas G 2002 *Europhys. Lett.* **59** 786
[7] Knaebel A, Bellour M, Munch J P, Viasnoff V, Lequeux F and Harden J L 2000 *Europhys. Lett.* **52** 73
[8] Bellour M, Knaebel A, Harden J L, Lequeux F and Munch J-P 2003 *Phys. Rev.* E **67** 031405
[9] Donth E 2001 *The Glass Transition* (Berlin: Springer)
[10] Chang I, Fujara F, Geil B, Heuberger G, Mangel T and Sillescu H 1994 *J. Non-Cryst. Solids* **172** 248
[11] Kegel W K and Van van Blaaderen A 2000 *Science* **287** 290
[12] Berne B and Pecora R 2000 *Dynamic Light Scattering* (New York: Wiley)
[13] Götze W 1991 *Liquids, Freezing and Glass Transition* ed J P Hansen, D Levesque and J Zinn Justin (Amsterdam: North-Holland) p 464
[14] Watzlawek M and Nägele G 1997 *Phys. Rev.* E **56** 1258
[15] Bergenholtz J, Horn F M, Richtering W, Willenbacher N and Wagner N J 1998 *Phys. Rev.* E **58** R4088