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Aging of rotational diffusion in colloidal gels and glassesS. Jabbari-Farouji,^{1,2} G. H. Wegdam,¹ and Daniel Bonn^{1,3}¹*LPTMS, CNRS and Université Paris-Sud, UMR8626, Bat. 100, 91405 Orsay, France*²*Van der Waals-Zeeman Institute, Institute of Physics (IoP) of the Faculty of Science (FNWI) University of Amsterdam, 1098 XH Amsterdam, the Netherlands*³*Laboratoire de Physique Statistique de l'ENS, 24 rue Lhomond, 75231 Paris Cedex 05, France*

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We study the rotational diffusion of aging Laponite suspensions for a wide range of concentrations using depolarized dynamic light scattering. The measured orientational correlation functions undergo an ergodic to nonergodic transition that is characterized by a concentration-dependent ergodicity-breaking time. We find that the relaxation times associated with rotational degree of freedom as a function of waiting time, when scaled with their ergodicity-breaking time, collapse on two distinct master curves. These master curves are similar to those previously found for the translational dynamics; the two different classes of behavior were attributed to colloidal gels and glasses. Therefore, the aging dynamics of rotational degree of freedom provides another signature of the distinct dynamical behavior of colloidal gels and glasses.

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I. INTRODUCTION

Understanding the nature of arrested states of matter such as colloidal gels and glasses has been an active and challenging field of research in recent decades [1] and is still far from being well understood. What makes these ubiquitous soft glassy materials a fascinating subject of study is their complex dynamical behavior that differs from that of equilibrium liquids. What makes studying their dynamics interesting is the observation of universal dynamical features in different systems, such as molecular, colloidal, metallic, and ionic glasses [2]. A very important common feature in such glassy materials is a dramatic slowing down of the diffusion of particles or molecules concomitant with a huge increase of viscosity on approaching the glass transition. The slowing down of dynamics expresses itself as a nonexponential relaxation of the translational and rotational degrees of freedom in supercooled liquids and nondecaying plateaus deep into the glassy phase. Another significant feature is *aging*, i.e., the evolution of the physical properties of the system with waiting time, the time elapsed since the quench into glassy phase.

An important question that arises in this respect is how the motion of orientational and translational degrees of freedom are influenced upon the transition from a liquid-like to a disordered solid-like state and if the slowing down of the two degrees of freedom are correlated. In a low-viscosity liquid far from the supercooled regime, the translational and rotational diffusion coefficients of particles follow the Stokes-Einstein and Debye-Stokes-Einstein equations, respectively, that relate the diffusion coefficients to temperature and viscosity [3,4]. According to these relations the translational and rotational diffusion coefficients are not independent and should both have a linear temperature dependence and be proportional to the inverse of the viscosity. While there have been some comprehensive studies on rotational motion of several molecular glass formers [5–8], there are fewer studies on rotational dynamics of glassy colloidal systems [9–12]. Here, we present the results of a systematic investigation of aging of the translational and rotational diffusion of charged colloidal platelets of Laponite studied for a wide range of concentrations and as a function of waiting time.

Laponite is a synthetic clay [13] that is widely used as a rheology modifier in industrial applications. Laponite particles, when suspended in water, form a suspension that evolves from a low-viscosity water-like liquid to a highly viscoelastic fluid over time [14–22]. In other words, the suspension exhibits a strong aging behavior and undergoes an ergodic to nonergodic transition. This behavior is observed at moderately low volume fractions $\phi \approx 0.001$ – 0.015 [14,15]. The aging dynamics of translational diffusion and structure factor in both ergodic and nonergodic regimes have been studied extensively over the past decade [14,15,23,24], revealing a dramatic slowing down of the translational motion. Interestingly, the intermediate scattering function measurements of Laponite suspensions have revealed that low and high concentration samples evolve in a distinctly different manner [14,15,23]. Based on different aging behaviors of the translational diffusion as well as the structure factor, the nonequilibrium states of Laponite suspensions in pure water have been identified to be a colloidal gel at low concentrations $C < 1.5$ wt% and a colloidal glass at higher concentrations $C > 1.5$ wt% [15,23,24].

Here, we study the behavior of rotational diffusion when varying the concentration from the gel to the glass region. In prior works [9,12], we have studied the aging dynamics of rotational diffusion in a colloidal glass of Laponite at concentrations around 3 wt%. We showed that orientational correlation function of the system also shows a nonexponential decay and the rotational relaxation time dramatically slows down during the aging; this happens at a rate faster than that of translational degree and viscosity. Here, we would like to know how the aging of rotational dynamics is correlated with the translational dynamics during the aging as we vary the concentration and consequently if the rotational dynamics of colloidal gels and glasses can also be classified into two distinct groups (gels and glasses). To this end, we perform a systematic study of the orientational correlations for a wide range of concentrations. We observe that the orientational dynamics of both colloidal gels and glasses slows down during the aging. However, the rotational dynamics of colloidal gels and glasses behave distinctly differently, in line with observations for the translational dynamics, thus providing

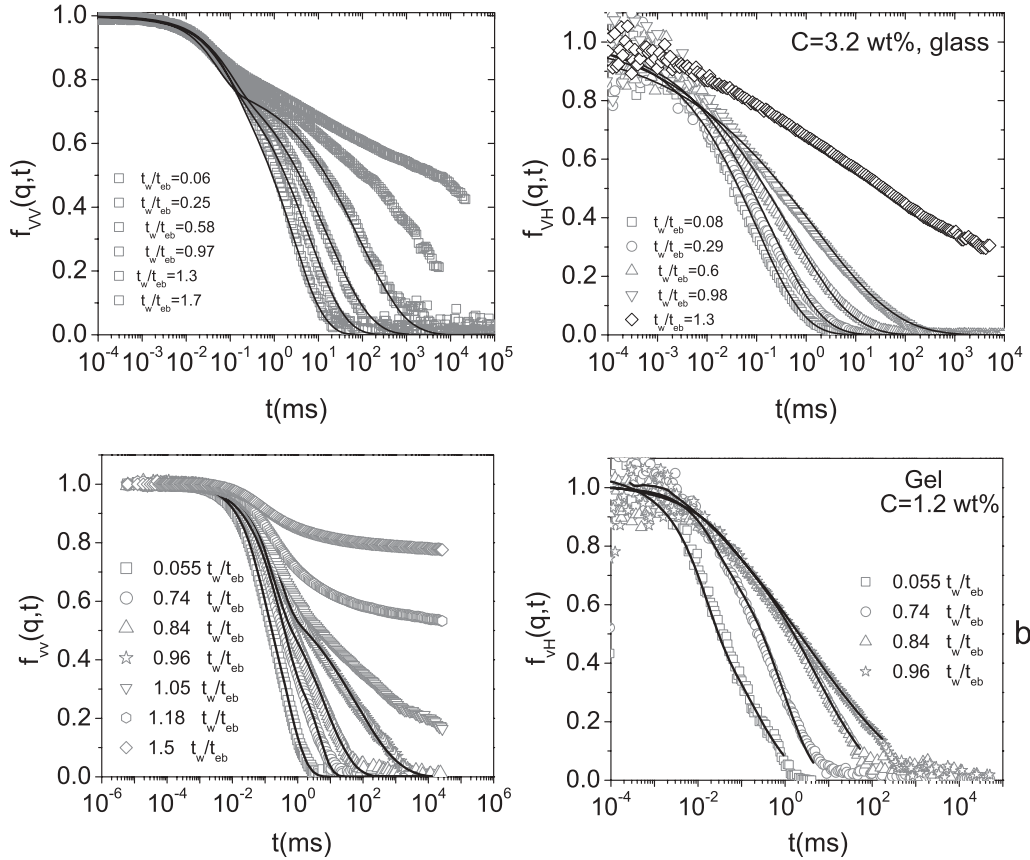


FIG. 1. Evolution of polarized (VV) and depolarized (VH) intensity correlation functions (symbols) and their corresponding fits (solid lines) to Eq. (4) (a) for a glass (Laponite 3.2 wt%, pure water) and (b) for a gel (Laponite 1.2 wt%, pure water) measured at a scattering angle of 90° . The waiting times are shown in the legends. Note that here only the correlations in the ergodic regime of aging are fitted. The ergodicity-breaking times are: $t_{eb} = 340$ min for Laponite 3.2 wt% and $t_{eb} = 18$ days for Laponite 1.2 wt%.

another criterion for discerning the two states. Also, we find that in both colloidal gels and glasses, the orientational relaxation time grows at a faster rate than the translational one, suggesting that orientation and translation become decoupled upon approaching the nonergodic state.

The remainder of this paper is organized as follows. First, we present the experimental aspects of the sample preparation and dynamic light-scattering measurements in Sec. II. Subsequently, we briefly review the theory of dynamic light scattering from anisotropic particles in Sec. III. Section IV is devoted to the results of our measurements on rotational dynamics for colloidal gels and glasses of Laponite. In Sec. V, we summarize our main findings and discuss our results in relation to experiments on other glass-forming materials.

II. EXPERIMENTAL

A. Materials

The Laponite that we used for our experiments is Laponite XLG, which consists of charged platelets with an average diameter of 30 nm and thickness of 1.2 nm [13]. Laponite can absorb water, increasing its weight up to 20%. Therefore, we first dried it in an oven at 100°C for one week and subsequently stored it in a desiccator.

We prepare a number of samples with different concentrations of Laponite in pure water. Laponite dispersions are prepared in ultrapure Millipore water ($18.2\text{ M}\Omega\text{cm}^{-1}$) and are stirred vigorously by a magnetic stirrer for 1.5 h to make sure that the Laponite particles are fully dispersed. The dispersions are filtered using Millipore Millex AA $0.8\text{-}\mu\text{m}$ filter units to obtain a reproducible initial state [18]. This instant defines the zero of waiting time, $t_w = 0$.

B. Dynamic light-scattering setup

Our dynamic light-scattering setup (ALV) is based on a He-Ne laser ($\lambda = 632.8$ nm, 35 mW) and avalanche photodiodes as detectors. An ALV-60X0 correlator directly computes the intensity correlation functions $g(q,t) = \frac{\langle I(q,t)I(q,0) \rangle}{\langle I(q,0) \rangle^2}$, at a scattering wave vector $q = \frac{4\pi n}{\lambda} \sin(\frac{\Theta}{2})$, in which Θ is the scattering angle.

In our experiments, the polarization of scattered light is detected in two modes: the VV mode, in which the polarization of the incident and scattered light are both vertical, and the VH mode, in which the polarization of the scattered light is horizontal and perpendicular to the vertical polarization of incoming light. The VV and VH intensity correlation functions were measured at a fixed scattering angle $\Theta = 90^\circ$ ($q = 1.87 \times 10^7 \text{ m}^{-1}$) regularly at a rate depending on the speed of aging of Laponite suspensions.

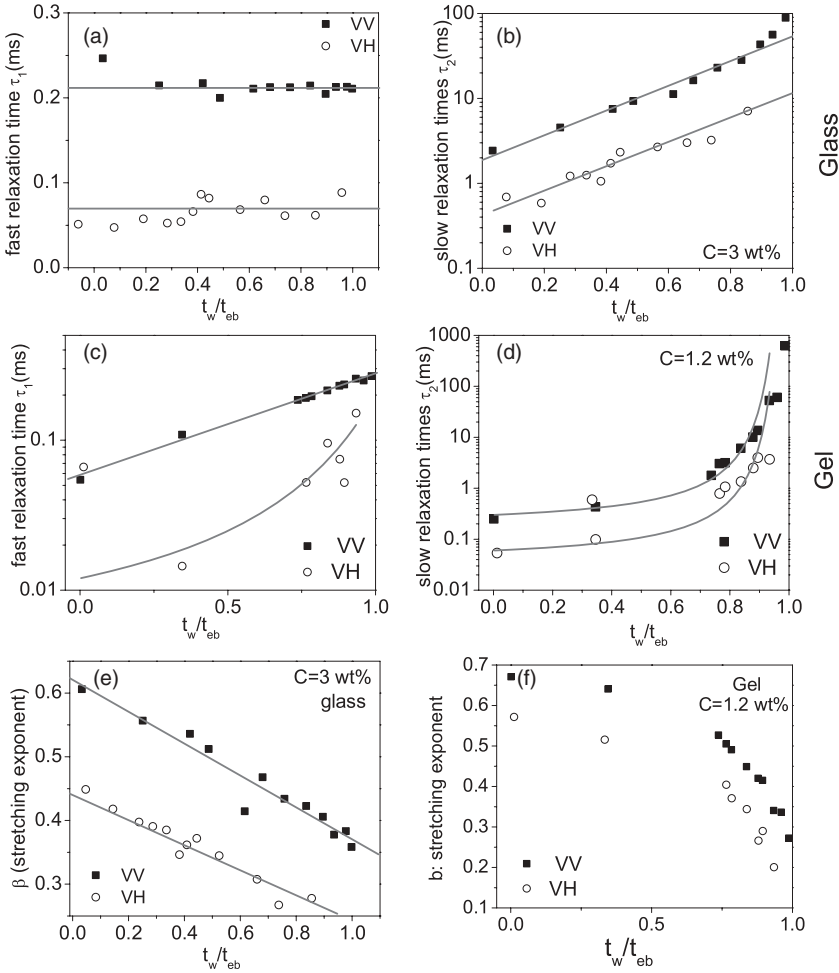


FIG. 2. Evolution of fast (τ_1) and slow (τ_2) relaxation times and the stretching exponents β of VV and VH correlation functions plotted versus scaled waiting time t_w/t_{eb} for a glass (Laponite 3 wt%, pure water, $t_{eb} = 450$ min) and a gel (Laponite 1.2 wt%, pure water, $t_{eb} = 26\,000$ min). The lines show the fits of relaxation times with the general form $\tau_i(t_w) = \tau_0 \exp(B \frac{t_w}{t_w^\infty - t_w})$ [14].

III. DYNAMIC LIGHT SCATTERING FROM ANISOTROPIC PARTICLES

The anisotropy in shape of particles gives rise to an anisotropic polarizability tensor. For particles with axial symmetry such as disks and rods, the eigenvectors of polarizability tensor correspond to the directions perpendicular and parallel to the symmetry axis and their resultant eigenvalues are γ_\perp and γ_\parallel , respectively [25]. The total electric field scattered by such particles for linearly polarized incident light in the vertical direction has two components. The first is the vertically polarized component E_{VV} with an amplitude proportional to the average polarizability, $\gamma = (\gamma_\parallel + 2\gamma_\perp)/3$. The second one is the horizontal depolarized component E_{VH} . Its amplitude is proportional to the intrinsic particle anisotropy $\beta = \gamma_\parallel - \gamma_\perp$, which is the difference between the polarizabilities parallel and

perpendicular to the optical axis. In depolarized dynamic light scattering (DDLS), one measures the correlation functions of the scattered light intensity whose polarization (horizontal) is perpendicular to the polarization of incident light (vertical), i.e., g_{VH} , as opposed to the g_{VV} , for which the polarization of scattered and incident light are both vertical. These intensity correlations are related to their corresponding intermediate scattering functions:

$$f_{VV}(q, t) = \frac{\langle E_{VV}(\mathbf{q}, t) E_{VV}^*(\mathbf{q}, 0) \rangle}{\langle I_{VV}(\mathbf{q}) \rangle} \quad (1)$$

$$f_{VH}(q, t) = \frac{\langle E_{VH}(\mathbf{q}, t) E_{VH}^*(\mathbf{q}, 0) \rangle}{\langle I_{VH}(\mathbf{q}) \rangle},$$

through the Siegert relation, i.e., $g_{VV(H)} = 1 + C |f_{VV(H)}|^2$, where C is a set-up-dependent coherence factor [25].

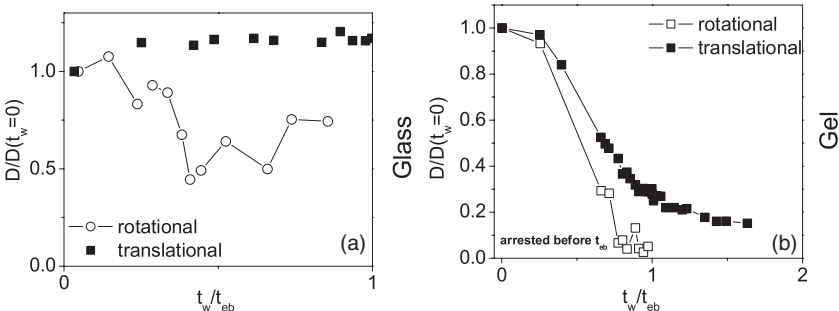


FIG. 3. Short-time translational and rotational diffusion coefficients normalized to their values at $t_w \approx 0$ as a function of scaled aging time t_w/t_{eb} (a) in a glass of Laponite C = 3 wt% and (b) in a gel of Laponite C = 1.2 wt%.

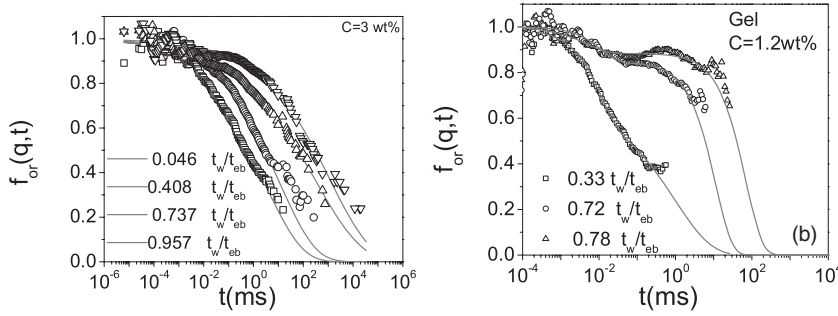


FIG. 4. The orientational correlation functions defined as $f_{\text{VH}}/f_{\text{VV}}$ at different waiting times in a glass (Laponite 3 wt%, pure water) and a gel (Laponite 1.2 wt%, pure water). The lines show the fits with the sum of single and stretched exponential as in Eq. (4).

Assuming that the suspensions are dilute enough so that orientations and positions of different particles are uncorrelated, one can obtain the VV and VH intermediate scattering functions in terms of the translational and rotational diffusion coefficients and average polarizability γ and anisotropy of polarizability β [25]. The resulting intermediate scattering functions factorize into a product of a purely local (not q -dependent) orientational correlation and a q -dependent translational correlation and can be written as [25]:

$$f_{\text{VV}}(q,t) = \frac{[\gamma^2 + \frac{4}{45}\beta^2 \exp(-6D_r t)] F_s(q,t)}{\gamma^2 + \frac{4}{45}\beta^2}, \quad (2)$$

$$f_{\text{VH}}(q,t) = F_s(q,t) \exp(-6D_r t), \quad (3)$$

where $F_s(q,t) = \langle \exp(i\mathbf{q}[\mathbf{r}_i(0) - \mathbf{r}_i(t)]) \rangle$ is the self-translational correlation function. The contribution of the rotational motion to the VV correlation is proportional to $\frac{4}{45}\beta^2/\gamma^2 \propto I_{\text{VH}}/I_{\text{VV}}$, which turned out to be smaller than 0.02 in our experiments. Therefore, we can neglect the rotational contribution to f_{VV} in our data. Hence, the dynamics of f_{VV} mainly reflects the translational diffusion of the particles, while f_{VH} is determined by both translational and rotational motion.

The translational and rotational diffusion coefficients of dilute solutions of hard disks can be obtained as the limiting case of the general formula for diffusion of oblate spheroids with major semi-axis b and minor semi-axis a [25]. For disks taking $a = 0$ and $b = R$, we can obtain in the infinite-dilution limit, the translational diffusion coefficients parallel and perpendicular to the symmetry axis of the disk, respectively, as: $D_{\parallel}^t = \frac{k_B T}{16\eta R}$ and $D_{\perp}^t = \frac{3k_B T}{32\eta R}$ giving an average translational diffusion $D_0^t = 1/3(D_{\parallel}^t + 2D_{\perp}^t) = \frac{kT}{12\eta R}$; the rotational diffusion coefficient follows as $D_0^r = \frac{3kT}{32\eta R^3}$. In DLS experiments in the VV mode, we measure the average translational diffusion D^t that for dilute suspensions should be D_0^t . From depolarized

DLS (VH mode), we can extract the rotational diffusion coefficient D^r .

IV. AGING DYNAMICS OF ROTATION AND TRANSLATION IN GELS AND GLASSES OF LAPONITE SUSPENSIONS

Measuring the intensity correlations of scattered light from aging Laponite dispersions, one always observes two regimes of aging in the evolution of the intensity correlations [15,17,18]. In the first regime of aging, the correlation functions decay to zero within the experimental accessible time scales. In the second regime of aging, the ensemble-averaged correlations do not decay to zero and a plateau in intermediate scattering function develops [see Fig. 1(a)]. The waiting time for which the correlation functions (i) no longer decay to zero within the experimental time-scale and (ii) the time-averaged correlation functions are not equal to their ensemble-averaged values defines the ergodicity-breaking time t_{eb} . The t_{eb} is a strong function of concentration and the smaller the concentration is, the longer the ergodicity-breaking time becomes. The dependence of t_{eb} on concentration is discussed in more details in Ref. [26].

Studying the aging dynamics of VV and VH correlation functions simultaneously, we find that the VH correlations become nonergodic at nearly the same time as VV correlations. Therefore, we take the same t_{eb} value for both VV and VH correlations. To be able to quantify the relaxation times for rotational and translational diffusion, here we only focus on aging dynamics in the first ergodic regime of aging.

Figure 1 shows the evolution of VV and VH intermediate scattering functions for a sample of low and a sample of high concentration measured at different stages of aging. As can be observed in the figure, for both the VV and VH intermediate scattering functions a two-step relaxation can be observed

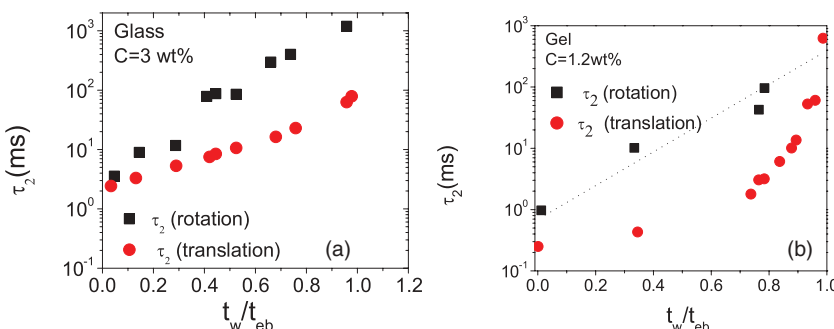


FIG. 5. (Color online) The orientational and translational relaxation times versus scaled waiting time measured for a Laponite suspension of (a) $C = 3$ wt% (glass) and (b) $C = 1.2$ wt% (gel).

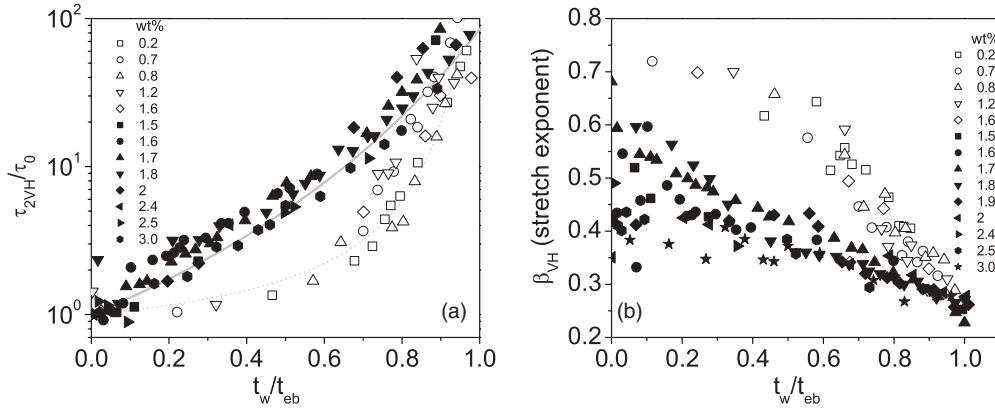


FIG. 6. The evolution of (a) the slow relaxation time normalized to its initial value τ_2/τ_0 and (b) the stretching exponent β of VH correlations versus scaled waiting time t_w/t_{eb} for different Laponite samples. The colloid concentrations are shown in the legend. Similar to the translational degree of freedom, the samples can be divided into two groups according to the evolution of the slow relaxation times of VH correlations. In both figures the open symbols correspond to gels, the filled symbols to the glass. In panel (a) the solid and dashed line correspond to the glass and gel lines obtained from growth of relaxation time of translational diffusion.

[14,15,19], and in both samples the average relaxation times of VV and VH correlations increase with increasing waiting time. In order to consistently describe these two-step relaxations quantitatively, we fit the normalized correlation functions, both VV and VH, by the sum of an exponential and a stretched exponential [9,14,19]:

$$f(q,t) - 1 = A \exp(-t/\tau_1) + (1 - A) \exp[-(t/\tau_2)^\beta], \quad (4)$$

where A determines the relative contribution of exponentially decaying fast relaxation time τ_1 and b is known as the stretching exponent characterizing the broadness of the distribution of slow relaxation modes that contribute to the correlation function. The smaller b is, the broader the distribution of the slow relaxation times is. The slow relaxation time τ_2 gives us an idea about the mean relaxation time that can be obtained as $\tau_m = \tau_2/b\Gamma(1/b)$, where Γ is the gamma function. 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 of $\ln[f(q,t) - 1]$ for short times ($t < 0.005$ ms), corresponding to the short-time diffusion. We subsequently use the extracted value of τ_1 to obtain A , b , and τ_2 from fitting within Eq. (4).

The results of fits of the VV and VH correlations for both samples are depicted in Fig. 2. For the high-concentration sample, the fast relaxation times are roughly independent of the waiting time [Fig. 2(a)], while they grow in the low-concentration sample, as presented in Fig. 2(c). The short-time translational D_s^t and rotational D_s^r diffusion coefficients can be extracted from the fast relaxation times as $D_s^t = 1/(\tau_1^{VV} q^2)$ and $D_s^r = 1/(6\tau_1^{VH}) - 1/(6\tau_1^{VV} q^2)$. The resulting short-time diffusion coefficients normalized to their initial values ($t_w \approx 0$) for both samples are plotted in Figs. 3(a) and 3(b), respectively. Figure 3(b) clearly demonstrates that the short-time rotational diffusion coefficient (D_s^r) in the low-concentration decreases at a faster rate than the translational one (D_s^t). In contrast, for the high-concentration sample, both short-time translational and rotational diffusion coefficients show only a weak dependence

on the waiting time. The short-time rotational diffusion already indicates that the aging of two types of samples are different.

We now turn to the behavior of the slow relaxation times. Figure 2(b) is similar to what was reported in previous works for the colloidal glass of Laponite [9]: the slow relaxation times associated with translational and rotational degrees of freedom grow exponentially with waiting time and remain parallel to each other. In the low concentration samples that were previously identified as gels [15,23,24], the slow relaxation time grows faster than exponentially for both VV and VH correlations as shown in Fig. 2(d). Looking at the stretching exponent b , we observe that b decreases with waiting time for both VV and VH correlations in both the gel and the glass [Figs. 2(e) and 2(f)]. However, the stretching exponents of the translational and rotational degree in the gel decreases at a faster rate than in the glass, pointing to a different character of aging in gels and glasses.

Before going further with interpreting these results, one should bear in mind that both translational and rotational degrees of freedom contribute to the VH correlations in contrast to VV correlations, which reflect almost exclusively the dynamics of translational motion. In order to gain a more direct insight into the rotational dynamics, we extract the orientational correlation functions defined as the ratio $f_{or}(t) = \frac{f_{VH}(t)}{f_{VV}(t)}$. The obtained orientational correlations for the glass and the gel at different stages of aging are depicted in Fig. 4. The orientational correlations of both gel and glass can also be fitted with Eq. (4).

The slow relaxation times extracted from the orientational correlations are presented in Fig. 5, together with the relaxation times for the translational degree of freedom. From this figure, we observe that for both gel and glass samples the slow relaxation time of the orientational degree of freedom grows more rapidly with t_w than the translational one. Furthermore, the orientational relaxation time of the gel ages in a manner that is different than in the glass. The difference in the slow relaxation times for orientational and translational correlations is an indication of the decoupling of translational degree

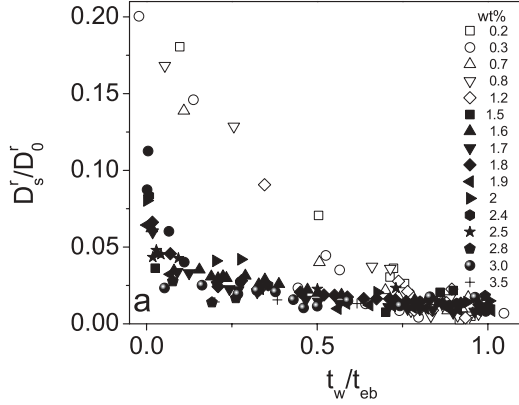


FIG. 7. The short time rotational diffusion coefficients normalized to those of infinitely diluted hard disks of radius $R = 15$ nm: D_0^r .

of freedom from the translational degree of freedom. The fact that also the orientational correlation functions are also well described by a stretched exponential (Fig. 4) indicates that the rotational degrees also have a broad distribution of relaxation times. Furthermore, the decrease of the stretching exponent with increasing waiting time expresses the fact that the distribution of these relaxation times becomes wider as the system ages, again similar to earlier observations for the translational dynamics [14,19].

Having investigated in detail the aging of translational and rotational diffusion in a gel and a glassy sample and characterizing their differences, we now present our results for a wider range of samples studied. We measured the VV and VH time correlation functions for a series of Laponite samples ranging from 0.2 wt% to 3 wt%. From these measurements, we find that the aging behavior of rotational degree of freedom between the low (gel-like) and high (glassy) concentration samples is distinctly different. Plotting the quantities τ_2 and β for VH correlations as a function of scaled waiting time t_w/t_{eb} , we find that, similar to the slow relaxation time of VV correlations, the data from all the samples collapse onto two distinct master curves (Fig. 6). These two master curves can be identified as gels and glasses in agreement with the classification based on the aging of the translational degree of freedom in Refs. [14,15].

Looking at the aging behavior of the short-time rotational diffusion of all the samples, again we distinguish two groups of samples. Figure 7 presents the short-time rotational diffusion coefficients D_s^r , normalized to the rotational diffusion of hard disks in the infinite dilution limit $D_0^r = k_B T / 32\eta R^3$ (taking $R = 15$ nm: $D_0^r = 1.1 \times 10^5$ s $^{-1}$) as a function of the scaled waiting time t_w/t_{eb} . We find a moderate decrease of D_s^r for the glassy samples, while the short-time rotational diffusion decreases very significantly in the gels.

As can be observed in Fig. 7, the rotational diffusion at the early stages of aging is considerably slower in glassy samples and is almost concentration-independent on approaching the nonergodic state. Therefore, one can deduce that in the nonergodic state the rotational diffusion of both gels and glasses is hindered. The rotational motion of particles in the glass is constrained from the very beginning due to crowding

of particles at high concentrations (glass), while in the gel the rotational motion of particles is obstructed as they become part of a network or clusters of particles.

V. CONCLUSION

We have studied the evolution of both the translational and rotational dynamics during aging for a wide range of concentrations of Laponite particles, including both colloidal gels and glasses. We find that the dynamics are qualitatively similar between the two degrees of freedom in all the samples. Concomitant with the slowing down of the translational motion, the rotational motion slows down as well, however, at a faster rate. More precisely, both the short-time rotational and translational diffusion decrease significantly during gel formation while these quantities remain almost constant during the formation of the glass. The slow relaxation times, characterizing the translational and orientational degree of freedom at longer delay times, decrease at a faster rate in the gel compared to the glass. All these findings point to the different mechanisms involved in gel and glass formation. The enormous slowing down of short-time rotational diffusion in the gel indicates that the rotational motion of particles in a gel becomes very restricted as a result of the formation of small clusters or network-like structures. Similar to the translational degrees of freedom that was reported previously [14,15,24], the aging dynamics of rotation in colloidal gels and glasses is different. One can observe two distinct routes of evolution for the rotational dynamics, providing us with another criterion [15,23,27] to distinguish colloidal gels (low concentrations) and glasses (high concentrations).

The faster rate of slowing down of rotational motion compared to that of translation in both colloidal gels and glasses, points to a decoupling of translational and rotational motion during the aging of colloidal gels and glasses and is usually interpreted in terms of dynamical heterogeneity [12,28]. The nonexponential behavior of both translational and orientational correlations and their description by a stretched rather than a simple exponential also points to a broad distribution of relaxation times, as thus also heterogeneous dynamics. Our data also suggest that the decoupling is stronger in spatially heterogeneous samples (gels) than the spatially homogeneous ones (glasses), as the difference in the aging behavior of rotational and translational degrees of freedom is more pronounced in gels. These observations agree with the existing literature, where it is found that the dynamic heterogeneity plays a central role in the decoupling between rotational and translational diffusion [5–7,28].

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