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Slow dynamics and intermittent quakes in soft glassy systems

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We present measurements of the thermal fluctuations of the free surface of oil-in-water emulsions which exhibit a glassy behavior. The Surface Fluctuation Specular Reflection (SFSR) technique was applied to measure the free surface fluctuations. When the volume fraction of the oil droplets is close to or larger than the disordered packing volume fraction, the emulsion ages and its free surface exhibits abnormal fluctuations, consisting of rare but large amplitude quakes. From a statistical analysis of the signal, we observe that the relative importance of such intermittent quakes grows as the system ages. More precisely, we observe for the first time that the kurtosis of the fluctuations increases with aging time with an exponent of about 1.3. These quakes correspond to large changes in the local slope of the free surface over a few tenths of a second. We conjecture that such quakes reflect the dynamics peculiar to glassy systems driven by the relaxations of internal stress.

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I. Introduction

Systems which are quenched into a glassy state exhibit aging, *i.e.*, slow evolution of their physical properties. If their response functions are measured over a short period of time, they exhibit quasi-equilibrium properties over the measurement period. However, when measured over a long period of time, these response functions substantially drift with the elapsed time as the material will have aged to a new state. Although the generic features of aging in glassy systems have been investigated for several decades,[1–3] further theoretical and experimental approaches are required to elucidate their essential microscopic mechanisms.

One of the characteristics of glassy systems is the existence of heterogeneities, which are spatial as well as temporal. Small neighboring domains can exhibit very different dynamics. Within one of those domains, the dynamics are intermittent, consisting of periods of intense activity interspersed between periods of relative calm. Those intermittencies are linked to the dynamical heterogeneities, *i.e.* the coexistence of slow and fast regions.[4,5] Experimentally, the occurrence of intermittencies has been investigated either microscopically[6–9] or macroscopically[10] in different glass-forming systems, such as polymer films at a temperature slightly above the glass transition temperature, a polymer glass quenched below the glass transition temperature, and glassy phases of colloidal suspensions with a net attractive interaction between particles.

In particular, glassy colloidal suspensions provide systems which are easier to study since the involved length scales are larger than in the ones in polymeric systems. Previously, dynamical heterogeneities in glassy colloidal systems have been evidenced by particle tracking using optical microscopy[11–13] or by light scattering techniques.[6,14] In ref. 6, Duri *et al.* reported that it is possible to observe time fluctuations of the decorrelation function by light scattering, which indicates intermittency in the fluctuation dynamics. However, recently it was also noticed by Cardinaux *et al.*[15] for an oil-in-water emulsion that the length scale of such intermittency can reach a considerably large size of order several tens or hundreds of microns. Experimental characterization of intermittent behaviour is needed in order to provide a clear overview of the length and time scales that are associated with heterogeneous dynamics.

In this article, we present measurements of the free surface on the glassy colloidal system that consists of Brownian oil droplets dispersed in water. Emulsions are known as suitable model systems to study glassy dynamics since they offer a wide range of accessible sizes and controllable parameters, and the particles have good stability with sharp boundaries.[16,17]

The thermal fluctuations of the free surface of the emulsions were measured by the Surface Fluctuation Specular Reflection (SFSR) technique that consists of measuring the local slope of the surface using a reflection of a laser beam projected on that surface.[18,19] This technique sensitively detects surface fluctuations at a mesoscopic scale of about 30 μm, which is larger than the individual particle and smaller than the entire system and covers

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an appropriate scale for intermittencies in our emulsion system. We demonstrated that the intermittencies are signaled by rare and large quakes of the free surface, which are growing in importance as the system ages. Using a statistical estimator, we measured the distribution of the fluctuation amplitudes and calculated its kurtosis, which reveals non-Gaussian statistics. We quantified the increase of the kurtosis with the aging time, and we suggest an interpretation of the intermittent behavior we observed.

II. Experimental section

A. Materials

An oil-in-water (O/W) emulsion was used as the glassy colloidal system. The base O/W emulsion is composed of 90% by weight of silicone oil (polydimethylsiloxane) ($d = 0.968$, $\eta = 350$ cSt; Sigma-Aldrich, USA), 7 wt% of distilled water, and 3% of a non-ionic surfactant (Ifralan D 0205; IFraChem; this surfactant is a mixture of two polyoxyethylene molecules: pentaethylene glycol mono *n*-dodecyl ether and pentaethylene glycol mono *n*-decyl ether). The emulsion was obtained by progressively incorporating the oil into the aqueous phase under gentle stirring with a spatula. Then the emulsion was sheared in a Couette-type set-up described in ref. 20 at a shear rate 14 280 s^{-1}. Under appropriate formulation and shearing conditions,[21,22] a quasi-monodisperse emulsion was obtained, characterized by a volume averaged diameter equal to 0.89 μm and a polydispersity index $P = 19.3\%$ (ref. 23) or equivalently a span equal to 0.60.[24] These data were confirmed by a static light scattering measurement performed with a Mastersizer 2000 Hydro SM device (Malvern) using Mie theory. This system is known to be very stable over at least one year, as neither coalescence nor Ostwald ripening occurs on this time scale.

The emulsion was then diluted by adding distilled water without alteration of its drop size distribution. Samples of various emulsion particle volume fractions φ_o from 0.55 to 0.70 were prepared. We have checked that the droplets are Brownian, *i.e.*, at the volume fractions probed, no significant creaming of the emulsions occurs over the duration of the optical measurements. Prior to an experiment, the emulsion was rejuvenated by strongly stirring it for at least 30 minutes.

B. Measurement setup

The fluctuation of the free surface of O/W emulsion was measured using techniques of Surface Fluctuation Specular Reflection (SFSR) spectroscopy. The SFSR technique measures the height of the fluctuations of a free surface by the reflection of a laser beam. A schematic of the setup is shown in Fig. 1. The suspension was poured into a cylindrical sample cell of diameter 26 mm, and the height of liquid was *ca.* 2 mm. The sample cell was covered by a glass lid to prevent water evaporation. A laser beam was focused by a lens ($f = 60$ mm) on the free surface of the target liquid, then its specular reflection from the surface was sent to a position-sensitive detector which consists of a two-quadrant photodiode.

After appropriate current to voltage conversion and pre-amplification, the difference of the voltages delivered from each quadrant $\delta V(t) = V_+ - V_-$ was acquired through second

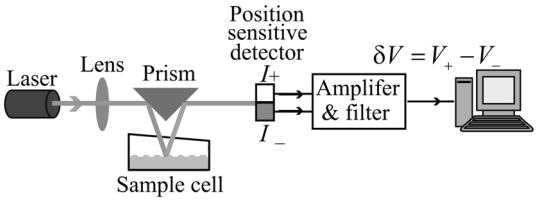

Fig. 1 A schematic of the SFSR setup. A laser beam is focused onto the free surface of the liquid in the sample cell. The position of the reflected part is detected using a position sensitive detector which consists of 2 quadrant diodes. The difference of the voltages delivered from each quadrant $\delta V(t) = V_+ - V_-$ was acquired.

amplification and anti-aliasing filtering. $\delta V(t)$ is a fluctuating signal of zero average which provides the fluctuations in the position of the beam reflected by the free surface. More precisely, $\delta V(t)$ normalized by $V_{total} = V_+ + V_-$ is related to the average slope of the free surface over the area of the circular laser spot of radius 30 μm. The normalized voltage $\delta V/V_{total}$ scales as the ratio of the angle variation and the divergence angle of the laser beam, the latter is of 5 mrad in the experiments we describe. We have shown that the fluctuations of $\delta V/V_{total}$ can be quantitatively related to the propagation of thermally excited waves at the probed surface (see ref. 18, 19 and 25 for details).

In the present experiment, $\delta V(t)$ was digitized at a sampling rate of 2 kHz. The duration of one data acquisition was 512 s, 2048 s and 4096 s depending on the reference time of aging t_a. More than 10^6 data points are thus acquired during each run.[26]

Alternatively, the dynamics of the emulsion in volume was measured by diffusing-wave spectroscopy (DWS).[27,28] The sample liquid in a rectangular glass cell of thickness 1 mm was illuminated with an expanded laser beam (λ: 488 nm, beam width: 5 mm). The multiply scattered light was collected in transmitting geometry onto photo-detectors through a lens and a diaphragm. Two types of photo-detectors were used. A photo multiplier connected to a correlator was used for measuring the time-averaged autocorrelation between short time intervals (10^{-7}–1 s). In order to measure ensemble averaged autocorrelation function between long time interval (10^{-1}–10^4 s), a CCD camera (480 × 480 pixels) was used. From the CCD camera, scattered light intensity from many speckles was collected, then we computed the autocorrelation of transmitted intensity between the images taken at reference time t_a and that taken at time $t_a + t$ for each pixel and averaged over the pixels. This technique is called multispeckle DWS(MS-DWS). The intensity autocorrelation function g_2 at time t_a is a function of the time t, written as

$$g_2(t_a, t) = \frac{\left\langle I(t_a + t)I(t_a)\right\rangle_E}{\left\langle I(t_a + t)\right\rangle_E \left\langle I(t_a)\right\rangle_E} \quad (1)$$

where $\langle\cdots\rangle_E$ denotes the ensemble average over the speckle pattern.

III. Experimental results

In this section, we present the result of two different experiments: DWS that measures the dynamics of the oil droplet

averaged over the whole sample volume in order to characterize the relaxation times of the system, and SFSR that probes the fluctuations of the free surface at a mesoscopic scale, and thus reflects the dynamics within a volume of roughly 30 μm × 30 μm × 30 μm.

A. Dynamics of droplets in volume

Fig. 2 shows the intensity autocorrelation functions $g_2(t_a, t)$ measured by DWS for O/W emulsions of two oil droplet volume fractions φ_o: (a) 0.57 and (b) 0.66. A remarkable difference is observed between these two suspensions. For the dilute emulsion of $\varphi_o = 0.57$, the system exhibits a single relaxation with a relaxation time $\tau \approx 10^{-4}$ s. This emulsion does not show aging, *i.e.*, τ does not vary as a function of the aging time t_a. On the other hand, for the concentrated emulsion of $\varphi_o = 0.66$, two relaxation modes are observed; the faster β relaxation originating from the diffusion of particles in a Brownian "cage" formed by the neighboring particles, and the slower α relaxation corresponding to the collective rearrangement of the particles. Looking at the α relaxation by MS-DWS as shown in the insets in Fig. 2(b), the aging of the system is observed, *i.e.*, the α relaxation time τ_α increases with t_a and finally it goes beyond the measurement timescale. The difference in the g_2 curves clearly demonstrates that at a volume fraction φ_o between 0.57 and 0.66, the system changes its behavior from liquid to glassy.

To investigate the critical volume fraction for the glass transition precisely, we conducted MS-DWS experiments for emulsions of various φ_o, and summarized the change of dynamics in Fig. 3. Fig. 3(a) shows a plot of the α relaxation time τ_α against the aging time t_a in systems of two different φ_o: 0.62 and 0.66. In each dataset, τ_α was obtained by fitting the curve of $g_2 - 1$ with a double stretched exponential function $c_\beta e^{-(t/\tau_\beta)^{\gamma_\beta}} + c_\alpha e^{-(t/\tau_\alpha)^{\gamma_\alpha}}$ which describes the dynamics of glassy systems empirically (the examples of the curve fitting are shown in the inset of Fig. 2(b)). Although both the emulsions exhibit the slow α relaxation mode, the aging of α relaxation proceeds more prominently for the concentrated emulsions $\varphi_o = 0.66$.

In Fig. 3(b), we plot the relaxation time τ_α at a fixed aging time t_a = 10 000 s as a function of φ_o. Up to $\varphi_o = 0.61$, the system shows only β relaxation, while from $\varphi_o = 0.62$, the α relaxation appears which drifts to a longer time with aging. In ref. 29, Gang *et al.* reported that emulsions become glassy at a volume fraction of about 0.58, like a suspension of hard spheres.[9,30] Above the random packing volume fraction, the deformable droplets are in a jammed state that also exhibits aging. In the oil in water emulsions we study, we observed a second relaxation drifting with t_a for volume fractions larger than 0.61, which is slightly larger than the expected value of 0.58. Note that, unlike as in other studies,[15] we use surfactants that are non-ionic, meaning that the repulsion between drops is mainly steric with a shorter range.

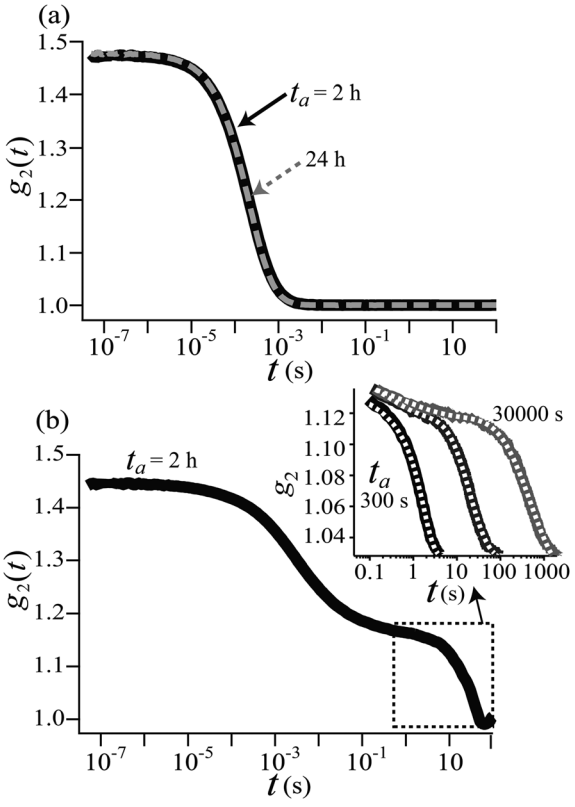

Fig. 2 Plot of the autocorrelation functions $g_2(t)$ measured by DWS at different aging times t_a. (a) Data of droplet volume fraction $\varphi_o = 0.57$. The system has a single relaxation and does not show any sign of aging. (b) $\varphi_o = 0.66$. The system has two relaxation modes and exhibits aging. In the inset, the evolution of the slower relaxation (α relaxation) measured by MS-DWS is shown at three different aging times (t_a = 300 s, 3000 s, 30 000 s). The fitting curves of a double stretched exponential function $g_2(t) = 1 + c_\beta e^{-(t/\tau_\beta)^{\gamma_\beta}} + c_\alpha e^{-(t/\tau_\alpha)^{\gamma_\alpha}}$ are superposed as white dashed lines.

B. Dynamics of the free surface: appearance of intermittent events on glassy systems

Fig. 4 shows the temporal signals of free surface fluctuation $\delta V(t) = V_+ - V_-$ measured by SFSR. In Fig. 4, $\delta V(t)$ is normalized by $V_{total} = V_+ + V_-$, and data of two different droplet volume fractions are shown: (a) $\varphi_o = 0.57$ and (b) 0.66. The signal was acquired 24 h after the sample initiation. We recall that SFSR provides a measurement of the slope of the free surface over a length given by the laser beam radius R (*ca.* 30 μm). Therefore, it

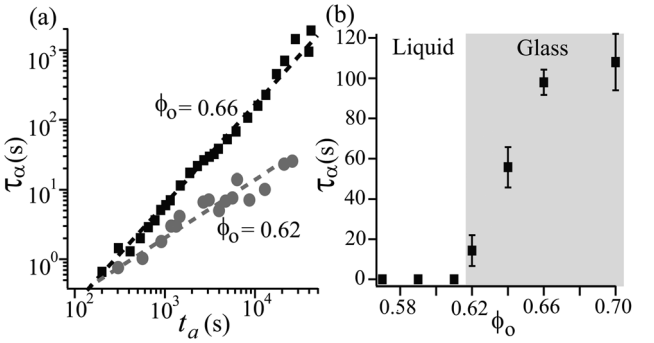

Fig. 3 (a) Plot of the characteristic time of α relaxation τ_α against the aging time t_a. Data of two different droplet volume fractions ($\varphi_o = 0.62$ and 0.66) are plotted. (b) Plot of τ_α at fixed t_a (10 000 s) as a function of φ_o. The α relaxation appears at a volume fraction $0.61 < \varphi_o < 0.62$.

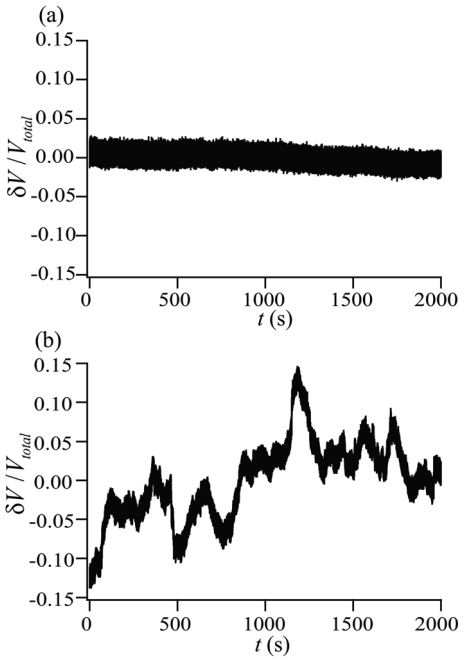

Fig. 4 Typical SFSR signals of 2 different samples which are below and above the glass transition volume fraction. The volume fractions φ_o are (a) 0.57 and (b) 0.66, and the signals were acquired 24 hours after the rejuvenation. The maximal surface angle is larger when the emulsion is glassy (about 50 μrad in (a) and 750 μrad in (b)) owing to an additional low frequency fluctuation.

probes the dynamics of a domain of surface R^2, extended vertically over R.

The behaviors of both systems are dramatically different.

• For the dilute emulsion below the glass transition volume fraction ($\varphi_o = 0.57$), the free surface fluctuates continuously. Meanwhile, when we observe the signal during a long period of order 100–1000 s, the mean value remains constant. The fluctuations we measured here correspond to the propagation of surface modes of wavelength close to the beam radius R, which reflects the rheological properties of the system.[19]

• For the concentrated emulsion above the glass transition volume fraction ($\varphi_o = 0.66$), an additional low-frequency fluctuation is observed. When we observe the mean value of the signal at a time scale of order 100–1000 s, a large shift of the value occurs intermittently. We call this type of fluctuation the "intermittent quake".

In order to detect the intermittent quakes from the signals of $\delta V(t) = V_+ - V_-$, we have conducted a sensitive statistical estimator based on the method reported in ref. 25 and 31. The signal $\delta V(t)$ was convolved with a Mexican-hat function $M(t, \tau)$:

$$M(t,\tau) = \frac{-2}{\sqrt{3\sqrt{\pi}}} \exp\left[\frac{-3}{2}\left(\frac{t}{\tau}\right)^2\right] \cdot \left[1 - 3\left(\frac{t}{\tau}\right)^2\right] \qquad (2)$$

and an estimator $\Delta(t, \tau) = \delta V(t) * M(t, \tau)$ was obtained. The function $M(t, \tau)$ is the normalized, second derivative of a Gaussian function of variance $\tau^2/3$. The estimator $\Delta(t, \tau)$ provides a second-order difference of the signal at a given time scale τ. Large values of $\Delta(t, \tau)$ correspond to the bursts of large events at the free surface over times of order τ.

We have found that the burst of each quake occurs over times of several tenths of a second (*Note*: the detailed result will be shown in the later Section III C and in Fig. 7(a)). Therefore, we set the value of time τ as 600 ms and calculated the estimator $\Delta(t, \tau)$ from each $\delta V(t)$ signal, then we counted the frequencies of events as a function of Δ. In Fig. 5, we plot the histogram of Δ distribution for emulsions (a) $\varphi_o = 0.57$ and (b) 0.66. For comparison, the value of $\Delta(t, \tau)$ was normalized by its standard deviation σ, and the count is normalized by the count at $0 \pm 0.05\sigma$. The curves of different aging time t_a are shown.

The histogram of Δ clearly emphasizes the existence of large intermittent quakes on the surface of the concentrated emulsion.

• For the dilute emulsion ($\varphi_o = 0.57$), the $\Delta(t, \tau)$ distribution is well described by the Gaussian distribution, and the distribution does not change with the aging time t_a. This behavior is the same as the one observed in systems in thermodynamical equilibrium; for instance, silicone oil of viscosity $\eta = 1$ kPas.

• For the concentrated emulsion in the glassy state ($\varphi_o = 0.66$), the distribution of Δ systematically deviates from a Gaussian as the system ages. When the emulsion is "young", corresponding to an aging time t_a of a few hours, the $\Delta(t)$ distribution is well described by a Gaussian curve like as it is observed in the emulsions of $\varphi_o = 0.57$. However, at longer t_a, the Δ distribution becomes broader and exhibits tails at large values of $\Delta(t)$. This indicates that over the time scale close to τ, large events occur more than they would if the distribution was Gaussian.

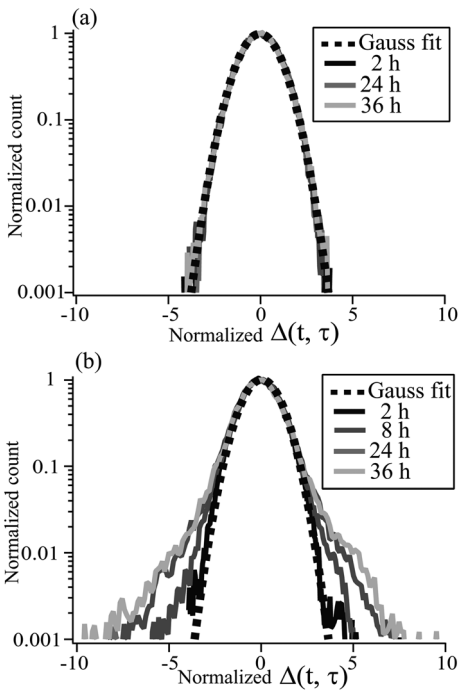

Fig. 5 Histograms of the values $\Delta(t, \tau)$ that give the second-order difference of the signal at time scale τ. τ is fixed at 600 ms. The volume fractions φ_o are (a) 0.57 and (b) 0.66, and curves of different aging times t_a are shown in each sample. For reference, the Gaussian fit to the data at $t_a = 2$ h is shown as a black dotted line. The values of $\Delta(t, \tau)$ have been normalized by the standard deviation of the signal σ, and the count is normalized by the count at $0 \pm 0.05\sigma$.

From the data of concentrated emulsions, we have further characterized these large bursts on the free surface that cause the deviation from a Gaussian distribution. The occurrence of each burst can be detected by reporting the time at which Δ is larger than a threshold value. Here, the threshold value has been arbitrarily chosen to be $\pm 3.5\sigma$ where the frequency of the value is less than 0.1% in the case of Gaussian distribution. An example of the events identified by this procedure is shown in the inset of Fig. 6. They correspond to large variations of the slope of the free surface occurring within a few tenths of a second. At $t_a \approx 30$ h, between 200 and 350 events are detected during the measurement of duration 4096 s.

We now focus on the temporal correlations between those events. By using the data of three different measurements of duration 4096 s at $t_a \approx 30$ h, we plotted the distributions of intervals δt between two events in Fig. 6. The distribution $P(\delta t)$ exhibits power law distributions $P(\delta t) \propto (\delta t)^b$ with an exponent $b = -1.2 \pm 0.1$, instead of an exponential function. Such power law statistics prove that in our O/W concentrated emulsion, non-trivial correlations between large events exist. Similar correlations were previously observed in other systems close to the glass transition: *e.g.* polymer glasses and coagulating suspensions.[32,33]

C. Effect of particle volume fraction

In order to investigate how the intermittent events on the free surface depend on the oil droplet volume fraction φ_o, we conducted SFSR measurements on emulsions of various φ_o. By varying the time τ from 0.005 s to 10 s, we convolved the signals δV with $M(t, \tau)$, and obtained $\Delta(t, \tau)$ as a function of τ. Furthermore, to characterize the statistics of each $\Delta(t, \tau)$, we calculated the kurtosis K of Δ. The kurtosis $K(\tau)$ is expressed as:

$$K(\tau) = \frac{\left\langle (\Delta - \bar{\Delta})^4 \right\rangle}{\sigma^4} - 3, \qquad (3)$$

where $\bar{\Delta}$ and σ respectively correspond to the mean value and standard deviation of Δ. The value $K(\tau)$ characterizes whether the distribution of Δ is expanded or contracted compared to the Gaussian distribution. If it has a positive value, the Δ distribution is expanded, *i.e.*, large events are counted more than in the case of Gaussian distribution.

In Fig. 7(a), we plot the kurtosis of Δ as a function of τ. Curves for four 4 different droplet volume fractions are shown ($\varphi_o = 0.57$, 0.62, 0.64, 0.66), while the aging time is fixed at $t_a = 36$ h for all data.

For a dilute emulsion below the glass transition (volume fraction $\varphi_o = 0.57$), the value of $K(\tau)$ is 0 in the entire region of τ. Therefore, Δ always corresponds to the Gaussian distribution over all the time scales probed τ. For φ_o larger than the glass transition volume fraction, a peak of $K(\tau)$ appears at 0.1 s $\leq \tau \leq$ 10 s. Those peaks of $K(\tau)$ clearly indicate that on the surface of the glassy emulsions, abnormally frequent large events are always observed over time scales ranging from 0.1 s to 1 s. By comparing the data of different particle volume fractions, it is also observed that K becomes larger with the increase of φ_o.

To observe how the $\Delta(t, \tau)$ statistics reflect the effect of aging, we also plot K as a function of the aging time t_a in Fig. 7(b). The plotted value is the mean value of $K(\tau)$ around the peak: 0.5 s < τ < 1 s, and data of two different emulsions ($\varphi_o = 0.62$ and 0.66) are shown. For both emulsions, the value of K becomes larger with the increase of the aging time $K(\tau) \propto t_a^c$, giving an exponent $c \approx 1.3$. The increase of K implies that the large quakes grow in importance as the system ages.

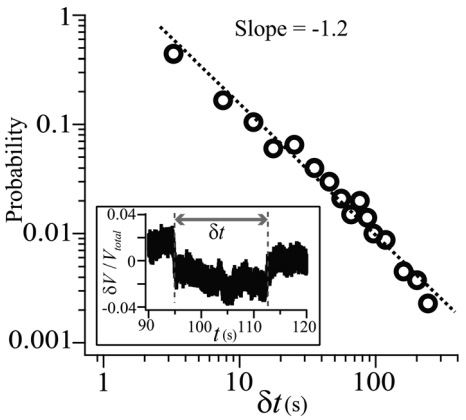

Fig. 6 Plot of the distribution of intervals δt between different intermittent events (an example of δt is shown in the inset). Data of the emulsion of volume fraction $\varphi_o = 0.66$ at $t_a \approx 30$ h are used.

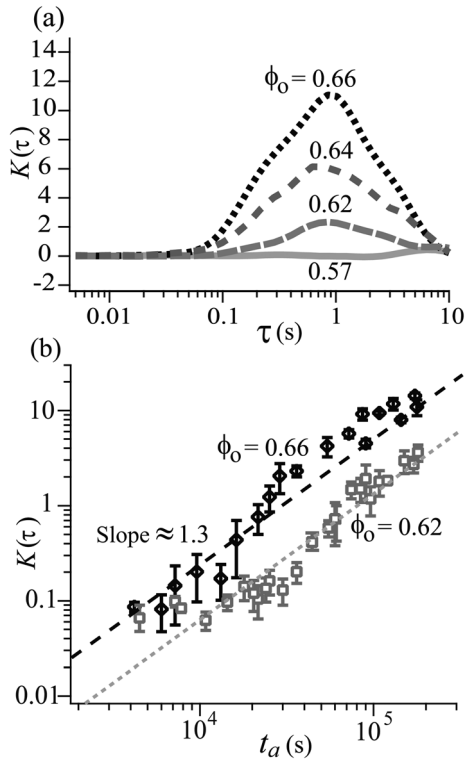

Fig. 7 (a) Plot of the kurtosis of $\Delta(t, \tau)$ as a function of τ. The data of four droplet volume fractions ($\varphi_o = 0.57$, 0.62, 0.64 and 0.66) are plotted, while the aging time is fixed at $t_a = 36$ h. For glassy emulsions, the signal statics deviate from Gaussian at 0.1 s < τ < 10 s. (b) Evolution of the kurtosis as a function of t_a. The plotted value is the mean value of kurtosis at 0.5 s < τ < 1 s. For each φ_o (0.62 and 0.66), data of three different measurements are superposed.

IV. Discussion

In what precedes, we have analyzed the fluctuation dynamics of the surface of aging emulsions. Using the SFSR technique, we have measured $\delta V(t)$, which reflects the local slope of the surface and further computed its second order difference at time τ: $\Delta(t, \tau)$. By analyzing the distribution of Δ, we have found that: (i) when we plot the value of its standard deviation σ in Fig. 8, it decreases with the aging time t_a. (ii) The distribution is non-Gaussian (Fig. 5(b)) and its kurtosis K increases with t_a, following a power law with an exponent ≈ 1.3 (Fig. 7(b)). Although we have no interpretation of that scaling behavior, let us discuss the meanings of results (i) and (ii) in the light of the specific features of glassy systems.

A glassy state is a state characterized by heterogeneous dynamics, or equivalently to a broad distribution of relaxation times, resulting in a distribution of local stiffness. As the glassy system ages, the relaxation times are shifted to longer times and their distribution broadens as well. Consequently, the system becomes more rigid and the elastic modulus increases logarithmically with the aging time t_a. As shown in Fig. 8, we have observed the slow decrease of σ (the width of the Δ distribution) in our aging emulsions, indicating that the mean amplitude of the surface fluctuations decreases. The decrease of σ results from the increase of the mean stiffness on the probed surface, which is consistent with the slow logarithmic increase of the elastic modulus measured in glassy colloidal systems.[34]

In addition to the system becoming stiffer, we measured a strong deviation of the distribution of Δ from Gaussianity since its kurtosis increases with the aging time according to a power law with an exponent larger than 1. To discuss that behavior more quantitatively, we follow the analysis suggested by Colin *et al.*[35] Here we assume that the non-Gaussian distribution of Δ is a consequence of the superposition of Gaussians, whose widths ω are distributed with a distribution function $f(\omega)$. The probability of Δ is thus written as

$$p(\Delta) \propto \int \exp(-\Delta^2/\omega^2) f(\omega) \mathrm{d}\omega. \quad (4)$$

We assume for simplicity that the widths of the Gaussians ω are themselves distributed following a Gaussian of width ψ:

$$f(\omega) \propto \exp\left(-\frac{\left(\omega - \langle\omega\rangle\right)^2}{\psi^2}\right). \quad (5)$$

Experimentally, the mean value of ω approximately equals to the standard deviation of Δ: $\langle\omega\rangle \approx \sigma$. The Kurtosis of the distribution of Δ simply writes as

$$K = \frac{3\psi^4}{\langle\omega^2\rangle^2}. \quad (6)$$

Hence, and more generally, the kurtosis varies proportionally with ψ, the width of the distribution of the widths of the superimposed Gaussian fluctuations, to the power 4.

At present, we cannot evaluate these dependencies quantitatively from the experimental data as the value $\langle\omega^2\rangle$ is not accessible. However, going back to the experimental data on the aging emulsions, we can qualitatively predict that the strong increase of K is explained not only by the decrease of ω, but as well results from an increase of the width ψ. Looking at the data of $\varphi_o = 0.66$ in Fig. 7(b) and 8, the value of K increases about 100 times between $t_a = 10^4$ s and 10^5 s, meanwhile the value of σ varies quite little during that moment ($\sigma/\sigma_i = 0.8$ at $t_a = 10^4$ s and 0.6 at 10^5 s).

Indeed, the kurtosis increases because the rigid fluctuations are superimposed on some soft-like fluctuations. The latter fluctuations result in the occurrence of low frequency and large amplitude events, although the system becomes more rigid as it ages. Such modes are not predicted in the classic picture of dynamic heterogeneity. However, similar large amplitude events have been observed in several aging systems of different nature.[36]

In the aging emulsion, we find that the number of intermittent events increases with the aging time, and that these quakes are correlated in time, as the distribution of time intervals between them follows a power law with an exponent larger than 1 (Fig. 6). We suggest that internal stresses gradually accumulate during aging, and are intermittently released by local plastic strains, which induce a long range displacement.[37] The lifetime of the quakes is of the order of a few tenths of a second, corresponding to the time τ for which the kurtosis reaches a maximum (Fig. 7(a)). As the system ages, more and more internal stress is stored, resulting in an increase of the number of plastic events relaxing the internal stress. The time correlation between those events may result from their elastic coupling: the stress release does not occur completely randomly, but is likely to be related to the increase of internal stress induced by aging. New models are needed to improve the understanding of such intermittent aging dynamics.

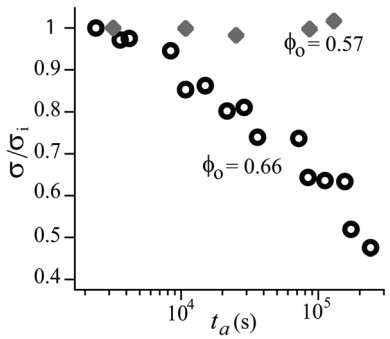

Fig. 8 Plot of the standard deviation of $\Delta(\varphi_o = 0.66)$ at $\tau = 600$ ms. The values of σ are normalized by the initial value σ_i. For reference, data of dilute emulsion ($\varphi_o = 0.57$) are plotted as gray rhombic symbols.

V. Conclusion

In this article, we have presented measurements of the fluctuations of the free surface on a glassy colloidal system that consists of Brownian oil droplets dispersed in water. The particle dynamics in volume was explored by the diffusing-wave spectroscopy (DWS), and the Surface Fluctuation Specular

Reflection (SFSR) technique was applied to measure the free surface fluctuations.

We have observed that between below and above the glass transition volume fraction, the liquid surface behavior dramatically changes. For dilute emulsions, the surface exhibits Gaussian fluctuations. For concentrated emulsions, large and intermittent quakes appear on the liquid surface as the system ages. Such intermittent quakes correspond to large changes in the local slope of the free surface over a few tenths of a second. By a statistical estimator, we have detected these quakes sensitively. We have observed for the first time that the kurtosis of the fluctuations ages with time with an exponent of about 1.3.

We finally suggest that those quakes reflect the dynamics peculiar to glassy systems driven by the relaxations of internal stress. During the aging, the internal stresses accumulate in the system, then they intermittently relax by the local plastic strain, inducing long range displacements.

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24 The span is another way for describing the drop size distribution, defined as: $\frac{D_{0.9} - D_{0.1}}{\overline{D}}$ where $D_{0.9}$ and $D_{0.1}$ are the diameters for which the cumulative undersized volume fraction corresponds to 90% and 10% respectively.
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