Crackling of a coagulating suspension

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A way of analyzing the intermittent dynamics of nonstationary systems is introduced. It is used to study the dynamics of a concentrated suspension while it is flocculating, probed by diffusing wave spectroscopy. When the repulsion interactions between the particles are slowly decreased their motion appears to be intermittent. It is characterized by rapid crackling periods, separated by arrested dynamics. Duration of the crackling periods exhibit a power-law distribution function.

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The cohesion of solids arises from attractive interactions between their elementary components. From a structural point of view, solids may be considered as force networks [1]. Nodes of a force network consist on the elementary components (atoms, molecules, or larger objects such as colloidal particles), with each segment connecting two nodes supporting a negative force dipole. When a disordered solid is made, for instance by aggregating colloids, a force network is progressively built. The creation of each new force dipole creation puts the existing network under tension, diminishing its number of degrees of freedom. At some point, the number of degrees of freedom becomes too low for the network to be able to sustain a new force dipole. This isostatic point, well studied in the case of central force networks [2], is of particular importance in many systems, including granular media [3], molecular glasses [1], colloidal gels [4], and engineering design. If force dipoles continue to be created at the isostatic point, then the system must rearrange in order to sustain them. This may lead to microscopic heterogeneities, or even macroscopic fractures, of the material [5]. We are interested here in the dynamic properties of attractive colloidal gels as a model system to study the dynamics of building a force network. As a first step, a stable suspension of colloidal particles is prepared in water. Their interactions are then slowly changed, either by increasing the ionic strength of the suspension, or by decreasing the surface charge of the particles, so that they become attractive. The system thus acquires elasticity.

When concentrated suspensions are used, this is the first step in the process of creating ceramics by direct casting coagulation; a concentrated liquid suspension is molded, flocculated, dried, and eventually sintered [6]. However, depending on the details of the coagulation procedure, the coagulated suspension, called wet green body by ceramists, exhibits very different mechanical properties that range from brittle to ductile [7]. Understanding how particles rearrange in order to sustain new force dipoles is thus of crucial importance for industrial applications. Rheological experiments have been performed [8] to monitor the increase of the elasticity of the system, but the linear regime of this fragile structure is extremely small, if it exists. One may wonder whether any deformation, no matter how small, does not break the weakest existing force connections.

The aim of this article is to study the dynamics of a concentrated suspension during flocculation. Diffusing wave spectroscopy (DWS) has already been used to monitor the short time dynamics of the particles during coagulation [9]. This is a light scattering technique that is applied to very turbid systems, serve a nonding as a nondestructive probe of the dynamics of the suspension. Generally, disordered concentrated systems exhibit two distinct relaxation times. The shorter one corresponds to the motion of the particles inside cages defined by their neighboring particles. The longer one is associated with long-time cage rearrangement. As expected, the amplitude of the shorter time decreases while the suspension flocculates. However, in order to understand the low frequency mechanical properties of the system, the long-time rearrangements that occur while the system is flocculating need to be monitored. The standard DWS technique consists of a running average over time and does not suit this task. Multispeckle DWS (MSDWS) overcomes this difficulty by averaging diffused light over different speckles [10,11]. It has been observed that fluctuations of the intensity diffused by concentrated systems exhibit non-Gaussian statistics [12,13]. Such findings suggest that the dynamics of concentrated systems are intermittent and reminiscent of the dynamics of driven disordered systems. When such systems are slowly driven, they respond with discrete events of a variety of size and duration; we will call these events crackling events [14]. Nevertheless, these experiments do not allow for the study of temporal properties of crackling events, such as how long an event lasts or the wait time between two crackling events. We present here a way of handling correlation data that allows for the analysis of intermittent dynamics.

We use a concentrated aqueous suspension of alumina particles (AK P30, Sumimoto) with a mean diameter of 350 nm and a refractive index $n=1.65$. An organic molecule derived from catechol, tiron, $4,5\text{–}(OH)_2\text{–}C_6H_2\text{–}1,3\text{–}(SO_3Na)_2$, is used to stabilize the suspension at a high volume fraction, up to 54% [8]. The volume fraction of alumina particles is varied from 32% to 44%. Tiron adsorbs at the surface of alumina particles by formation of an inner sphere complex between the metal ions on the surface and the alcohol groups in the molecule. Hydroxyaluminum diacetate powder is then added to the suspension at a concentration of 0.45 M. This

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powder is almost insoluble in water, but slowly decomposes to release acetate and dialuminum ions. These ions increase the ionic strength of the suspension [8] thus screening the repulsive interactions between colloids, causing the suspension to flocculate. The decomposition rate of hydroxyaluminum diacetate may be controlled by varying the temperature. At 45 ° C, the characteristic decomposition time as measured by the ionic strength of the solution is 20 min, but the diacetate salt continues to decompose for several hours. All the experiments presented here are performed at this temperature. The dynamics of the particles are monitored during 5 h after the diacetate salt is added. The elastic modulus of the alumina suspension diverges at a time corresponding to the dissolution time of the diacetate powder, in 20 min. When the suspension flocculates, we do not observe any retraction of the system or water repulsion. In the range of alumina volume fraction studied, expelled water measured by γ-densimetry is inferior to 2%. Shrinkage of the suspension under gravity is thus not observed.

The sample is placed in a 1 mm thick cell and illuminated with an enlarged laser beam (argon, SpectraPhysics), of diameter 5 mm and wavelength 514 nm. At the studied concentrations, the sample is very turbid, and light is multiply diffused. The turbidity of the sample may be characterized by its photon scattering mean free path, l^* [15]. We measured l^* by comparing the intensity transmitted by the system with the intensity transmitted by a latex suspension of known scattering mean free path [16]. The scattering mean free path is then deduced, and its value, 5 ± 0.5 μm remains constant throughout the experiment while the suspension flocculates. An interference pattern forms, depending on the position of the scatterers and a CCD camera (Pulnix TM9701) records the speckle image, in the backscattering geometry. The correlation value between two images is then computed by averaging the intensity fluctuations over the entire image, containing $\sim 10^4$ speckles. The smallest spatial motion of the scatterers that can be detected is ~ 3 Å. If a reference image is chosen and its correlation with all subsequent images is computed, the following correlation function emerges:

$$g_2(\tau) = \frac{\langle I_p^0 I_p(\tau)\rangle_p}{\langle I_p^0\rangle_p \langle I_p(\tau)\rangle_p} - 1, \qquad (1)$$

where $\langle \ldots \rangle_p$ represents averaging over the pixels, and index 0 corresponds to the reference image. One thus has access to the instantaneous dynamics of the system. However, depending on the reference image chosen, the correlation functions exhibit very different decay times and shapes (Fig. 1). From these functions, it appears that the dynamics of the suspension are temporally heterogeneous.

In order to quantify these dynamics, the correlation value of any two speckle images separated by any time lapse τ is computed. We record the images (at a frequency of 6 Hz) and then construct the surface correlation as outlined below. The value of the correlation between two images taken at t and $t+\tau$ is given by Eq. (2):

$$c(t,\tau) = \frac{\langle I_p(t) I_p(t+\tau)\rangle_p}{\langle I_p(t)\rangle_p \langle I_p(t+\tau)\rangle_p} - 1, \qquad (2)$$

$c(t,\tau)$ is thus a two-variable function, both of the total elapsed time t since the addition of the acetate salt, and of the time interval τ between two images. It has been defined by Bissig *et al.* in [12], and the statistical properties of the one-variable function, $c_{\tau_0}(t)=c(\tau_0,t)$ have been studied. The authors follow the aging of concentrated colloidal suspensions and observe that $c_{\tau_0}(t)$ exhibits non-Gaussian fluctuations. The probability density function of $c_{\tau_0}(t)$ is asymmetric, and possesses a tail for low-value correlations. This led the authors to the conclusion that the aging dynamics of concentrated suspensions is intermittent. Nevertheless, more detailed properties of the intermittencies, such as their duration, or the elapsed time between them have not been studied. The goal of this article is to fully exploit the two-time dependency of the correlation function $c(\tau,t)$ in order to have access to statistical properties of intermittent events.

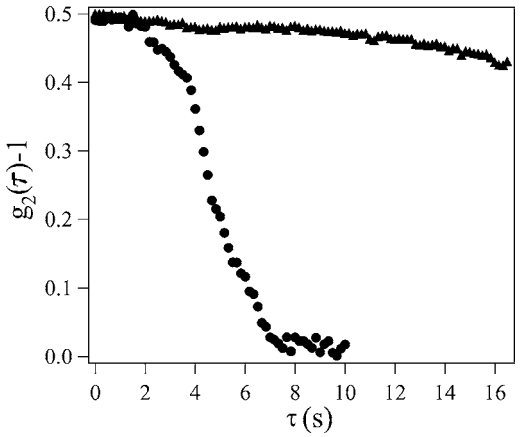

FIG. 1. Correlation functions of backscattered intensity for two different reference images (▲) : reference image is taken at $t=12\,500$ s. (●) : time of reference image is 12 483 s. No polarizer is used in the detection optics. The expected limit of the correlation function when $\tau \to 0$ is thus 0.5.

Let us thus plot Eq.(2) as the height of a surface (Fig. 2). As previously [Eq. (1)], $I_p(t)$ is the intensity collected on speckle p at time t, and $\langle .. \rangle_p$ is the average over the pixels [17]. This representation exhibits the following properties:

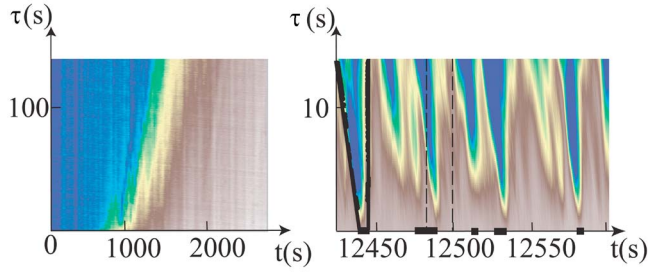

FIG. 2. (Color online) Future-past correlation surfaces for a suspension with volume fraction 34%. Correlation increases from 0 to 0.5 from blue to red. Left: short time correlation surface, when the transition from a fluid to an elastic behavior occurs. Right: Zoom of the correlation surface at longer times, between $t=12\,450$ and $t=12\,600$ s. Duration of the longer crackling events are plotted as thick lines on the abscissa axis. Lines of slope -1 and ∞ are the borders of the wedges, determined as anomalously low correlation values (Fig. 4). Correlation functions plotted in Fig. 1 are read along vertical dashed lines.

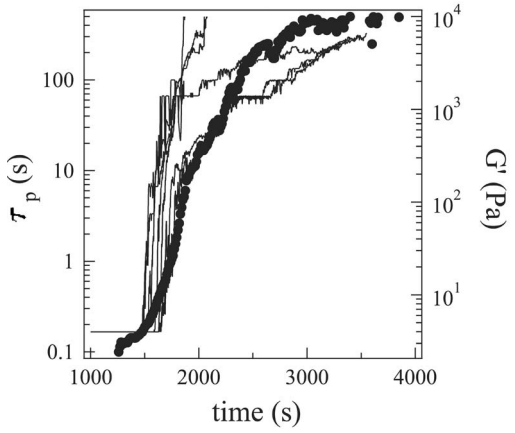

FIG. 3. Characteristic time of the correlation function, τ_p, as a function of time, t. Each curve corresponds to a given concentration. From left to right at short times: $\phi=32\%$, 34%, 36%, 38%, 42%, 44%, and 46% Plain circles (●) represent the evolution of the elastic modulus, of a suspension whose $\phi=36\%$, measured in a cone-plate geometry, with a constant controlled stress, $\sigma=1$ Pa, at a frequency $\nu=1$ Hz.

All the correlation values associated with a given image taken at time t belongs to two straight half-lines. Along a line of either slope ∞, or of slope -1, crossing the abscissa axis at time t, one reads the correlation value between the image recorded at time t and all images in the future (slope ∞) or past (slope -1).

The correlation between two images separated by a given time lapse τ is read along the horizontal line of ordinate value $y=\tau$ [12].

A transition from smooth dynamics at short times t to heterogeneous temporal dynamics at longer times is observed. At short times ($t<2000$ s), the characteristic decay time of the correlation functions smoothly increases, whereas for sufficiently long times (Fig. 2), the dynamics associated with some images is anomalously fast. Along some lines of slopes -1 and ∞, the correlation values are anomalously low.

Let us first describe the transition from smooth to intermittent dynamics. The time τ_p needed, at each instant, for the intensity, to become half-correlated, allows to describe this transition (Fig. 3). At the beginning of the experiment, τ_p is too short to be measured with the temporal resolution of our apparatus, ($\tau_p<0.17$ s). Its value then abruptly increases and the instant at which τ_p begins to diverge is almost independent of the volume fraction of the sample. This divergence is related to the time at which the suspension acquires an elastic modulus. Thus, as long as the suspension remains fluidlike, the motion of the particles is temporally continuous. On the contrary, as soon as an elastic network is formed in the suspension, crackling occurs.

We now move on the dynamics of the suspension at long times. It is important to remember that the diacetate salt continues to dissolve after the suspension exhibits an elastic modulus. Because of this, the preexisting elastic network is put under tension, and we are measuring the response of the suspension to this driving force. The dynamics of the suspension are thus nonstationary, and we aim at describing their time irreversibility properties. Let us first compute the probability distribution of the correlation value between any two images separated by a constant time lag, τ, i.e., along a line of ordinate value τ (Fig. 4) [12]. For a situation of stationary dynamics, the correlation value would be constant. On the contrary, once the transition to elastic behavior occurs, these isotime lag curves have a constant mean value, but are extremely noisy: anomalous correlation losses are observed. Therefore, the probability distribution functions are asymmetric and exhibit long tails at low correlation values (Fig. 5). Beyond the Gaussian fluctuations due to the normal motion of scatterers and the noise of our apparatus, large fluctuations are observed. These large fluctuations allow us to define a criterion to identify anomalous dynamics of the scatterers. This criterion is a correlation value smaller than the most probable correlation value minus twice the width of the Gaussian noise. The anomalous dynamics, identified by com-

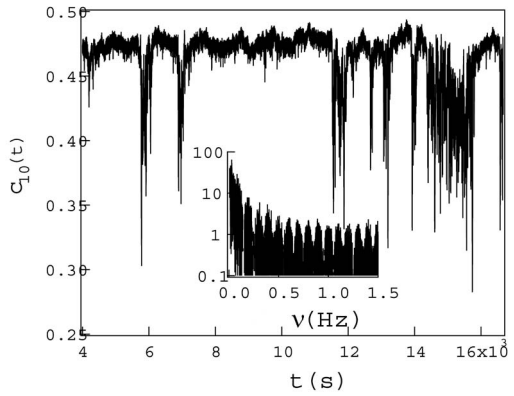

FIG. 4. Isotime lag function, $c_\tau(t)$, for $\tau=10$ s, as a function of time, $t>4000$ s, i.e., after the increase of the elastic modulus. Concentration of the suspension is $\phi=34\%$. Inset: Fourier transform of $c_{10}(t)$. It exhibits a frequency of 0.1 Hz.

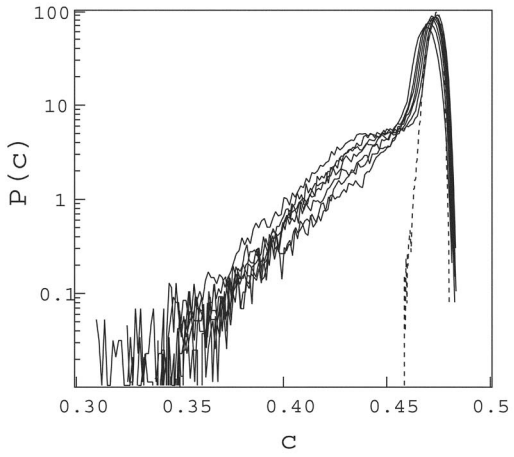

FIG. 5. Probability density function of the isotime lag curve, for $\phi=34\%$, and different values of the lag time. When the time lag increases, the curves are shifted towards lower c values. From right to left: $\tau=10$ s, $\tau=14$ s, $\tau=18$ s, $\tau=20$ s, $\tau=24$ s, $\tau=27$ s, $\tau=33$ s. Dashed curve is the probability density function obtained for a sample of identical optical properties, at 45 °C, but without dynamics. It shows the Gaussian noise of our apparatus.

paring two images at $t-\tau$ and t, do not allow a determination of which of these two images is responsible for the correlation loss. This shows up more clearly by considering the Fourier transform $\tilde{c}_\tau(\nu)$ of the isotime lag curve. It exhibits periodic oscillations at frequencies multiple of $1/\tau$ (Fig. 4, inset), indicating that redundant information is stored at two points separated by time lag τ.

Indeed, $c_\tau(t)$ is in fact a two-variable function whose one of them, the lag time τ, has been hidden. Thus, the value $c_\tau(t)$ is by construction correlated with the value $c_\tau(t-\tau)$. As a consequence of the Wiener-Khinchin theorem, this autocorrelation shows up in the Fourier transform: $\tilde{c}_\tau(\nu)$ is periodic, with a period $1/\tau$. Thus, if an anomalously low value of the correlation value c_τ is observed at time τ, one cannot distinguish whether the anomalous dynamics occurred at time t or at time $t-\tau$. In order to easily raise this ambiguity, one needs to consider at least two correlation functions, $c_\tau(t)$ for two different values of τ. As any choice of two values of τ would be arbitrary, and in order to reduce the noise, we consider hereafter the entire set of $c_\tau(t)$ for $0<\tau<100$ s, plotted in Fig. 2.

In order to unambiguously identify the time at which crackling events occur, we report the points of anomalously low dynamics in the plane (t,τ). They all belong to wedge-shaped surfaces whose slopes are -1 and ∞. These surfaces appear in blue and light grey in Fig. 2. This is an important observation, as it implies that the anomalously fast dynamics are due to the rapid motion of the scatterers during a short amount of time. Indeed, any two images inside a given wedge are correlated, while an image inside and one outside suffer a correlation loss. The duration of a crackling event may thus be measured by counting the number of images that are not correlated with either preceding of subsequent images.

A series of samples with volume fractions varied from 32% to 44% was studied. The analysis described above was performed during the coagulation of these suspensions, after the transition to elastic behavior. Each experiment lasts 5 h and the total number of crackling events recorded is on the order of 10^3. We first observe that the mean duration as well as the mean waiting time between two events remain constant while coagulation occurs. The probability density function (PDF) of the crackling events duration is in fact a stationary property of the coagulating suspension. We report in Fig. 6 the PDF of the crackling events duration, which spreads over a wide range of times (Fig. 6, inset). It is apparent that their PDF is a power-law distribution, $P(\tau)\propto\tau^{\alpha}$ with a slope comprised between -1.9 and -2.1.

This technique allows us to have access to the time intervals between two successive crackling events, $\delta\tau$. At short times, $\delta\tau<3$ s, the distribution function obeys a power-law function of slope -2 (Fig. 7). These non-Poissonian statistics imply that short-time correlations exist between two successive crackling events. At longer times, the probability distribution function exhibits a cutoff. Nevertheless, for each concentration, the total number of crackling events is of the order of 10^3. The number of events recorded for $\delta\tau>3$ s is of the order of 100. The number of events recorded in each channel of the histogram is thus smaller than 5. This low statistical resolution prevents us from finding an analytical form of the tail of the density of probability of $\delta\tau$.

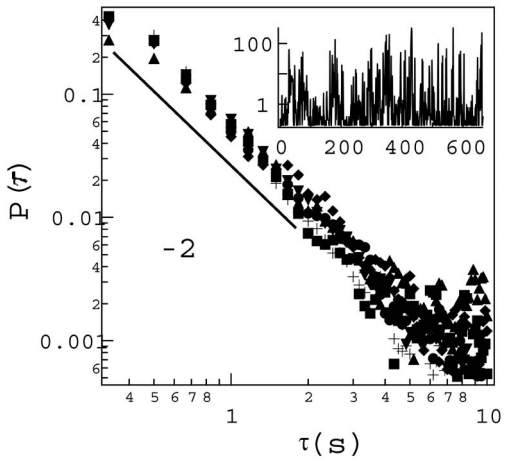

FIG. 6. Probability density function of the duration of cracks, τ, for ϕ=32% (●), 34% (■), 36% (▲), 38% (▼), 42% (♦), and 44% (+). Inset: Time duration of a crack, τ, in seconds, as a function of the crack number.

Moreover, in the range of volume fractions studied, we observed no variation in either crackling events duration, or the waiting time between two crackling events (Fig. 7, inset). Additional volume fractions could not be studied because suspensions of higher concentration are not fluid enough to be loaded into our cell and lower volume fraction samples exhibit retraction. Let us emphasize that the average duration of crackling events and the mean waiting time between two of them are of the same order. This is in contrast with one might expect from intermittent behavior, where the events are much scarcer. Indeed, similar dynamics, characterized by an absence of time scale are characteristic of many slowly driven disordered materials [14], from magnetic materials [18] to compressed ice [19]. In such cases, the dynamics is

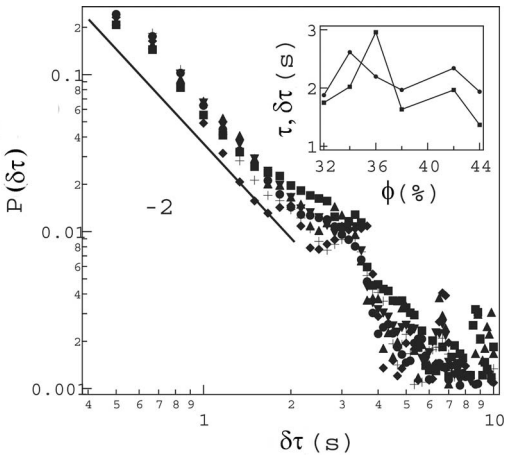

FIG. 7. Probability density function of the time duration between two successive cracks, $\delta\tau$, for ϕ=32% (●) 34% (■), 36% (▲), 38% (▼), 42% (♦), and 44% (+). Inset: mean value of the crack duration, τ (■), and waiting times, $\delta\tau$ (●), as a function of the volume fraction.

governed by the intermittent motion of grain boundaries. On the contrary, in the case of concentrated suspensions, crystallization and grain boundaries are not observed. Molecular dynamics simulations [20], as well as cryoscanning electron microscopy images [21], show that when coagulation occurs, compact flocs with a fractal dimension of 3, develop. Particles belonging to the same floc are in close contact, and lie in the first Van der Waals minimum of their interaction potential [21]. As particles of the same floc cannot move relative to one another, the crackling events we observe are due to a reorganization of dense flocs that leave large voids responsible for the fragility of the final system. This motion of dense structures may be responsible for the longer duration of the crackling events.

As a conclusion, we have developed a way of analyzing correlation data that allows the study of intermittent dynamics. Although this method has been applied to light scattered by a concentrated suspension, it may be used to search for intermittency in any fluctuating signal.

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[16] We use a series of suspensions of polystyrene particles whose volume fractions are comprised between 0.8% and 3%. The diffusion coefficient is independently measured by quasielastic light scattering after dilution, and is $D=2.8\times10^{-12}\,\mathrm{m}^2s^{-1}$. For each suspension, the scattering mean free path is determined according to the following procedure. We measure the correlation function of light diffused by each suspension, both in backscattering and transmitted geometry, and fit the obtained curves with two free parameters: the photon scattering mean free path l^* and the penetration depth z_0 [15]. The measured mean free path are comprised between 85 μm and 250 μm. These samples are thus approximately one order of magnitude less turbid than our sample. Using two calibrated optical densities OD ($OD=11.3\pm0.4\%$ and $OD=1.25\pm0.04\%$ at 514 nm), we then construct a reference curve of the transmitted intensity vs. the product OD. l^* for these reference samples. Reporting the intensity transmitted by our system (in the same cell) without optical density, we deduce its scattering mean free path.
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