Slow dynamics in glasses, gels and foams

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Abstract

Slow dynamics and aging effects in disordered, out-of-equilibrium systems are a rich and fascinating topic, yet still poorly understood. Recent developments in light scattering methods, such as the multispeckle technique, combined with new theoretical approaches that underline the analogies between different glassy materials are bringing a better understanding of these phenomena.

Keywords: Aging; Lightscattering; Glass; Gel; Colloids; Rheology

1. Introduction

Disordered, out-of-equilibrium systems are ubiquitous: they include structural, polymer [1], or spin glasses [2], granular materials [3], and many 'soft' materials [4], such as gels, pastes, concentrated emulsions and foams. Their use in industrial applications is widespread and they represent an active field of research subject to an intense debate [5]. Because the mobility of their constituents is extremely reduced, these systems are frozen (or 'jammed' [6*]) in configurations far from thermodynamical equilibrium. As a result, they exhibit unusually slow relaxations and aging effects: measured quantities such as response or correlation functions often depend on the time elapsed since the material was first quenched in the disordered phase. Remarkable analogies between widely different systems have been pointed out; however, these phenomena are still poorly understood.

For many soft materials, dynamic light scattering (DLS) [7] is an ideal experimental tool for studying aging, since it allows the dynamics to be directly probed without perturbing the system. New techniques that overcome the difficulties traditionally posed by non-ergodicity and ultra-long relaxation times have been recently developed: these methods will certainly contribute to gain a better understanding of the dynamics of disordered materials. In this review, we report mainly on light scattering investigations of jammed soft condensed matter systems published in the past 2 years; rheology experiments and new theoretical advances will also be discussed briefly.

2. Recent developments of light scattering techniques

Traditional light scattering experiments probe the sample dynamics by measuring the time autocorrelation function of the fluctuations of the intensity scattered within a single speckle or coherence area [7]. For ergodic samples, ensemble averages and time averages are equivalent; therefore, the desired ensemble-averaged correlation functions are obtained by extensively averaging over time, the measurement time being typically three to four orders of magnitude longer than the system relaxation time. Out-of-equilibrium systems pose a three-fold challenge to this approach: (i) the sample is non-ergodic; (ii) the dynamics is often very slow, thus making the measure-
ment duration impractically long; (iii) the dynamics may be time-dependent, e.g. for aging systems. Correction schemes have been developed to address: (i) [8,9]; unfortunately, these methods are not apt to access the slow dynamics. An alternative approach consists in averaging the autocorrelation function not only over time, but also over a large number of different speckles. For a point detector (e.g. a phototube), this can be achieved either by slowly rotating the sample (‘interleaved’ method [10]) or by periodically oscillating it (‘echo’ DLS [11]), so that the same speckle will fall onto the detector after a full rotation or oscillation. Even more efficiently, correlation functions for thousands of different speckles can be calculated in parallel and then averaged by using a two-dimensional detector, usually the chip of a CCD camera. This ‘multispeckle’ approach drastically cuts the required measurement time and applies to non-ergodic samples as well. It has been adopted in several experimental configurations, both in the single [12–14] and multiple [15*,16,17] scattering limit, as well as for X-ray photon correlation spectroscopy (XPCS) [18,19]. Multispeckle methods are rapidly becoming a widely used, powerful technique to investigate the slow dynamics of non-ergodic, non-stationary systems.

3. The jamming transition

Liu and Nagel [6*] have recently presented a scheme to unify a wide range of fluid-solid transitions by introducing the concept of jamming and proposing a three-dimensional jamming transition phase diagram. Trappe et al. [20**] have shown that a jamming phase diagram can indeed be established to account for the fluid–solid transition in a large variety of attractive colloidal systems. This phase diagram is shown in Fig. 1; its axes are the inverse volume fraction $\varphi^{-1}$, the ratio between thermal energy and the interparticle attractive potential, $k_B T/U$, and an applied stress $\sigma$. The jammed phase occupies the inner octant: a system jams above a $\varphi$- and $U$-dependent critical volume fraction, or above a $\sigma$- and $\varphi$-dependent critical $U$; conversely, a jammed system is fluidized when a stress is applied that exceeds a $U$- and $\varphi$-dependent critical value. Remarkably, the same critical-like divergence of the viscosity and onset of the elastic modulus are observed when crossing the different boundaries of the phase diagram: these observations support the fundamental concept of jamming and demonstrate its validity as a universal tool to rationalize the solid–fluid transition.

Fig. 1. The jamming phase transition diagram for attractive colloids (reproduced with permission from Nature (http://www.nature.com): Trappe V, Prasad V, Cipelletti L, Segrè PN, Weitz DA, Jamming phase diagram for attractive particles, Nature 2001;411:772–775 [20**]). A system may jam when increasing the volume fraction $\varphi$ or the interparticle attractive energy $U$ above a critical value; conversely, an applied stress $\sigma$ can re-fluidize it. The jammed phase, which occupies the inner octant, is characterized by a dramatically reduced particle mobility and the onset of aging effects.
4. Dynamics at the jamming transition

As the jamming transition is approached, the dynamics dramatically slows down and the system is confined in an increasingly reduced region of the phase space, giving rise to non-ergodicity effects. This process can be effectively followed by DLS. Historically, much effort has been devoted to the investigation of hard spheres [21], a model system for the glass transition in simple liquids. For hard spheres, the slowing down of the dynamics is due to the crowding of the particles when approaching the glass transition volume fraction $\varphi = 0.58$; in the phase diagram of Fig. 1, this corresponds to a cut towards the jammed phase along the $\varphi^{-1}$ axis. The correlation functions measured by DLS typically exhibit a two-step decay: an initial decay ($\beta$-relaxation), due to the particle motion within the cage formed by their neighbors, is followed by a plateau and a final decay ($\alpha$-relaxation), which corresponds to the cage-escape process. As the glass transition is approached, the plateau height increases and the $\alpha$-relaxation characteristic time diverges. Recent work in this area includes a DLS investigation of the glass transition in a binary mixture of hard spheres [22•]. (Note that binary mixtures are often used in simulation work to prevent crystallization [23].) Charged colloids form glasses that exhibit a behavior similar to that of hard spheres (‘Wigner’ glass) [24,25•], the particle volume fraction being replaced by an effective volume fraction, which accounts for the long-ranged interaction.

Similarly to hard spheres, attractive systems can undergo a fluid–solid transition, as it is widely documented in the literature on polymer or particle gel formation. Although analogies between the dynamics in gels and glassy systems have been pointed out in the past [26], only recently has a unifying view of gelation and the glass transition begun to emerge. Bergenholtz et al. [27] have analyzed the gelation of short-range attractive colloids in the framework of the Mode Coupling Theory [28], originally developed for glasses. They propose that gelation be triggered by the slowing down of local dynamics due to the creation of long-lived interparticle bonds. Segrè et al. have measured the dynamics of suspensions of weakly attractive colloids as a function of both volume fraction and interparticle attraction, thus exploring the jamming transition in the $\sigma = 0$ plane of Fig. 1 [29•]. They stress the deep analogies between the glass and the gelation transitions and conclude that both result from a kinetic arrest due to the crowding of clusters (for gels), or individual particles (for glasses).

A full description of attractive colloidal systems must include also the effects of the hard core repulsion at particle contact. Pham et al. [30••] use a combination of experiments, theory and simulations to thoroughly study the jamming transition for sticky hard spheres, which interact via the depletion potential (more details on the simulations can be found in Puertas et al. [31]; a DLS investigation on a similar system is presented in Eckert and Bartsch [32]). The phase diagram shown in this paper (which can be mapped to the $\sigma = 0$ plane in Fig. 1) is in good agreement with the predictions of the Mode Coupling Theory [33]. It exhibits the existence of two qualitatively different glassy states, dominated by repulsion and attraction, respectively. In this framework, gelation and the (repulsive) glass transition are therefore unified as manifestations of the onset of glassy (or jammed) states. Interestingly, the existence of multiple glassy states is also found in a completely different system, block-copolymer micelles [34•], which interact via a potential qualitatively similar to that reported in Pham et al. [30••]. This analogy further supports the generality of the jamming picture.

5. Slow dynamics and aging of jammed systems

Systems quenched in the jammed phase are far from thermodynamical equilibrium; as a consequence, their properties continuously evolve with time. In particular, correlation functions measured by DLS depend not only on the time delay $t'$, as for time-translation invariant systems, but also on the waiting time $t_w$ since the system was jammed (i.e. the sample age). Typically, the dynamics becomes progressively slower as the sample ages. To our knowledge, the first light scattering experiments where aging phenomena were observed are described in [35,36] (hard spheres colloidal glass); a slowing down of the dynamics after initialization by applying a strong shear to the sample has also been reported for glassy suspensions of charged synthetic clays (Laponite) [24]. These early works used either traditional DLS or the interleaved method; to fully characterize the aging behavior of jammed systems, however, CCD multispeckle methods are generally preferable as demonstrated both in single [37•,38••] and multiple scattering experiments [15•,39••,40].

A remarkable finding of multispeckle experiments is the existence of ultraslow relaxations in jammed systems, leading to a full decay of the intensity autocorrelation function. This result is particularly surprising for small angle experiments [37•], where the dynamics is probed on length scales as large as several tens of micrometers, thus demonstrating that particle rearrangements may occur over nearly macroscopic distances, while the structure, as probed by static light scattering, often hardly changes. Both attractive [37•] and repulsive [38••] systems where found to exhibit the same very unusual dynamics: the dynamic struc-
ture factor decays as a ‘compressed’ exponential $\exp(-\langle\tau/\sigma\rangle^p)$, with $p \approx 1.5$ and $\tau \sim q^{-1}$, where $q$ is the scattering vector. This dynamics has been interpreted as ‘ballistic’ motion resulting from the relaxation of internal stresses (see [41*] for a more refined model). Remarkably, a distribution of velocities similar to that measured in these works has been reported for the flow of dislocations in a stressed ice crystal [42**]. Although these dynamics seem to be quite general, other functional forms and different $q$-dependencies have also been observed [25*,43*].

Diffusing wave spectroscopy (DWS) [44] probes the dynamics on much smaller length scales. Knaebel et al. report age-dependent slow supra-diffusive motion of probe particles in a Laponite glass [15*], while the evolution of the local dynamics after applying a shear to the sample is investigated in Cohen-Addad and Höhler [39**] and Viasnoff and Lequeux [40] for a foam and a colloidal glass, respectively. Since all $q$-dependent information is lost in DWS, the interpretation of the dynamics is less straightforward than in DLS: in our view, with the exception of foams [45], more effort will be required for a complete understanding of the DWS correlation functions of jammed systems.

A more complete picture of the aging in jammed systems may be obtained by combining different experimental techniques. Rheology can play a major role, because applied and internal stresses influence the jamming transition and the dynamics in the jammed phase. Moreover, rheology is a well-established tool for studying aging since the pioneering work of Struik [46] on polymer glasses. Experiments in the linear regime [38**,47*,48] measure the (age-dependent) response of the system to a small mechanical perturbation. Recent theoretical models [49,50**], inspired by Bouchaud’s trap model for spin glasses [51], interpret the results in terms of relaxation of stress when the locally varying strain exceeds a local yield strain. A simpler rheological model has also been proposed [52]. One of the features common to most light scattering and linear rheology studies is the asymptotic power-law scaling of the characteristic relaxation time with sample age: $\tau \sim t_c^\mu$, with the aging exponent $\mu$ often close to one (linear or simple aging). Note that a faster growth has been observed in some cases, mainly in the initial stages of aging [25*,37*]. Intriguing analogies exist with other disordered systems, such as spin glasses and polymer melts [53], for which the same behavior has been observed.

For soft condensed materials, a strong shear is often used to initialize or partially rejuvenate the system. Berthier et al. [54] shows that the competition between aging and shear rejuvenation manifests itself as a bifurcation in the stress-dependent viscosity. Rheology can therefore be used to study the jamming transition by cutting the phase border of Fig. 1 along a line parallel to the $\sigma$ axis [47*]. This is analogous to a temperature variation in hard condensed matter systems, such as structural glasses; this analogy has been investigated in theoretical work [55*,56], where the concept of an effective temperature related to an external mechanical drive has been introduced. Diffusing wave spectroscopy has been used to measure the dynamics of colloidal glasses [40] and foams [39**] after applying a strong shear. While for the former system the relaxation time is reduced after shearing and increases with age, for the latter the opposite behavior is observed. The apparently counterintuitive results for foams are nicely explained [39**] by assuming that shearing erases the highest internal stresses, responsible for the faster rearrangements. With aging, coarsening of the bubbles rebuilds internal stresses, leading to a faster relaxation time. Finally, we note that for materials with low yield stress, such as gels at low $\phi$ or with weak interparticle attractive energy, gravitational stress greatly influences the system rearrangements and its aging [57*,58,59].

### 6. Conclusions and future directions

Recent advances in light scattering techniques have opened new exciting possibilities for studying the slow dynamics and the aging of far-from-equilibrium systems, a domain not accessible to traditional methods. The jamming picture provides a unifying conceptual framework for investigating these phenomena in a wide range of different systems. Further progress will increasingly require the combined use of different techniques. In this direction, we note that dielectric relaxation (a technique usually adopted for studying structural glasses) has recently been used for colloidal glasses [60]. Conversely, soft condensed matter methods such as multispeckle DLS have the potential to be powerful tools for the investigation of supercooled liquids [61]. This cross-breeding between the methods used for soft glassy materials and structural or spin glasses has already proved to be fruitful in the theoretical approach.

In our view, future directions of research will include the characterization of spatial and temporal heterogeneities in the dynamics, memory effects and rejuvenation, and the universality of the slow dynamics and the aging. Intermittent dynamics has been observed in foams [45,62**] and dislocation flow [42**]; in supercooled colloidal fluids and colloidal glass, spatial heterogeneities are proposed theoretically [5,63] and have been evidenced by confocal microscopy [64*,65*]. These effects are most likely ubiquitous in disordered materials; new scattering
methods will be necessary to address this issue. On a theoretical level, models that go beyond a phenomenological approach by providing a system-specific microscopic description in real space are needed; Bouchaud and Pitzard [41] is one example of such models. Memory effects and rejuvenation have been observed in spin glasses [60]; they are now increasingly studied in soft matter systems [40,67]. Finally, despite the striking similarities in the dynamics and the aging of very different systems, the universality of these phenomena as well as its physical roots are still under debate.

Acknowledgements

We thank all the authors that responded to our request of reprints and preprints for this review paper.

References and recommended reading

- of special interest
- of outstanding interest


The authors propose a phase-diagram to rationalize the similarities in the behavior of glasses and granular matter. The ‘jammed’ phase occupies the inner octant of the phase-diagram with temperature, load and 1/density as axes.


First example of the use of multispeckle diffusive wave spectroscopy technique to investigate the non-stationary dynamics of a colloidal glass. The decay time of the autocorrelation functions is found to increase linearly with sample’s age.


Experimental data from three different colloidal suspensions are combined to construct the phase-diagram shown in Fig. 1.


This optical contrast variation study shows that the addition of small particles slows down the motion of the large spheres within their neighbors’ cage (slower β relaxation), but ‘lubricates’ the escape from the cage (faster α relaxation).


Standard dynamic light scattering study of the formation of a laponite glass. The correlation function exhibits a two-step decay: both the slow and the fast relaxation times scale as q−2; they are interpreted in terms of diffusion within cages and cage escape, respectively.


Detailed static and dynamic light scattering study of gelation for weakly attractive colloids. When U approaches 0, the fluid–solid boundary in the ζ−1, U−1 plane of the jamming phase diagram is found to extrapolate to the hard sphere glass transition volume.
fraction. The scattering vector dependence of the $\alpha$-relaxation characteristic time is similar to that observed for colloidal glasses (Sebè RN, Pusey PN. Scaling of the dynamic scattering function of concentrated colloidal suspensions. Phys Rev Lett 1996;77:771–774).


This paper nicely combines experiments, theory and simulations to study the glass formation in a suspension of sticky hard spheres. It demonstrates that two qualitatively different glass transitions exist, one driven by the repulsion between particles and one driven by their attraction. They are at the origin of the experimental re-entrant glass transition observed by the authors and by others [32].


The concentration and temperature-dependent kinetic arrest observed in the investigated micellar system is due to the existence of an attractive tail in the interparticle potential. The shape of the dynamic structure factor is in agreement with the predictions of the Mode Coupling Theory [33].


Detailed low-angle multispeckle dynamic light scattering study of a aging fractal colloidal gel. The very peculiar features of the slow relaxation of the dynamic structure factor (a decay faster than exponential, whose characteristic time scales as the inverse scattering vector), are interpreted in terms of internal stress relaxation.


Multispeckle DLS and linear rheology experiments are combined to probe the slow dynamics and aging of a dense arrangement of soft spheres. The same age dependence of the rheology and light scattering characteristic times is observed, thus suggesting that the two techniques probe similar physical processes: the relaxation of applied or internal stresses for rheology or DLS respectively.


The rate of local rearrangements in foams following a mechanical perturbation is investigated using multispeckle diffusive-wave spectroscopy. This study nicely illustrates the subtle interplay between the slow dynamics, the aging of a foam, and its macroscopic deformation.


A microscopic model is developed, based on the build-up of internal stress due to random micro-collapses in the gel. The model reproduces the very unusual features of the slow dynamics of a fractal colloidal gel [57].


The flow of dislocations in stressed single ice crystals is investigated by acoustic techniques and simulations. The authors show that the dynamics is intermittent and that the distribution of the velocity of dislocations asymptotically decays as a power law with exponent $-1.5$.


Dynamic and static light scattering study in the vicinity of the gel point for colloidal spheres whose stickiness is controlled by temperature. The slow relaxation, whose characteristic time scales as $q^{-0.51}$, is interpreted as due to rare, thermally induced, bond breaking.


The aging of a dense arrangement of soft spheres is studied by rheology. The authors find that the aging exponent $\mu$ decreases when the applied stress increases and is equal to 0 at the yield stress. They propose that $\mu$ can be used to quantify the partial rejuvenation of the system due to an external stress.


A model, based on the trap model for the dynamics of glasses [51], is developed to account for the rheology of jammed systems. Local structural rearrangements play a central role in this approach. In this paper, the role of aging in the linear and nonlinear rheology is studied in detail.


Extension of the mode-coupling approach used for glasses [28] to the case where a driving force, i.e. a shear rate γ, is imposed to the sample. The authors show that the drive leads to a stationary state. The γ-dependence of the viscosity and that of the scaling properties of the correlation functions are studied in the steady state.


Detailed experimental study of the collapse of a gel formed by colloidal particles with short-range attraction. The observed delayed sedimentation of a gel under gravity suggests the existence of slow rearrangements processes before the collapse. A theoretical analysis based on stress transmission in the gel is given in Evans and Starrs [58].


A novel optical method is presented to probe the grain dynamics for continuous or intermittent flows and also for the transition between these two states. The technique is based on diffusive wave spectroscopy with the use of higher order temporal correlation functions in the intensity of multiple scattered light. This original method could certainly be applied for turbid jammed soft materials.


Using confocal microscopy, dynamic heterogeneities in hard colloidal spheres close to the glass transition are directly observed. The existence of two sub-populations, a slow one and a fast one, is shown.


Experiments very similar to [64], except that the particles are tracked in three dimensions. The fast-moving particles belong to clusters whose shape, size and dynamics are characterized above and below the glass transition.
