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## REVIEW ARTICLE

## Slow dynamics in glassy soft matter

Luca Cipelletti§ and Laurence Ramos

LCVN UMR 5587, Université Montpellier II and CNRS, P. Bataillon, 34095  
Montpellier, France**Abstract.**

Measuring, characterizing and modelling the slow dynamics of glassy soft matter is a great challenge, with an impact that ranges from industrial applications to fundamental issues in modern statistical physics, such as the glass transition and the description of out-of-equilibrium systems. Although our understanding of these phenomena is still far from complete, recent simulations and novel theoretical approaches and experimental methods have shed new light on the dynamics of soft glassy materials. In this paper, we review the work of the last few years, with an emphasis on experiments in four distinct and yet related areas: the existence of two different glass states (attractive and repulsive), the dynamics of systems very far from equilibrium, the effect of an external perturbation on glassy materials, and dynamical heterogeneity.

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## 1. Introduction

A wide range of soft materials exhibit slow relaxations strongly reminiscent of the glassy dynamics observed in hard condensed matter. These materials include concentrated or strongly interacting colloidal suspensions, emulsions, surfactant systems, polymeric or colloidal gels, and foams [1]. Most of these materials are out of thermodynamical equilibrium: for systems far from equilibrium, a continuous evolution of the mechanical and dynamical properties is observed, in analogy with the slowing down of the dynamics in aging hard glasses. Several different terms are used in the literature to designate out-of-equilibrium soft materials, depending on the context and the authors' views: gels, glasses, and jammed [2] systems are but a few examples. Here, we will term them quite generally "soft glassy systems" [3] or simply soft glasses. Soft glasses are non-ergodic systems, since they are able to explore only a restricted portion of the total phase space. Experimentally, however, determining whether or not a given system is non-ergodic may prove to be a difficult task, since only a limited range of length and time scales can be probed. In the following we will therefore use the term "soft glassy system" with a wider connotation, including also materials that are ergodic but still exhibit very slow relaxations.

Soft glassy systems attract a wide interest. On the one hand, they are ubiquitous in industrial applications, for example in the food, cosmetic, paint, pharmaceutical, and oil recovery industry. For most applications, understanding and controlling their dynamical and rheological properties, as well as their long term evolution and stability is of fundamental importance. On the other hand, soft glasses are much studied at a more fundamental level. For example, systems such as colloidal hard spheres are taken as model systems for investigating the general behavior of glasses, their relevant time and length scales being more easily accessible than in molecular glasses. Moreover, soft systems allow one to control in great detail and to significantly vary the interactions between their constituents. Therefore, it is possible to investigate how different interactions influence the dynamical behavior of soft glassy materials and the generality of the behavior observed for model systems can be tested.

Until very recently, the experimental characterization of the dynamics was limited to relatively short time scales (e.g. up to a few hundred seconds in light scattering experiments) and only the average dynamics were accessible. Theoretically, very few quantitative models were available, and their applicability was restricted to a few model systems (e.g. the mode coupling theory, MCT [4], applied to colloidal suspensions

interacting via a hard sphere potential). Recent advances include progress both on the conceptual and experimental side. The concept of jamming [2] was proposed to describe in a unified way —albeit somehow qualitatively— the ergodic to non-ergodic transition in many systems, including molecular glasses, granular materials, and colloids. On the other hand, the MCT has been extended to include concentrated systems with attractive interactions (for a review see reference [5]) and attempts have been made to extend its validity to more diluted attractive systems [6], thus bridging the gap between colloidal gels and glasses. Thus, both the jamming picture and the MCT attempt to give a unified vision of the ergodic to non-ergodic transition, the scope of the former being wider and the latter providing more quantitative predictions. Finally, dynamical heterogeneity has emerged as a key feature of the slow dynamics of glassy systems [7] and many theories have been developed based on or incorporating dynamical heterogeneity.

On the experimental side, recent advances include both the design of new systems with interactions that can be fine-tuned and the development of new methods and techniques to measure very slow and heterogeneous relaxations in out-of-equilibrium systems. Experimentally, controlling the transition to non-ergodicity (possibly in a reversible way) is often quite difficult. As a consequence, systems for which a transition from a fluid to a solid state can be reversibly obtained are particularly interesting. They include thermoresponsive systems such as thermoreversible sticky hard spheres [8, 9] or emulsions [10, 11], swellable microgel particles [12, 13], star polymers [14, 15, 16], and surfactant systems [17, 18, 19].

The most popular techniques for probing the dynamics of soft systems are probably optical microscopy and dynamic light scattering: both of them have benefited of major improvements in the last years. Time-resolved confocal microscopy, together with digital image processing, allows the trajectories of thousands of fluorescently dyed particles to be measured simultaneously [20], thus providing detailed information on the dynamics at a microscopic level. Motion on very long time scales (up to several days) has been measured by bleaching a cubic volume of the sample and by measuring the fluorescence recovery due to the diffusion of the unbleached particles [21].

In light scattering experiments, information on the sample dynamics are obtained by measuring the time autocorrelation function of the scattered intensity,  $g_2(t)$ . In the single scattering regime [22], the dynamic structure factor (or intermediate scattering function)  $f(q, t)$  is proportional to  $\sqrt{g_2(t) - 1}$ , where the intensity autocorrelation function is measured at a scattering vector  $\mathbf{q}$  and the proportionality factor depends on the setup detection. The advent of high brilliance coherent X-ray sources has made possible X-photon correlation spectroscopy (XPCS) [23], which extends dynamic light scattering experiments to much higher values of  $q$ . For highly multiply scattering samples, the diffusing wave spectroscopy (DWS) [24] formalism allows the particle mean squared displacement to be extracted from  $g_2(t)$ , provided that the dynamics be homogeneous. Until recently, the applicability of light scattering and XPCS techniques to soft glasses has been severely limited by the need to average the measured intensity autocorrelation function over a duration much longer than the system relaxation

time. This limitation has been overcome by the so-called multispeckle technique [25, 26, 27, 28], where a multielement detector is used (typically a CCD camera) and the intensity autocorrelation function is averaged not only over time, but also over distinct speckles corresponding to different elements of the detector. This scheme allows one to drastically reduce the duration of a measurement, thus making dynamic scattering techniques suitable for systems with very slow or non-stationary dynamics. A conceptually similar approach is followed in the so-called interleaved method, where a point detector is used and the sample is slowly rotated in order to illuminate sequentially the detector with different speckles [29]; for each speckle the intensity correlation function is calculated for time delays multiple of the period of rotation of the sample and  $g_2$  is finally obtained by averaging over all speckles. A recent implementation of this scheme, more simple and efficient, is described in reference [30]. To conclude this brief overview of recent advances in scattering methods, we remark that most scattering experiments probe the average dynamics and hence are not sensitive to dynamic heterogeneities. Information on temporal heterogeneity of the dynamics can be extracted from higher order correlation functions [31, 32] or using the Time Resolved Correlation (TRC) method [33], as it will be discussed in some detail in section 5.

In this paper we will review the experimental work of the last few years on soft glassy systems, with an emphasis on microscopy, light scattering and, to a less extent, rheology experiments. References will be made also to some of the numerical and theoretical investigations related to experiments, as well as to experiments on granular materials that share intriguing analogies with soft glasses. The literature is very abundant, reflecting the growing interest in this field. We have chosen to focus on four areas that seem to us particularly interesting and promising. Section 2 deals with the observation of two types of colloidal glasses (repulsive and attractive), and the success of the MCT in modelling the slow dynamics of these systems. Systems very far from equilibrium, where stress relaxation appears to play a major role in the slow dynamics are reviewed in section 3. Section 4 discusses the effect of a perturbation on a glassy system, both in the linear and in the non-linear regime. Finally, dynamical heterogeneities in the slow dynamics are addressed in section 5.

## **2. Attractive and repulsive glasses: experiments and the mode-coupling theory**

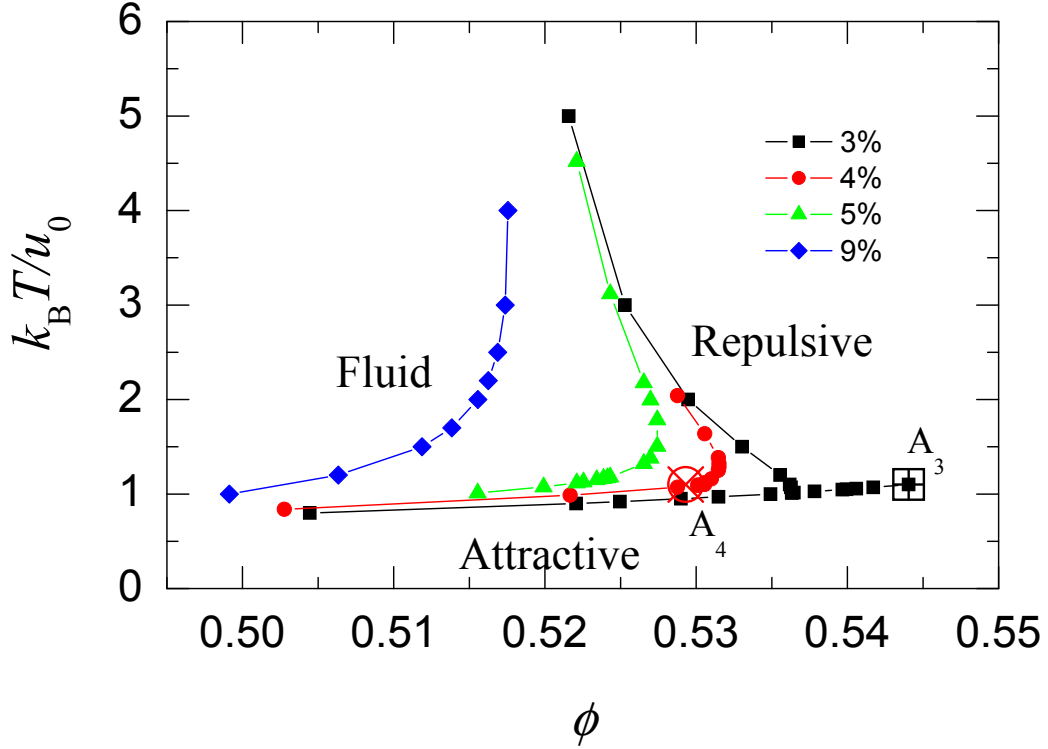
Hard spheres have been investigated as a model system for the glass transition for many years. Experimentally, colloidal particles such as poly(methyl methacrylate) (PMMA) spheres sterically stabilized and suspended in an organic solvent have been shown to behave as hard spheres, forming a glass phase when the volume fraction,  $\phi$ , becomes larger than  $\phi_g \approx 0.58$  [34, 35]. On the other hand, the mode-coupling theory (MCT) introduced by Götze [4] provides detailed predictions on the dynamics of hard spheres when approaching the glass transition. For a supercooled liquid of hard

spheres|| the MCT predicts a two-step decay of the dynamic structure factor  $f(q, t)$ . The initial relaxation ( $\beta$  relaxation) is due to the rattling of the particles inside the cage formed by their neighbors. The  $\beta$  relaxation is followed by a plateau and a second relaxation ( $\alpha$  relaxation), due to cage-escape processes. At the glass transition, the ideal MCT predicts that the characteristic time of the  $\alpha$  relaxation diverges and thus that the plateau extends to all times, indicating a complete dynamical arrest. Note however that on very long time scales ergodicity may be restored by thermally activated processes (hopping), and attempts have been done to include such processes in the MCT [4]. Good agreement has been found between the MCT and dynamic light scattering measurements of the dynamic structure factor of hard sphere colloidal suspensions (for a review on experimental tests of the MCT, see [36]), although the critical packing fraction  $\phi_g^{\text{MCT}} = 0.525$  predicted by the MCT is smaller than the experimentally measured glass transition volume fraction  $\phi_g \approx 0.58$ . To overcome this discrepancy, the *relative* volume fractions  $(\phi - \phi_g)/\phi_g$  and  $(\phi - \phi_g^{\text{MCT}})/\phi_g^{\text{MCT}}$  are often used when comparing experiments and theoretical or numerical work [37].

In hard spheres, the dramatic slowing down of the dynamics when approaching  $\phi_g$  is due to the cage effect: the motion of any given particle is increasingly hindered by its neighbors as the particles are packed more tightly. The glass transition is therefore driven by the repulsive (excluded volume) interaction between the spheres, and the arrested phase thus formed is termed *repulsive* glass. Recent theoretical [38, 39, 40] and experimental [41, 42, 43, 44] work has shown that the addition of short-ranged, low-energy attractive interactions can lead, surprisingly, to the melting of such a repulsive glass. This can be understood in the framework of the cage effect: particle bonding due to attractions results in the increase of the available free volume, thus loosening and eventually opening the cage. If the strength of the attraction is increased further, however, a new arrested phase is formed, because the bonds are sufficiently long-lived to effectively confine the particles. This arrested phase is referred to as an *attractive* glass, although the term gel is also found in the literature. For a short general introduction to the topic of attractive *vs* repulsive glass, see [45]. A brief and clear review of the experimental work on this topic is given in [46], while reference [5] discusses recent theoretical advances. In the following, we will briefly recall the main results of MCT and then focus on the experimental work.

Figure 1 shows the theoretical phase diagram for particles interacting via a hard-core repulsion ( $U(r) = \infty$  for  $r < 2R$ , where  $U$  is the inter-particle potential and  $R$  is the particle radius) and a square well attraction ( $U(r) = -u_0$  for  $2R < r < 2R + \Delta$ ) [40]. The different curves are labelled by the relative width of the attractive well,  $\xi = \Delta/(2R + \Delta)$ . Although the exact location of the lines depends on the detailed shape of the potential and the chosen approximated expression for the static structure

|| For hard spheres, the temperature quench that is used in molecular systems to obtain a supercooled fluid would correspond to a rapid increase of volume fraction, above the crystallization volume fraction  $\phi_{\text{cryst}} = 0.494$  and below  $\phi_g$ . Although in some experiments centrifugation is used to realize such a quench, in most cases supercooled samples are prepared by shear melting.



**Figure 1.** Theoretical phase diagram for hard spheres of radius  $R$  with a square well attractive interaction of width  $\Delta$  and depth  $u_0$  (data from reference [40]). The different curves are labelled by the relative well width,  $\xi = \Delta/(2R + \Delta)$ . Note the reentrant shape of the lines separating the fluid region to the glassy regions for  $\xi \leq 5\%$ . For  $\xi = 3\%$  a line separating the attractive and the repulsive glass phases ends in the  $A_3$  singular point. The  $A_4$  singular point (circled cross) is estimated to be located on the  $\xi = 4.11\%$  line (not shown for clarity).

factor, the features shown in figure 1 are quite general. The lower part of the phase diagram corresponds to strong attractions ( $u_0 \gg k_B T$ ) and is occupied by the attractive glass. The upper-right region is occupied by the repulsive glass, while the upper-left part corresponds to the fluid phase. Note that at small enough  $\xi$  (typically less than about 0.1) the phase diagram has a reentrant shape: there exists a range of volume fractions for which, at constant  $\phi$ , a sample may be in the fluid phase or in either the attractive or the repulsive glass phase, depending on the strength of the attractions. For very short-ranged attractions ( $\xi$  less than about 0.04), at high  $\phi$  the attractive and repulsive glass regions are contiguous, separated by a line ending in the so-called  $A_3$  singular point (open square with plus in figure 1). When  $\xi$  increases, the line separating the attractive and the repulsive glasses progressively shrinks, until the line and the  $A_3$  singularity vanish and the so-called  $A_4$  singularity is observed (open circle with cross in figure 1). In the vicinity of the  $A_3$  and  $A_4$  singular points, as well as at the intersection of the attractive and repulsive glass lines, the system is predicted to relax with a very broad distribution of time scales, resulting in a logarithmic decay of the dynamic structure

factor  $f(q, t)$  and a power law behavior of the particle mean squared displacement [47, 48, 49]. Simulations performed by using either a square-well [50, 51, 52] or the Asakura-Osawa potential [53, 54, 55], have confirmed the predictions of the MCT.

Experimentally, the more extensive tests of the two glasses scenario have been performed by three independent groups. Pham and coworkers [42, 57] have used nearly monodisperse, sterically stabilized PMMA particles to which polystyrene, a non-adsorbing polymer, was added to induce a short-ranged attraction via the depletion effect, leading to an attraction well described by the Asakura-Osawa potential (for a review on this much studied experimental system, see [58]). The strength of the attraction can be controlled by changing the amount of the polymer, while the range is of the order of the radius of gyration of the polymer. In references [42, 57] the phase diagram of this system is established and both the structure and the dynamics of the glass phases are studied in detail by means of light scattering. The so called two-color technique [59] is used to suppress multiple scattering, and a recently introduced “echo” scheme [30] is used to obtain properly ensemble-averaged measurements even when dealing with non-ergodic samples. As expected from the MCT, at fixed  $\phi$  the non-ergodicity—or Debye-Waller—factor  $f(q, t \rightarrow \infty)$  for the attractive glass is found to be higher than that for the repulsive glass, because the motion of clustered particles is more restrained than that of repulsive spheres, which can rattle in the cage formed by their neighbors. Accordingly, the liquid-order peak in the static structure factor,  $S(q)$ , shifts to larger  $q$  vectors when going from the repulsive to the attractive glass. Additionally,  $S(q)$  is less sharp for attractive glasses, since they are locally more disordered than repulsive glasses. In the vicinity of the  $A_3$  point, a logarithmic decay of  $f(q, t)$  is observed over more than three decades in time. Beyond the  $A_3$  point, where the MCT predicts that the attractive and repulsive glasses should merge into a single arrested phase, the non-ergodicity factor becomes independent of attraction strength, suggesting that indeed the two glasses phases are indistinguishable. However, quite intriguingly, the short-time behavior of  $f(q, t)$  remains different, a feature also reported in reference [60].

Similar detailed investigations, leading to comparable results, are presented by Eckert and Bartsch and by Chen and coworkers. Eckert and Bartsch study a concentrated suspension of microgel particles, to which linear polystyrene is added to induce an attraction via the depletion effect [41, 61]. The microgel particles are bidisperse so as to suppress crystallization. This two-component system is mapped onto an effective (polydisperse) one-component system of slightly soft spheres (the repulsive barrier is modelled by an inverse power potential  $U(r) \sim r^{-35}$ ), and is studied by static and dynamic light scattering. The multispeckle technique [26, 61] is used to access the long time dynamics and for studying non-ergodic samples. Chen and coworkers [19, 43, 60] investigate by small angle neutron scattering (SANS) and dynamic light scattering (DLS) a concentrated aqueous solution of L64, a triblock copolymer of the Pluronics family. L64 is composed of two end sections of polyethylene oxide (PEO) and a central section of polypropylene oxide (PPO). Both PPO and PEO become increasingly hydrophobic when the temperature  $T$  is raised, but PPO does so at a



faster rate. As a consequence, when  $T$  is increased micelles are formed with a PPO core and a PEO corona. At high enough temperature, the PEO corona becomes sticky because of hydrophobic interactions, thus providing an attraction between the micelles. The experimental control parameters for this system are  $T$  and the block copolymer concentration,  $C$ . For comparison with the MCT phase diagram, the  $T$ - $C$  experimental phase diagram is mapped onto a  $\phi$ - $u_0$  diagram by fitting the static structure factor obtained by SANS to that predicted for adhesive hard spheres. Note that the DLS data are taken at a  $q$  vector much smaller than that corresponding to the peak of  $S(q)$ , in contrast to the work of Pham *et al.* and Eckart and Bartsch.

Several features of the two glasses scenario predicted by the MCT have been observed also in other systems. References [44, 62] report a rheology, SANS and dynamic light scattering investigation of a solution of soft spheres, made of diblock copolymer micelles. An attraction can be induced by synthesizing diblock polymers with a controlled amount of stickers (ethyl acrylate units). Two distinct glass phases and a reentrant behavior are observed. The rheology experiments show that the elastic modulus  $G_0$  of the attractive glass is larger than that of the repulsive glass, a feature predicted by the MCT. Note, however, that for these soft objects the difference in  $G_0$  for attractive and repulsive glasses (about a factor of 2) is much less marked than for attractive hard spheres (more than a decade, see [63]). The melting of a glass of soft spheres (star polymers) and a reentrant gelation upon the addition of a linear polymer has been observed by Stiakakis and coworkers [64]. Although the phenomenology is strongly reminiscent of that observed in other systems with depletion interactions, the authors point out that the melting is due to the decrease of the range of the soft repulsion between stars upon addition of the linear polymer, while the gelation results from bridging flocculation induced by the long polymers chains. Finally, the existence of a reentrant glass transition in Laponite suspensions has been speculated, but not yet proved experimentally [65].

Qualitatively, the experiments mentioned above strongly support the MCT picture of attractive and repulsive glassy states and show that this scenario is robust with respect to changes in the exact shape of the potential. A quantitative comparison is however much more difficult. Indeed, even for the experimental system closer to the theoretical models, i.e. the hard spheres with depletion interactions studied by Pham and coworkers, it is difficult to exactly locate a sample on the theoretical phase diagram, because of uncertainties in the parameters describing the potential and in the relative volume fraction  $(\phi - \phi_g)/\phi_g$  of a sample [57]. A comparison of the experimental and theoretical phase diagrams is given in reference [63], showing that the MCT somehow underestimates the extent of the fluid pocket in between the attractive and repulsive glass regions.

In view of the success of the MCT in modelling suspensions of attractive particles at high volume fraction, attempts have been made to extend it to lower  $\phi$ , in order to describe as a glass transition the “weak gelation” observed in attractive systems where particle bonds are non-permanent. In the “cluster mode-coupling theory” of

Kroy and coworkers [6], the MCT is applied to clusters of particles, rather than to the particles themselves. This theory predicts the existence of a cluster phase that may freeze if the effective cluster volume fraction is large enough. Recent simulations [66, 67] and experiments [68] are consistent with this picture. A more detailed discussion of the delicate interplay between aggregation, dynamical arrest and phase separation that arises in relatively low  $\phi$  suspensions is given in [55]. For a discussion of colloidal gelation in connection to the glass transition, see also the review by Trappe and Sandkühler [69], which focuses on the elastic properties of these materials.

In spite of the large amount of theoretical, numerical and experimental work of the last years, several questions are still open. We mention here two topics that are likely to focus the interest of researchers in the next future and are connected to the subject of this review: dynamical heterogeneities and aging. Simulations on high  $\phi$  attractive glasses suggest that, although the MCT correctly captures the average dynamics, the particle motion is very heterogeneous [55], a feature also observed at intermediate volume fractions ( $\phi = 0.4$ ) [56]. New experiments are needed to characterize dynamical heterogeneity in attractive glasses and the new approaches described in section 5 may prove useful. No systematic experimental investigation of the aging behavior in attractive *vs* repulsive glasses is available yet, although preliminary DLS data are presented in reference [57]. They suggest a different aging in attractive and repulsive glasses: for the former, the dynamics keep slowing down for up to 10 days, while no significant aging effects beyond 2 days are reported for the latter. The destabilization of the attractive glass with time, due to activated dynamics (bond breaking), has also been investigated in a series of numerical works [70, 71, 72].

### 3. Out-of-equilibrium soft systems

The slow dynamics of out-of-equilibrium soft materials have been investigated experimentally for a wide variety of systems, ranging from model systems of hard spheres to more complicated materials. Quite generally, these experiments demonstrate that the dynamics at very long time scales are not completely frozen: many soft materials in the glassy phase have been shown to exhibit ultra-slow relaxations. After reviewing these investigations, we will describe the aging behavior that is very often associated with the slow dynamics. Finally, internal stress relaxation will be discussed as a possible mechanism for slow dynamics and aging in many soft glassy materials very far from equilibrium.

#### 3.1. Ultra-slow relaxations

As discussed in section 2, the ideal MCT predicts the divergence of the  $\alpha$  relaxation time at the glass transition: therefore for  $\phi > \phi_g$  the dynamic structure factor should exhibit a plateau after the initial decay ( $\beta$  relaxation). The pioneering dynamic light scattering experiments on colloidal hard spheres glasses of van Meegen and coworkers [73, 74] hinted

however at a second decay of  $f(q, t)$ , after the plateau. Unfortunately, the accessible time delays were too short to properly characterize this slow relaxation. Qualitatively similar results are obtained by Pham and collaborators [57]. Recent experiments confirm indeed that a hard sphere glass is not a fully arrested state and cage-escape plays a decisive role even in the glass phase. Using a confocal scanning microscope, Simeonova and Kegel [21, 75] follow in real-time the fluorescence recovery after photo-bleaching of a small volume within a concentrated suspensions of hard spheres and derive from their measurements the mean squared displacement (MSD),  $\langle r^2 \rangle$ , of the colloids. In the glass phase, they find a subdiffusive behavior  $\langle r^2 \rangle \sim t^{0.30}$ , which extends over seven decades in time. The largest displacements are of the order of the particle size. This result is intriguing: it is fundamentally different from the ideal MCT predictions and is moreover different from the light scattering results of van Megen *et al.*, who observe an intermediate plateau of the MSD, before detecting a further increase of  $\langle r^2 \rangle$  at very large  $t$ . Interestingly, thanks to their extremely long experiments, Simeonova and Kegel have recently demonstrated that the subdiffusive power law growth of the MSD corresponds actually to a transient regime (lasting up to  $\sim 10^7$  Brownian times, or about 7 days!), after which a plateau is eventually reached [75].

Apart from these few reports, experiments probing the slow dynamics of hard spheres systems deep in the glass phase are still scarce. Other systems, however, provide an opportunity to investigate in details the dynamical state of soft materials far from the fluid-to-solid transition. Indeed, for several soft materials, the characteristic times are intrinsically smaller than that of hard-spheres systems, and a quench to a state far from equilibrium may be realized more easily. These systems include fractal colloidal gels, dilute suspension of colloidal charged platelets, concentrated suspensions (or pastes) of colloidal particles stabilized both by electrostatic and steric repulsions, and compact arrangements of soft deformable particles (multilamellar vesicles or polyelectrolyte microgels), the volume fraction of the latter being essentially 1. Thanks to the multispeckle dynamic light scattering method [25, 26, 27, 28], the dynamics have been probed for time delays as long as tens of hours. A remarkable result of these experiments is that, for several soft glassy materials, the intensity autocorrelation function  $g_2(t) - 1$  relaxes completely to zero at very long  $t$ , a behavior indicative of structural changes over the length scale probed by the experiment. These findings have been obtained by dynamic light scattering both in the multiple scattering (diffusing wave spectroscopy, DWS [24]) and in the single scattering regime (DLS) [22], as well as by X-photon correlation spectroscopy (XPCS) [23].

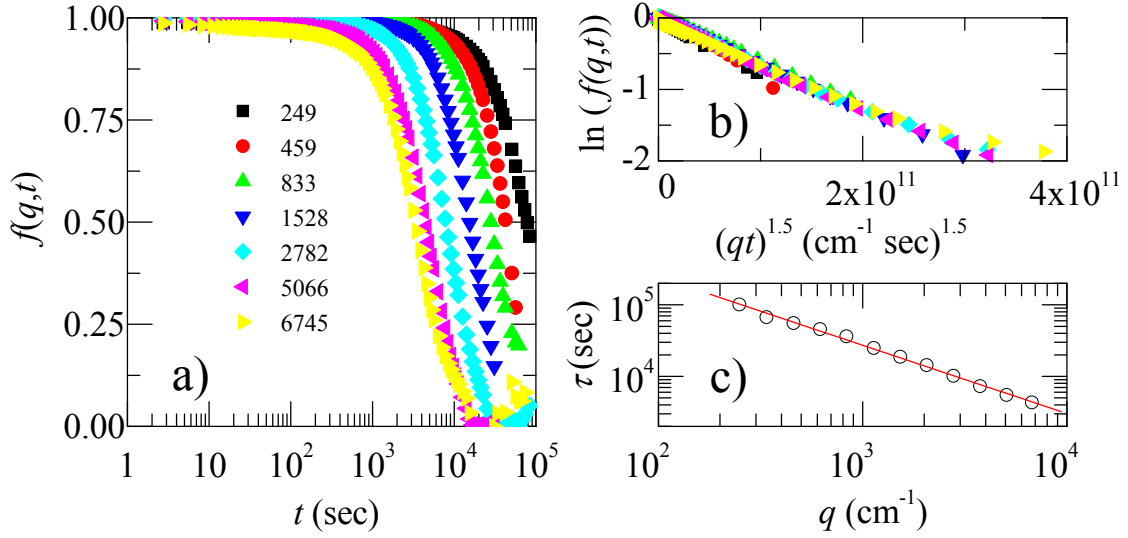
Diffusing wave spectroscopy measurements are performed on very turbid samples, or on transparent systems to which probe particles are added to increase the turbidity. Using DWS, a slow relaxation well separated from the fast dynamics by a plateau in  $g_2(t) - 1$  has been measured for systems as varied as dilute suspensions of charged clay platelets (Laponite) forming a “Wigner glass” [76], colloidal pastes [77], and concentrated colloidal gels [78]. The quantitative interpretation of the decay of  $g_2(t) - 1$  is not straightforward: the standard DWS formalism allows the MSD to be calculated

from  $g_2(t)$ , but it requires the motion of all scatterers to be spatially and temporally homogeneous [24], a condition that is likely to be violated in many glassy systems (see section 5). It is also worth noting that in these experiments the length scale probed is at most of the order of a few tens of nanometers, much smaller than the typical size of the sample constituents.

Qualitatively similar features have been observed in single scattering experiments on a variety of systems, including fractal colloidal gels with strong and irreversible [79] or weak, thermoreversible [8] bonds between the particles, compact arrangements of soft elastic spheres [17] or of emulsion droplets [80], polycrystals made of block copolymer micelles [80], and suspensions of Laponite [83, 84]. Note that DLS probes length scales much larger than those explored in a DWS experiment, typically up to the size of the sample constituents or more. The full decay of the dynamic structure factor extracted from DLS experiments is therefore particularly significant, since it is indicative of slow rearrangements that eventually change the system configuration on length scales comparable to or larger than the size of its constituents. An additional valuable feature of DLS is the possibility to easily measure how the dynamics depend on length scale. This is accomplished by changing the  $q$  vector at which the experiment is performed. Several different  $q$ -dependencies of the characteristic time  $\tau$  for the slow relaxation have been measured. Abou and coworkers [84] have found  $\tau \sim q^{-2}$  for a suspension of clay particles (Laponite), as expected for a diffusive process, such as cage-escape mechanisms. However, less intuitive scaling laws have also been obtained by several groups on various samples. Solomon and coworkers [8] reported  $\tau \sim q^{-0.5}$  for a colloidal gel of adhesive particles, while Bellour and coworkers have found —for the same material as Abou *et al.* but in a different aging regime, see also subsection 3.2—  $\tau \sim q^{-1.3}$ . These results remain largely unexplained.

An intriguing  $\tau \sim q^{-1}$  scaling has been measured for a wide variety of materials, including both attractive systems (fractal colloidal gels [79]) and repulsive systems (compact arrangements of soft elastic spheres [17] or of emulsion droplets [80], a polycrystal made of copolymer micelles [80], and Laponite in XPCS experiments that probe the high  $q$  regime [81]). This scaling suggests that the slow dynamics be due to a “ballistic” motion of the particles, in the sense that the average particle displacement grows linearly with time (this ultra-slow regime should not be confused with the ballistic motion of colloids observed on very short time scales, before the onset of Brownian motion [82]). A very unusual shape of the dynamic structure factor accompanies always this scaling:  $f(q, t)$  decays as a “compressed exponential”, i.e.  $f(q, t) \sim \exp[-(t/\tau)^p]$ , with a “compressing” exponent larger than one,  $p \approx 1.5$ . Figure 2 illustrates both the  $\tau \sim q^{-1}$  scaling and the compressed exponential shape of  $f(q, t)$  for the colloidal fractal gel studied in [79]. Note that the same compressed exponential shape was observed in reference [83], although with a somehow smaller value of  $p \approx 1.35$ .

Because the relaxation is faster than exponential and due to the  $\tau \sim q^{-1}$  scaling, all models based on cage-escape processes must be ruled out. Instead, we have proposed [17, 79, 80] the dynamics to be due to randomly distributed internal stress sources acting



**Figure 2.** a): dynamic structure factor measured simultaneously at various scattering vectors for a fractal gel made of strongly attractive polystyrene particles, with  $\phi = 5 \times 10^{-4}$ . The curves are labelled by the magnitude of the scattering vector in  $\text{cm}^{-1}$ . b): the same data as in a) are plotted as  $\ln[f(q,t)]$  vs  $(qt)^{1.5}$ . All data collapse onto a straight line, thus demonstrating that  $f(q,t) \sim \exp[-(t/\tau)^p]$ , with  $p = 1.5$ . c): double logarithmic plot of the  $q$  dependence of the relaxation time  $\tau$ . The line has a slope of  $-0.96 \pm 0.02$ , suggesting a  $\tau \sim q^{-1}$  scaling. To avoid overcrowding the figure, not all the curves that were fitted to obtain the data shown in c) are plotted in a) and b). Data taken from reference [79].

on the sample, whose response is that of an elastic solid. Simple scaling arguments lead then to the observed peculiar shape of the dynamic structure factor [80]. A more refined model based on the microscopic description of local rearrangement events has been developed for the case of a colloidal gel [85]. Experiments testing the notion of internal stress as the driving force for the slow dynamics are reviewed in subsection 3.3. Finally, we note that there are strong indications that in this type of systems the dynamics is heterogeneous. The unusual dynamics reported above may therefore be due to a series of discrete rearrangement events, as it will be discussed in more details in section 5.

### 3.2. Aging

The properties of out-of-equilibrium systems continuously change with time as the system slowly evolves towards its equilibrium configuration. As a consequence, correlation functions, e.g. measured by dynamic light scattering, and response functions, e.g. stress or strain relaxation in rheological experiments, depend not only on time delay,  $t$ , as for time-translation invariant systems, but also on the waiting time or sample age,  $t_w$ . Typically, the dynamics becomes progressively slower as the sample ages and the system spends more and more time in the metastable states it visits, the energy of such states becoming increasingly lower (see references [86, 87] for an introduction to aging

phenomena). Very generally, age is defined as the time elapsed since the sample was quenched from a fluid to an out-of-equilibrium solid state. For hard condensed matter systems (e.g. structural, polymeric or spin glasses), this is usually realized by means of a temperature quench. By contrast, soft materials are very often (albeit not always) initialized by applying a strong mechanical shear; hence age is defined as the time interval between the end of the applied shear and the beginning of the measurement. Aggregation phenomena leading to a percolated network may also provide a route to an out-of-equilibrium state: in this case,  $t_w = 0$  is taken as the percolation (or gelation) time.

The first experimental reports of aging phenomena in soft condensed matter are light scattering experiments performed on hard spheres colloidal glass [73, 74]. Although the accessible time window in these experiments was too short to investigate in details the aging dynamics, the data unambiguously show a slowing down of the dynamics as the sample ages, when the volume fraction of the sample is larger than  $\phi_g$ . By contrast, no dependence of the dynamic structure factor with sample age can be detected when  $\phi$  is smaller than  $\phi_g$ . Hence, the results of van Meegen and coworkers nicely demonstrate the dramatic dynamical differences between a sample in the supercooled fluid state and one in the glass state, in spite of the minute differences in sample composition. More recently, Simeonova and Kegel [75], using the fluorescent recovery after photobleaching technique, have found clear evidence of aging behavior in hard sphere glasses, since they measure a particle MSD whose growth slows down with increasing  $t_w$ . Similar results have been obtained by Courtland and Weeks [88], who used confocal microscopy to follow in real-time the three-dimensional motion of individual particles in a colloidal glass. They find that the MSD initially grows linearly with time, then tends to plateau, and finally exhibits a slight upturn at very large time (similarly to what observed for the cage escape process in supercooled fluids). For glasses, the time scale of the upturn increases with  $t_w$ . They also find that the dynamics is both spatially and temporally heterogeneous, although characterizing dynamical heterogeneities is more difficult than in supercooled samples, because the particle motion is very restrained and the statistics is poorer (more details on dynamical heterogeneities can be found in section 5). At all ages the most mobile particles form clusters; however no obvious evolution of the cluster size or morphology with age is observed. To conclude the overview of experiments on the aging of hard spheres systems, we recall the preliminary dynamic light scattering results in reference [57], which compare the aging dynamics of a repulsive hard sphere colloidal glass to those of an attractive glass (see section 2) and suggest different behaviors: the repulsive glass seems to stop aging after about one day, while the dynamics of the attractive glasses keep on slowing down after 10 days.

Aging behavior has been most extensively investigated in soft materials which greatly depart from a hard spheres model system. These materials include colloidal pastes made of concentrated silica [89, 90] or polystyrene particles [77] (both stabilized by a combination of electrostatic and steric repulsions), diluted [79] or more concentrated [78] fractal colloidal gels of polystyrene beads, diluted suspensions of charged clay

platelets (Laponite) [83, 84] (to which polystyrene beads may be added to perform DWS experiments [76]), compact arrangements ( $\phi \sim 1$ ) of surfactant multilamellar vesicles [17], polyelectrolyte microgel particles [91], or polycrystals of copolymeric micelles [80].

For these systems, rheological tests are very often employed to probe aging phenomena, in addition to light scattering experiments. Rheological experiments, e.g. measurements of the stress relaxation following a step strain in the linear regime, are often compared to available theories, one of the most successful being the Soft Glassy Rheology (SGR) model of Sollich and coworkers [3, 92]. This model, derived from the trap model of Bouchaud [86, 94] accounts for the rheology of out-of-equilibrium materials. In brief, in the trap model non-interacting particles evolve through a hopping mechanism in an energy landscape with wells of depth  $E$ . The distribution of well depths is fixed and the evolution of  $P(E, t)$ , the probability for a particle to be in a trap of depth  $E$  at time  $t$ , is governed by thermally activated hopping. This model leads to aging phenomena when the average trapping time diverges. In the SGR model, the material is divided into elements which yield above a critical yield strain  $l_y$ , thus relaxing stress. Yield events (i.e. rearrangements of the particles) are seen as hops out of the trap, and yield energy is identified as the trap depth  $E$ . The activation barrier is  $E = E_y - \frac{1}{2}kl^2$  where  $E_y = \frac{1}{2}kl_y^2$  is the maximum elastic energy before yielding,  $l$  is the local shear strain of an element, and  $k$  is an elastic constant. The link between the microscopic parameters and the macroscopic strain applied to the sample is straightforward: in between rearrangements, the local strain follows the macroscopically imposed strain  $\gamma$ . In reference [93], Fielding, Sollich and Cates study the role of aging in the rheology of soft glassy materials. They describe several rheological tests suitable to investigate the (linear and non-linear) rheology of aging soft materials, whose features are qualitatively similar to experimental results.

Experimentally, aging behavior has been observed in DWS [76, 77, 78], single light scattering [17, 79, 83, 84], and linear rheology [17, 89, 90, 91] experiments. In all cases, the characteristic time  $\tau$  of the correlation functions (for light scattering experiments), of the stress relaxation (in a step strain experiment), or of the strain evolution (in a creep experiment) increases continuously with sample age. However, very different aging laws  $\tau(t_w)$  have been found for the various materials investigated. In many cases a power law  $\tau \sim t_w^\mu$  is observed, but the aging exponent  $\mu$  may significantly vary. Indeed, values of about 1 [76, 77, 79, 91], smaller than 1 ( $0.5 < \mu < 1$ ) [17, 89, 90], and larger than 1 ( $\mu \simeq 1.4$  and  $\mu \simeq 1.8$  in references [78] and [81], respectively) have all been observed, reflecting—in the language of glasses—full aging, sub-aging and hyper-aging, respectively. A peculiar, very fast aging regime has been observed both in fractal colloidal gels [79] and in Laponite samples [83, 84], for which  $\tau$  is found to grow exponentially with sample age. This fast aging regime is eventually followed by a slower growth of  $\tau$ , corresponding to full aging. Note that the work by Bellour *et al.* [83], who studied the aging of Laponite over a wide interval of  $t_w$  and observed both regimes, rationalizes the apparently conflicting findings of references [76] and [84], which were probing only the exponential and the full aging regime, respectively.

The experimental work reviewed in this section clearly shows that, albeit aging behavior is a ubiquitous feature of out-of-equilibrium soft materials, the detailed evolution of the dynamics with  $t_w$  greatly depends on the particular system that is investigated. The large spectrum of aging behaviors measured experimentally hints at differences in the microscopic mechanisms at play in the various samples and stands as a challenge for more detailed theories.

### 3.3. Internal stress relaxation

In subsec. 3.1, we have mentioned that a large variety of soft disordered materials were found to exhibit an unusual slow dynamics, with a compressed exponential shape for the dynamic structure factor ( $f(q, t) \sim \exp[-(t/\tau)^p]$ , with  $p \approx 1.5$  and  $\tau \sim q^{-1}$ ), indicative of ballistic motion [17, 79, 80, 81]. We have argued that these peculiar features could be rationalized with simple arguments, based on the concept that the dynamics be due to the relaxation of internal stresses. Several experimental observations hint at the key role played by internal stresses in leading to the final relaxation of  $f(q, t)$ . Cipelletti *et al.* and Manley *et al.* [79, 95] have observed particle syneresis in colloidal gels made of attractive particles. When the gel is strongly anchored to the container walls (as it is usually the case), tensile stress builds up in the sample as a result of the decrease of the interparticle distance, due to syneresis. Further evidence for the role of internal stress is provided by experiments on concentrated emulsions, whose dynamics was initialized by centrifugation [80]. The dynamics is systematically faster in the direction of the centrifugation acceleration, along which most of the internal stress has been presumably built in. For Laponite suspensions, Bandyopadhyay and coworkers argue that internal stresses are generated by the increase of the interparticle repulsion, due to the dissociation of ions at the surface of the particle, as revealed by the increase of the conductivity of the suspension with sample age [81]. Finally, similar dynamics were observed for a micellar polycrystal [80] and compact arrangements of multilamellar vesicles (MLVs) [17], two systems for which the fluid-to-solid transition is induced by a temperature jump. For these samples, we expect internal stress to be built up due to the rapid growth of randomly oriented crystallites or MLVs, respectively. Interestingly, linear rheology measurements on the MLVs [17] show that the characteristic time of the mechanical response of this material follows exactly the same aging law as the characteristic time of the final decay of  $f(q, t)$ . Since rheology probes the response to an external stress, while the final relaxation of  $f(q, t)$  is ascribed to internal stress, this concordance gives further support to the concept of stress relaxation as a key ingredient in determining the dynamics of disordered systems and their evolution with sample age.

Dense arrangements of MLVs [17, 18] provide ideal samples to test in great details the notion of internal stress as a driving force for the slow dynamics. As mentioned above, the fluid-to-solid transition of this material can be driven by a temperature jump. This has to be contrasted with most soft glassy systems, where the fluid-to-solid transition is obtained upon cessation of a large applied shear, which certainly influences



the initial configuration of internal stress. For the MLVs, the physical origin of the internal stress is the elastic energy stored in the deformation of the vesicles, which are expected to depart from a spherical, elastically relaxed shape, due to their rapid and disordered growth at the fluid-to-solid transition. On the other hand, the linear elastic modulus  $G_0$  is equal to the density of elastic energy stored by the material when it is deformed in the linear regime [18]. Therefore, both the internal stress and  $G_0$  share the same microscopic origin, i.e. the deformation of the MLVs. It follows that the slow dynamics should depend crucially on  $G_0$ , if indeed they are driven by the relaxation of internal stress. In order to test this conjecture, we have recently measured the aging dynamics of MLVs samples for which  $G_0$  was varied over more than one order of magnitude [96]. We find that the slow dynamics is faster for systems with a higher elastic modulus, in agreement with the hypothesis that the higher  $G_0$  the larger the internal stress. Remarkably, the slow dynamics and the aging can be entirely described by the evolution of an effective viscosity,  $\eta_{eff}$ , defined as the characteristic time measured in a stress relaxation rheology test times  $G_0$ . The concept of effective viscosity is found to be robust, since at all time  $\eta_{eff}$  is independent of  $G_0$ , of elastic perturbations, and of the rate at which the sample is driven from the fluid to the solid state. A simple model that links  $\eta_{eff}$  to the internal stress created at the fluid-to-solid transition is proposed. In this model, the ballistic motion of the MLVs results from a balance between a driving force, associated to the local internal stress acting on a region containing several MLVs, and a viscous drag. (Note that this model is similar to the one proposed in reference [97] to describe the fast dynamics associated with the rattling of soft microgel particles within the cage formed by their neighbors.) In this picture, aging results from a weakening of the driving force, due to the progressive relaxation of internal stress. Indeed, we find that  $G_0$  slowly decreases with  $t_w$ , as expected if the measured elastic modulus is the sum of a (constant) “equilibrium” elastic modulus (corresponding to an ideal, totally relaxed configuration of the sample, where all MLVs have a spherical shape) and the internal stress, which decreases with  $t_w$ .

Similar arguments should apply also to other soft systems, such as concentrated emulsions, whose elasticity, similarly to that of the MLVs samples, depends on the deformation of their constituents. By contrast, a very different behavior is observed for hard particles, for which the elasticity results essentially from excluded volume interactions (entropic origin). Derac *et al.* study the age-dependent rheology of a colloidal paste made of silica particles [90]. They find that the elastic modulus of the paste increases logarithmically with sample age, defined as the time elapsed since the system has been fluidified by a strong mechanical shear, while the elastic modulus of a MLV sample decreases. The authors suggest a link between the aging that they observe in stress relaxation experiments and the spontaneous increase of the elastic modulus. A phenomenological model which incorporates as main ingredients spontaneous aging and mechanical rejuvenation [89, 90, 98] is able to reproduce the essential features of the various rheological tests performed experimentally, in particular the stress relaxation experiments, although in the model the elastic modulus of the sample is fixed. The

same phenomenological model gives also results in good agreement with start-up flow experiments [90], where the time evolution of the stress is measured as a constant shear rate is imposed to the sample. They find both experimentally and theoretically that the stress overshoots before the system actually starts to flow. The amplitude of the overshoot increases with sample age, thus suggesting that the older the sample the larger the stress that has to be stored before flow can occur. This suggests that the system strengthens with age, in contrast with the decrease of  $G_0$  observed for the MLVs.

Interestingly, a similar link between slow dynamics, aging behavior and stress relaxation has been proposed to explain the dynamics of a gently vibrated granular pile [99]. Kabla and Debrégeas measure by multispeckle DWS the two-time intensity autocorrelation function of the light scattered by the pile,  $g_2(t, t_w)$ . The sample is vibrated by applying “taps”, whose amplitude is small enough not to induce macroscopic compaction, but large enough to trigger irreversible particle displacements on a microscopic scale. The characteristic decay time of  $g_2(t, t_w)$  increases roughly linearly with  $t_w$ , in surprising analogy with many glassy systems. By invoking arguments similar to those of Bouchaud’s trap model [86, 94], the authors explain this slowing down as the result of a slow evolution of the (gravitationally-induced) stress distribution in the pile. Weak grain contacts are progressively replaced by stronger contacts, leading to the observed aging of the dynamics and the strengthening of the pile.

The literature reviewed in this section indicates that internal stress and its time evolution are quite general ingredients in attempts to explain the slow dynamics and the aging of many glassy systems. However, internal stress may play very different roles, either acting as a driving force for the dynamics (as proposed, e.g., for the MLVs), or evolving in response to other processes (e.g. thermal activation or applied vibrations). The experiments reviewed here show that the role of internal stress, as well as the evolution of the elastic response during aging, may depend also on the way the samples are initialized and on the microscopic origin of the elasticity. Indeed, the internal stress can not be the same when a system is fluidized by applying a mechanical shear or, on the contrary, without perturbing it mechanically. Similarly, different aging behaviors of the stress distribution and the elasticity are to be expected in samples where the elasticity is due to the deformation or the bending of the individual constituents, or where it derives from excluded volume interactions.

#### 4. Response to an external perturbation

A great amount of experimental, numerical and theoretical work has been devoted to investigating the response of glassy soft materials to an external perturbation, usually a mechanical one. There are several reasons justifying such a broad interest. On one hand, these materials are ubiquitous in industrial applications, where their mechanical properties are of primary importance. On the other hand, applying a (large) mechanical perturbation is a way to modify the dynamical state and the aging behavior of a soft glass: in this case the dynamics may depend on the mechanical history, much as the

dynamics of a molecular or spin glass depends on its thermal history. This analogy lies on the similar role of temperature and, e.g., strain in driving the fluid-to-solid transition, as proposed by Liu and Nagel [2]. Finally, there is an intense debate on the relationship between response functions (in the linear regime) and correlation functions in glassy systems and the break down of the Fluctuation Dissipation Theorem (FDT).

In this section, we will first review experiments probing the response of a system to a strong perturbation (non-linear regime), and then discuss experimental work addressing the possible violation of the FDT.

#### 4.1. Non-linear regime: rejuvenation and overaging

Habdas *et al.* have performed original experiments [100] where they measure the average velocity and the velocity fluctuations of a magnetic bead submitted to a force,  $f$ , and immersed in a dense colloidal suspension (in the supercooled fluid state). As also observed in simulations [101], they find that the average velocity varies as a power law with  $f$ . They also find a threshold force  $f_0$  for motion to be observed, which initially increases with the colloid volume fraction, but eventually saturates, suggesting that  $f_0$  does not diverge at the glass transition. Moreover, they do not observe an increase of velocity fluctuations when approaching the glass transition, as one might have expected if the probe environment became more heterogeneous. They suggest that  $f_0$  be related to the strength of the cage and that the existence of  $f_0$  hints at local jamming even if the colloidal suspension is globally in a liquid phase. Two interesting extensions of this work would be *i)* to perform the same type of measurements in the glass phase and *ii)* to look at the rearrangements of the particles due to the forced motion of the magnetic probe. We note that experiments similar to *ii)* have been conducted in a two-dimensional granular material where one follows the motion of all grains in response to the forced motion of one grain [102]. Note that in the experiment by Habdas *et al.* the motion of the magnetic probe is much larger than the Brownian motion of the surrounding particles. As a consequence, this experiment probes —at a microscopic level— the non-linear rheology of the suspensions .

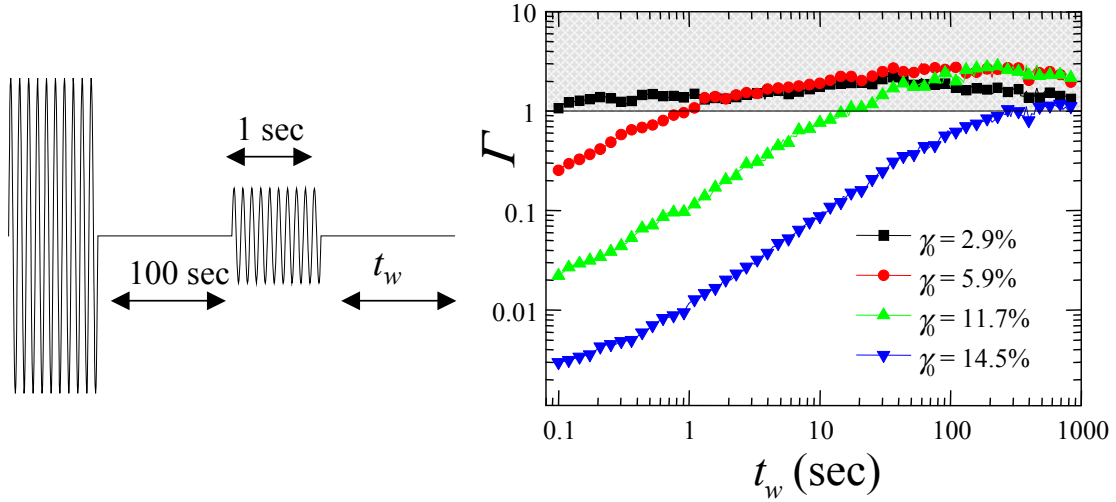
Macroscopic non-linear rheology experiments have been performed on a variety of systems. Although it has been known for several years, and has been widely used in experiments, that the dynamics of soft glassy materials can be initialized by submitting them to a strong shear, recent experiments have investigated in more details the effects of shear on the slow dynamics and the aging of these materials. One important issue is to understand how the slow and age-dependent evolution of the rheological properties correlates with the mechanical history of the materials. A first answer is provided by Cloitre *et al.* [91], who have studied a paste made of soft microgel colloidal particles. They measure the strain recovery and the creep of a sample (initially fluidified by applying a stress larger than the yield stress,  $\sigma_y$ ) submitted to a “probe” stress  $\sigma$  of variable amplitude. They find that the time evolution of the strain is age-dependent but that all the experimental data collapse on a master curve when the time is normalized

by  $t_w^\mu$ . The aging exponent  $\mu$  decreases continuously from 1 (full aging) to 0 (no aging) as  $\sigma$  increases ( $\mu = 0$  for  $\sigma = \sigma_y$ ). They propose that  $\mu$  can be used to quantify the partial mechanically-induced rejuvenation of the sample.

Light scattering has also been used extensively to investigate the interplay between slow dynamics and shear rejuvenation. Using the recently introduced light scattering echo technique [103, 104], Petekidis and coworkers [105] have looked at the effect of an oscillatory shear strain on the slow relaxation of a colloidal glass of hard spheres, finding support for a speedup of the slow dynamics due to shear. Bonn and coworkers [106] have measured by DWS the characteristic relaxation time  $\tau$  of a glassy suspension of Laponite particles, to which a shear of rate  $\dot{\gamma}$  has been applied. Similarly to the results of reference [105], they find that  $\tau$  decreases after imposing a shear; moreover  $\tau$  is smaller for larger  $\dot{\gamma}$ . The observed shear rejuvenation is in agreement with theoretical predictions [107].

More quantitatively, Ozon *et al.* [108] have shown using clay particles (smectite) that partial rejuvenation depends only on the amplitude of the applied strain and not on its frequency nor its duration. They find that the relative decrease of the relaxation time due to a sinusoidal shear varies exponentially with strain amplitude,  $\gamma$ , implying that the mechanical energy input is proportional to  $\gamma$ . This result is in contradiction with the Soft Glassy Rheology model of Sollich *et al.* [3, 92], which assumes a  $\gamma^2$  dependence, resulting from a local elastic response.

This discrepancy is only but an example of how subtle and counterintuitive the mechanisms for shear rejuvenation may be. By investigating in detail the dynamics of a colloidal paste subjected to an oscillatory mechanical strain of variable duration, amplitude and frequency, Viasnoff and Lequeux [77, 109] have indeed demonstrated that the characteristic relaxation time of the mechanically perturbed sample (as measured by DWS) may be either smaller or larger than that of an unperturbed sample. The former case corresponds to rejuvenation, while the latter has been termed “overaging”. An illustration of the rejuvenation and overaging effects is shown in figure 3. Note that overaging is reminiscent to observations of the dynamics of a foam by Cohen-Addad and Höhler [110], who have found that the bubble dynamics is strongly slowed down after applying a transient shear. Viasnoff and Lequeux interpret their findings using Bouchaud’s trap model for glassy dynamics [86, 94] (see subsec. 3.2 for a short description), assuming that shear is strictly equivalent to temperature. They calculate the probability for a particle to be in a trap of depth  $E$  a time  $t$  after a temperature jump of small amplitude. They find that the  $T$ -jump (correspondent to the shear perturbation in their experiments) modifies the lifetime distribution : at large times, the deep traps may be overpopulated compared to the unperturbed case, while populations of the shallow traps are equal in both cases. This change of the distribution of life times for the traps leads to an average relaxation time which is longer for the perturbed sample, and hence to overaging. Physically, overaging demonstrates that a moderate shear could help the system to find a more stable configuration, by allowing it to explore more rapidly a larger portion of the energy landscape.



**Figure 3.** (Left) Strain history and (Right) normalized relaxation time  $\Gamma$  (ratio of the relaxation time of the perturbed sample over relaxation time of the unperturbed sample) as a function of sample age. Rejuvenation corresponds to  $\Gamma < 1$  and overaging corresponds to  $\Gamma > 1$  (gray region). Curves are labelled by strain amplitudes. Overaging occurs for low strain amplitude. (Adapted from reference [109])

Shear rejuvenation may lead to very peculiar rheological responses. Coussot, Bonn and coworkers have indeed observed for several systems [111, 112] a critical stress above which the viscosity  $\eta$  continuously decreases with time and below which  $\eta$  increases until flow is totally arrested. The authors interpret the viscosity bifurcation as resulting from a competition between aging and rejuvenation and propose a simple phenomenological model that captures the main experimental observations.

An alternative way to perturb a system have been recently studied by Narita *et al.* [113]. The authors have measured by DWS the slow dynamics of concentrated colloidal suspensions upon drying. They consider that in this experimental configuration a uniaxial compressive stress is generated in the sample. They attempt to map their previous findings of mechanically-induced rejuvenation and overaging on their experimental results. Implicitly, they assume that the effects on the internal stress in the aging dynamics of the sample are similar to those of an external strain. Detailed experiments are clearly needed to address this issue.

Finally, recent experiments of Simeonova and Kegel [75] demonstrate that soft glasses can be considerably perturbed also by gravitational stress. By changing the solvent in which the colloids are suspended, the density difference between the colloids and the solvent,  $\Delta\rho$ , is varied. Two systems with gravitational lengths  $h$  equal respectively to 100 and 10  $\mu\text{m}$  ( $h = k_B T / (\frac{4\pi}{3} R^3 \Delta\rho)$ , with  $k_B$  the Boltzmann constant and  $R$  the radius of the colloids) are used. They find that gravity accelerates significantly the aging of the colloidal glass. Thus, a direct parallel with the overaging effect can be drawn: gravity, similarly to a moderate shear, can help the system to find a more stable configuration. On the other hand, gravity prevents a full exploration of the

configuration space, ultimately suppressing crystallization. Indeed, space experiments have shown that hard sphere suspensions that are in a glass phase on earth do crystallize in microgravity conditions [114]. How gravity couples to the particle rearrangements on a microscopic scale remains an open issue.

#### 4.2. Violation of the Fluctuation Dissipation Theorem and effective temperature

For systems at equilibrium, the response to an external perturbation is related to the correlation function of the observable to which the perturbation field is conjugated. Let us consider an observable  $A$  and its normalized time autocorrelation function  $C(t) = \frac{\langle A(t_0+t)A(t_0) \rangle}{\langle A(t_0)A(t_0) \rangle}$ . If the system is perturbed by a field  $h$  conjugated to  $A$ , the response function is  $R(t) = \frac{\delta A(t)}{\delta h(t_0)}$ . At equilibrium, the fluctuation-dissipation theorem (FDT) relates the time derivative of the correlation function with the response:  $\frac{dC}{dt} = -k_B T R(t)$  where  $k_B$  is the Boltzmann constant and  $T$  is the system temperature. Two common examples of the FDT are the Nyquist formula that relates the voltage noise across a resistor to the electrical resistance and the Stokes-Einstein relation, which relates the diffusion of a particle in a solvent to the solvent viscosity. In deriving the FDT, time-translation invariance is required: as this assumption is not fulfilled for out-of-equilibrium systems, for them the FDT does not hold. For out-of-equilibrium systems, it has been proposed [115, 116] that the FDT could be generalized by introducing an effective temperature,  $T_{\text{eff}}$ . The time derivative of the correlation function and the response function are then related through  $\frac{dC}{dt} = -k_B T_{\text{eff}} R(t)$ . Note that  $T_{\text{eff}}$  is expected to depend on the observation time scale and on the sample age and to be higher than the temperature  $T$  of a bath with which the out-of-equilibrium material is in thermal contact.

In the past, violations of the FDT have been experimentally observed for structural glasses [117], spin glasses [118], and polymer glasses [119]; moreover, an effective temperature has been introduced to describe granular materials [120, 121]. By contrast, experiments testing the FDT in out-of-equilibrium soft materials are still very rare. Using available data from the literature, Bonn and Kegel [122] examine the generalized Stokes-Einstein relation,  $D(\omega) = k_B T / [6\pi\eta(\omega)R]$ , for hard sphere suspensions. Here  $D(\omega)$  and  $R$  are the frequency-dependent diffusion coefficient and the radius of the particles, respectively, and  $\eta(\omega)$  is the frequency-dependent viscosity of the suspension. They derive  $D(\omega)$  from dynamic light scattering experiments and  $\eta(\omega)$  from rheology measurements of either the high shear rate viscosity of the suspension, when considering the short-time diffusion coefficient, or the complex modulus in the linear regime, when considering the long-time diffusion coefficient. They find that, in a wide range of volume fractions (between 0.032 and 0.59), the FDT is obeyed ( $T_{\text{eff}} = T$ ) for the short time diffusion coefficient, i.e., at the larger volume fractions, for the particle dynamics within the cage. By contrast, for supercooled suspensions the FDT is strongly violated at longer times. The departure from FDT is quantified by  $\frac{T_{\text{eff}}}{T} = \tilde{\eta}(\omega)\tilde{D}(\omega)$ , where  $\tilde{D}$  and  $\tilde{\eta}$  are reduced parameters given in units of the diffusion coefficient of the particle at

infinite dilution and of the solvent viscosity, respectively. They deduce that  $\frac{T_{\text{eff}}}{T}$  can be as large as 70 at low frequencies and for a volume fraction  $\phi = 0.52$ ;  $\frac{T_{\text{eff}}}{T}$  is found to decrease from  $\sim 70$  to  $\sim 10$  as  $\phi$  increases from 0.52 to 0.56. As expected theoretically, they find that  $T = T_{\text{eff}}$  at high frequency and that at low frequency  $T_{\text{eff}}$  is larger than  $T$  and decreases continuously with  $\omega$  following a power law. Finally, we point out that, although the violation of the FDT is clearly evidenced in this work, the exact values of the effective temperatures should be taken with extreme caution since they are derived from experiments carried out with different particles.

Abou and Gallet [123] have measured the effective temperature of a colloidal glass of clay particles (Laponite), using a modified Stokes-Einstein relation (the detailed theoretical formalism for the diffusion of a particle in an aging medium can be found in references [124, 125]). They seed the colloidal glass with micron-sized particle probes that can be tracked using light microscopy, and use these probes as a thermometer by measuring both the mean squared displacement and the mobility of the beads. From these measurements, they extract an effective temperature  $T_{\text{eff}}$  at a fixed frequency of 1 Hz. They find a non-monotonic variation of  $T_{\text{eff}}$  with sample age:  $T_{\text{eff}}$  is equal to the bath temperature  $T$  for a young sample, it increases up to  $\simeq 1.8T$  at intermediate age ( $t_w \simeq 150$  min) and then decreases when the sample further ages. The authors relate the non-monotonic variation of  $T_{\text{eff}}$  with sample age to the evolution of the characteristic time for the relaxation of the colloidal glass as measured by dynamic light scattering, and argue that  $T > T_{\text{eff}}$  when the characteristic frequencies of the slow modes measured in DLS are comparable to the frequency at which  $T_{\text{eff}}$  is measured. Measuring the frequency dependence of the effective temperature would be needed to confirm this interpretation.

The same experimental system has been investigated by the group of Ciliberto [126, 127, 128]. They probe the electrical and rheological properties of the material during the formation of the soft glass. For the dielectric experiments, the clay solution is used as a conductive liquid between two electrodes. The set-up allows the frequency dependence of both the electrical impedance and the voltage noise to be measured, from which an effective temperature is derived, by means of a generalized Nyquist formula. They find that  $T_{\text{eff}}$  is a decreasing function of frequency and reaches the bath temperature at high frequency. Moreover,  $T_{\text{eff}}$  decreases as the sample ages, while the FDT is strongly violated for young samples:  $T_{\text{eff}}$  can be larger than  $10^5$  K at low frequency (1 Hz) and small age [126, 127]. They show [128] that the origin of the large violation is the highly intermittent dynamics characterized by large fluctuations of the voltage noise (see section 5 for more details on the dynamic heterogeneities). We note that, in this line of thought, Crisanti and Ritort [130] have shown numerically how an effective temperature can be extracted from the probability distribution function of intermittent events. Because of the strong fluctuations of the noise in the experiments of Ciliberto and coworkers, the value of  $T_{\text{eff}}$  extracted from the voltage data is extremely sensitive to rare events and to the duration over which data are collected. This may explain the discrepancy between references [126, 127] and [128] concerning the numerical

value of the effective temperature obtained by dielectric measurements (about one order of magnitude). Bellon and Ciliberto [127] have also tested the FDT for the rheological properties of the same system. To that end, they have built a novel “zero-applied stress” rheometer [129], by which the (very small) strain induced by thermal fluctuations can be measured. Although strong aging properties are measured in the rheological responses of the material (as measured also for the dielectric properties), no violation of the FDT could be detected. The authors propose several possible explanations for the discrepancy between dielectric and rheological measurements. In particular, they point out that the strong fluctuations of the voltage noise could result from the dissolution of ions in the solution. Ion dissolution has been very recently confirmed by Bandyopadhyay and coworkers [81] who argue that the dissociation of the ions at the surface of the particles leads to the increase of the interparticle repulsion and is at the origin of the slow dynamics and aging of Laponite samples. Because the increase of the interparticle repulsion may lead to a rearrangement event only when the internal stress thus generated exceeds the (local) yield stress, fluctuations in the mechanical properties are expected to be much less strong than fluctuations of the dielectric properties, which are more sensitive to the release of charges. On the other hand, the rheology measurements of the group of Ciliberto are in principle similar (albeit not identical) to those of Abou and Gallet, since both probe the mechanical properties of the material. Abou and Gallet measure a weak violation of the FDT ( $T_{\text{eff}}/T$  is at most equal to 1.8 at a frequency of 1 Hz), while the measurements of Ciliberto’s group do not detect any violation. However, it should be pointed out that the rheology experiments of Ciliberto and coworkers may lack the sensitivity required to measure violations as small as those reported by Abou and Gallet. Whether these experimental results are indeed conflicting remains therefore an open question.

To conclude, we remark that experimental works are still scarce, owing to the difficulty of measuring simultaneously the response function and the fluctuation in experiments on soft materials. Laponite clay suspensions have been mostly investigated and the results obtained so far by two independent groups and using different techniques display both qualitative and quantitative discrepancies. On the other hand, simulations works on a binary Lennard-Jones mixture [131] have shown that the effective temperature is independent on the chosen observable, while it has been shown theoretically [132] that the effective temperature does depend on the observable in the glass phase of Bouchaud’s trap model. More theoretical, numerical, and experimental investigations are needed to rationalize these contrasting findings.

## 5. Dynamical heterogeneity

Dynamical heterogeneity is now recognized as a fundamental feature of the slow dynamics of supercooled fluids and glasses in hard condensed matter, thanks to the large body of experimental, numerical and theoretical work carried out in the last decade (a general review on dynamical heterogeneity can be found, e.g., in reference [7]).



Most early observations of heterogeneous dynamics focussed on temporal heterogeneity: the coexistence of different relaxation times was identified as the source of the non-exponential relaxations observed in glass formers. Spatial heterogeneity was often invoked as the most plausible physical origin of this coexistence (see [7] and references therein). Subsequent experimental and numerical work has shown that indeed the dynamics of glass formers is spatially heterogeneous, and spatial heterogeneity has been related to the cooperative nature of the slow dynamics (for reviews on spatial heterogeneity that focus on experimental and numerical work, see for example references [133] and [134], respectively).

Cooperativity plays a central role in many recent theories, where the glass transition is explained as a dynamical (as opposed to thermodynamic) transition driven by the divergence of the size of regions that undergo cooperative rearrangements. Following this approach, analogies have been drawn with critical phenomena, the static correlation length of the latter being replaced by a suitable dynamical correlation length [135, 136, 137, 138, 139]. It should be noted that most theories are developed in the framework of spin models or the so-called dynamically facilitated (or kinetically constrained) models [140], where the motion of on-lattice particles depends on the number of occupied neighboring sites. Making quantitative connections between the results for these systems and molecular glass formers or colloidal systems may be therefore difficult. However, we note that recent numerical and theoretical work has shown that the concept of the glass transition being a dynamical critical phenomenon can be successfully applied also to Lennard-Jones glass formers [136] and in the framework of the mode coupling theory [139].

Experimentally, soft materials provide a unique opportunity to study in great detail temporal and spatial heterogeneity in supercooled fluids and glasses, because the relevant length and time scales are more easily accessible than for hard condensed matter systems. In this section, we will review recent experiments that probe dynamical heterogeneity in a variety of systems, ranging from model hard sphere suspensions to more complicated glassy samples, such as colloidal gels and concentrated surfactant phases. Most experiments are performed using time-resolved confocal scanning microscopy [20] or recently introduced light scattering methods that allow temporal heterogeneities to be measured [33], as it will be discussed in the following subsections.

### *5.1. Optical microscopy experiments*

Optical microscopy and digital imaging processing allow one to follow simultaneously the individual trajectories of a large number of particles (up to thousands), tracking their position to an accuracy of a few tens of nanometers [141]. Three-dimensional motion can be studied thanks to time-resolved, laser-scanned confocal microscopy. Once the particle trajectories are known, a wide range of statistical quantities can be calculated in order to detect, characterize, and quantify dynamical heterogeneity. Direct comparison

with simulation work is possible, making optical microscopy a powerful experimental technique for investigating slow dynamics in glassy soft materials (for a recent review of video microscopy applied to colloidal suspensions, see reference [20]).

Early optical microscopy measurements of dynamical heterogeneities were performed by Kasper and coworkers, who studied the self diffusion of tracer particles in a concentrated hard sphere fluid [142]. The tracer particles have a core-shell structure: the outer layer is identical in composition to the host particles, while the inner core has a large optical contrast with the fluid and the host particles. The trajectories of the tracer particles are followed in a thin slice of a three-dimensional sample, allowing the mean squared displacement (MSD) and the self part of the van Hove correlation function,  $G_S(x, t)$ , to be calculated.  $G_S(x, t)$  represents the (density of) probability that a particle moves a distance  $x$  in a time step  $t$ . For a diffusive process,  $G_S(x, t)$  is a Gaussian distribution. Kasper *et al.* find that in concentrated suspensions  $G_S(x, t)$  departs from a Gaussian behavior, the deviations being increasingly marked as  $\phi$  approaches  $\phi_g$ . These deviations are due to a small but significant fraction of displacements  $x(t)$  larger than expected. Deviations from Gaussian behavior are quantified by the so-called non-Gaussian parameter  $\alpha_2$ , defined as the fourth moment of  $G_S(x, t)$ , properly normalized ( $\alpha_2 = 0$  for a Gaussian distribution).

Similar experiments are reported by Kegel and van Blaaderen [143], who use confocal microscopy to study in two dimensions the dynamics of concentrated suspensions of nearly density- and refractive index-matched colloids behaving as hard spheres. In contrast to the experiment of Kasper *et al.*, all particles are tracked (as opposed to tracer particles only), improving dramatically the statistics. For concentrated suspensions in the fluid phase,  $G_S(x, t)$  is reasonably well described by the sum of two Gaussian distributions, corresponding to two distinct populations of “fast” and “slow” particles. This result clearly demonstrates the heterogeneous nature of the dynamics, in agreement with several simulation works (see, e.g., reference [144]).

Weeks and coworkers performed the first three-dimensional optical microscopy investigation of the slow dynamics of supercooled colloidal suspensions [145]. They use PMMA particles stained with a fluorescent dye and suspended in an organic solvent that nearly matches both the density and the refractive index of the particles. Note that under the reported experimental conditions the particles are slightly charged [146]. They find a non-Gaussian  $G_S(x, t)$ , with a non-Gaussian parameter that has a peaked shape as a function of the time step  $t$ . The peak position corresponds to the characteristic time of the  $\alpha$  relaxation, and its height increases when  $\phi$  approaches  $\phi_g$ , indicating increasingly heterogeneous behavior. In the glass phase, no clear peak is observed. In analogy with previous simulation work [144, 147], Weeks and coworkers study the spatial arrangement of the most mobile particles (the mobility is measured for time intervals comparable to the  $\alpha$  relaxation time). They find that these particles form clusters that have a fractal morphology (fractal dimension  $\approx 1.9$ ) and whose size, for supercooled suspensions, increases with increasing  $\phi$ , up to a radius of gyration of about 10 particle radii. For glasses, defining the most mobile particles is more difficult, since no

$\alpha$  relaxation is observed and the cluster size depends sensitively on the way the mobility is calculated [88]. When the particle trajectories are slightly averaged over time to remove the contribution of Brownian motion, the clusters observed in glasses are similar to those observed for supercooled samples. Interestingly, no change in the cluster size is observed for glasses during aging, thus ruling out the increase of the correlation length of the dynamics as a possible origin for the slowing down of the dynamics [88].

In glassy systems, the relationship between dynamical heterogeneity and local structure is a long-standing open question. Various experiments suggest that particle mobility is related to the degree of local disorder and packing, although it should be stressed that very small changes in the local structure are associated to huge variations in the dynamics. In the same three-dimensional experiment discussed above, Weeks and Weitz have shown that the clusters of the most mobile particles occupy regions with lower local density and higher disorder [148]. Two-dimensional systems allow a more direct investigation of the relationship between local structure and dynamical heterogeneity. Cui and coworkers have studied the dynamics of a single layer of concentrated monodisperse particles confined in a quasi-two-dimensional cell [149] (note that this system does not exhibit a glass phase, but rather crystallizes at high enough volume fraction). At relatively high volume fractions and intermediate time scales, the dynamics is very heterogeneous, with two distinct populations of particles. The fast particles move in a string-like fashion —strongly reminiscent of that observed in simulations of supercooled fluids [147]— along channels formed by the disordered boundaries between regions of slowly-moving, quasi-ordered particles. On very long time scales, infrequent, large displacements are associated with transient regions of lower density created by density fluctuations. A very elegant realization of a two-dimensional colloidal glass former has been recently reported by König and coworkers [150, 151]. Superparamagnetic colloidal particles are confined at the water-air interface of a hanging liquid drop; the interactions between particles can be fine-tuned by applying a magnetic field, thereby fixing the “temperature” of the system [152]. Mixtures of particles of two different sizes are used, in order to prevent crystallization. The structure is analyzed in terms of locally ordered patterns of small and large particles that maximize the packing density [153, 154]. Dynamical heterogeneities appear to be associated with the regions where the local order is frustrated and the local packing is looser [150, 153].

## 5.2. Light scattering experiments

Although in light scattering experiments no microscopic information on the individual particle trajectories are available, this technique still presents some attractive features compared to optical microscopy. The scattering volume is typically larger than the sample volume imaged by microscopy, thus allowing a better statistics to be achieved. A large experimental volume may be particularly important when the dynamics is spatially correlated: for example, for samples near  $\phi_g$ , the size of the clusters of fast-moving particles measured in the experiments by Weeks *et al.* [145] was comparable to the full

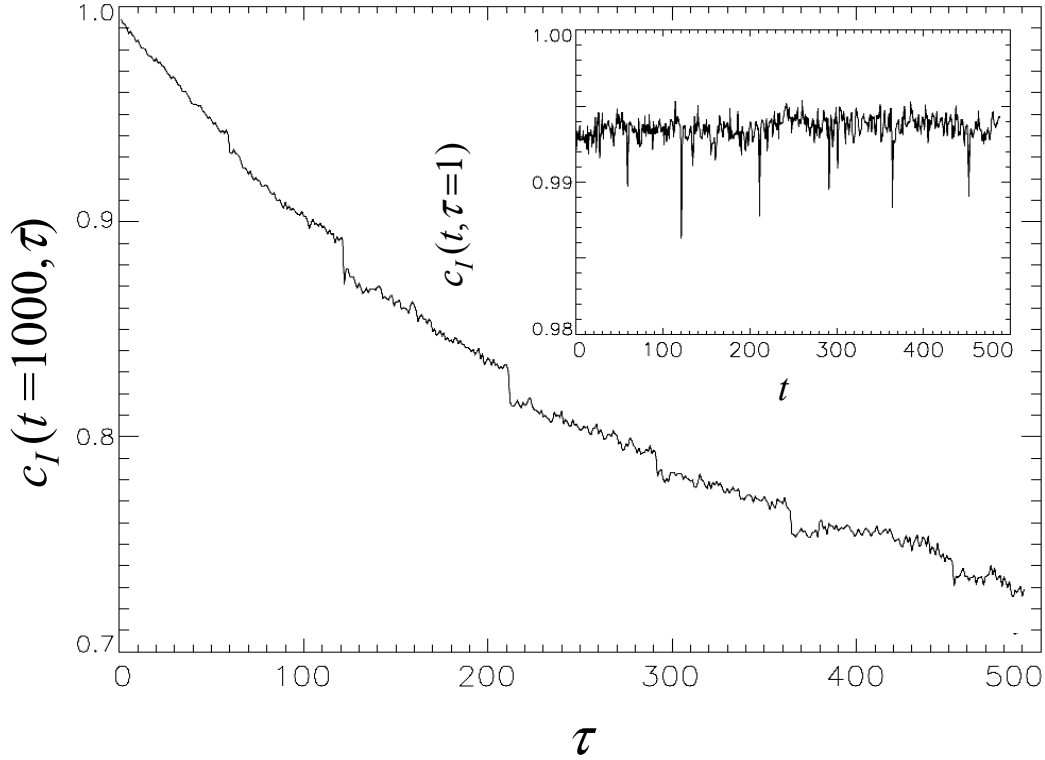
field of view, thus making difficult their precise characterization. Moreover, particles used in light scattering experiments are typically smaller than those used for imaging: as a consequence, the time scales of the slow dynamics are not as prohibitively long as for larger particles. In addition, small particles are less influenced by external fields such as gravity. Finally, experiments can be performed both in the single and in the strongly multiple scattering limits, thus extending the possible choice of systems (by contrast, optical microscopy requires nearly index-matched suspensions, except for two-dimensional systems).

Traditional light scattering techniques, however, do not provide direct information on dynamical heterogeneity, because of space and time averaging. In fact, the intensity correlation function  $g_2 - 1$  has to be averaged over extended periods of time in order to achieve an acceptable accuracy (typically up to four orders of magnitudes longer than the largest relaxation time in the system), and the detector collects light scattered by the whole illuminated sample. Indirect measurements of dynamical heterogeneities are still possible: for example, the non-Gaussian parameter  $\alpha_2$  that quantifies deviations from diffusive behavior can be measured (see e.g. reference [155]). However, it should be noted that a non-zero value of  $\alpha_2$  could be due either to the coexistence of fast and slow populations of particles, as discussed in the previous subsection, or to the same non-diffusive behavior shared by all particles. Traditional light scattering experiments lack the capability of discriminating between these two contrasting scenarios.

Higher-order intensity correlation functions contain more information on temporal heterogeneities of the dynamics [31, 32]. In particular, Lemieux and Durian have studied the dynamics of the upper layer of grains in a heap upon which grains are steadily poured at a flow rate  $Q$  [156]. They measure the 4-th order intensity correlation function,  $g_T^{(4)}(\tau) = \langle I(t)I(t+T)I(t+\tau)I(t+\tau+T) \rangle_t / \langle I \rangle_t^4$ , where  $I(t)$  is the multiply scattered intensity measured by a point-like detector and the average is over time  $t$ ¶. They show that, contrary to  $g_2$ ,  $g^{(4)}$  allows intermittent, avalanche-like processes (occurring at low  $Q$ ) to be distinguished from continuous dynamics (occurring at high  $Q$ ). Moreover, both the statistics of the avalanches and the motion of grains within a single avalanche can be obtained by analyzing  $g^{(4)}$ .

The technique proposed by Lemieux and Durian still requires to average the (higher-order) intensity correlation functions over time. This poses a problem when studying very slow or non-stationary processes, as it is often the case for soft glasses. Cipelletti and coworkers have recently proposed an alternative approach, termed Time Resolved Correlation (TRC) [33, 157], where one takes full advantage of the multispeckle method. In a TRC experiment, a CCD camera is used to record a time series of pictures of the speckle pattern of the light scattered by the sample (both single scattering and DWS measurements are possible). The dynamics is quantified via  $c_I(t, \tau)$ , the instantaneous degree of correlation between pairs of speckle patterns recorded at time  $t$  and  $t + \tau$ :

¶ In this section we follow the notation of most experimental works by indicating time by  $t$  and a time lag by  $\tau$ . This is different from the notation used in previous sections of this paper and in most numerical and theoretical works where  $t$  and  $t' - t$  are used, respectively.



**Figure 4.** Time Resolved Correlation measurements for a granular material gently tapped. The dynamics of this athermal system is due to the taps; therefore both the time,  $t$ , and the time delay,  $\tau$ , are expressed in number of taps. Inset:  $c_I(t, \tau)$  as a function of  $t$  for a fixed time delay  $\tau = 1$ . Note the rare, large drops of the TRC signal, indicative of intermittent dynamics. Main plot: for the same system,  $c_I(t, \tau)$  is plotted as a function of time delay, for fixed  $t = 1000$ . The step-like relaxation of  $c_I$  is due to large, rare rearrangement events similar to those that yield the downward spikes in the inset. Adapted from reference [159].

$c_I(t, \tau) = \frac{\langle I_p(t) I_p(t+\tau) \rangle_p}{\langle I_p(t) \rangle_p \langle I_p(t+\tau) \rangle_p} - 1$ . Here,  $I_p$  is the intensity measured by the  $p$ -th pixel and averages are over all CCD pixels. Because any change in the sample configuration results in a change in the speckle pattern,  $c_I(t, \tau)$  quantifies the overlap between sample configurations separated by a time lag  $\tau$ , as a function of  $t$ . The time average of  $c_I(t, \tau)$  yields the intensity correlation function  $g_2(\tau) - 1$  usually measured in light scattering, while the raw  $c_I(t, \tau)$  is analogous to the two-time correlation function studied numerically or experimentally for non-stationary (e.g. aging) systems. Note however that in most simulations and experiments the two-time correlation function is averaged over a short time window or over different realizations of the system, in order to reduce its “noise”. By contrast, the essence of the TRC method is to extract useful information from the fluctuations of  $c_I$ .

In order to investigate the temporal heterogeneity of the dynamics, it is useful to plot  $c_I(t, \tau)$  as a function of time  $t$ , for a fixed lag  $\tau$ . For temporally homogeneous dynamics, one expects  $c_I(t, \tau)$  to be constant (except for small fluctuations due to

measurement noise), as verified on dilute suspensions of Brownian particles [33, 157]. On the contrary, a large drop of  $c_I$  at time  $t$  would be indicative of a sudden rearrangement event occurring between  $t$  and  $t + \tau$  and leading to a significant change of the sample configuration. Large drops of  $c_I$  have been indeed observed in TRC measurements on a variety of systems, including colloidal fractal gels and concentrated surfactant phases [33, 78], flocculated concentrated colloidal suspensions [158], and granular materials [99, 159, 160]. As an example, the inset of figure 4 shows TRC data for the granular material studied in references [99, 159]: large drops of the degree of correlation are clearly visible, thus demonstrating the intermittent nature of the slow dynamics. These sudden rearrangements are also visible in the two-time correlation function, provided that no average is performed, as discussed above. The main plot of figure 4 illustrates this point by showing  $c_I(t, \tau)$  as a function of  $\tau$  for a fixed  $t$ , for the same system as in the inset. The rearrangement events result in a discontinuous, step-like relaxation of the correlation function (note that a similar behavior was observed in simulations on a molecular glass former, when the two-time correlation function was not averaged over different system realizations [161]). By contrast, the *average* intensity correlation function  $g_2 - 1$  is often indistinguishable from that of a system with homogeneous dynamics. This demonstrates that great care should be used in applying standard equilibrium methods to extract from  $g_2$  quantities such as the particles' MSD, because these methods usually assume the dynamics to be homogeneous. In particular, the preliminary experiments reported in reference [33] on the same systems for which the “ballistic” motion associated with internal stress relaxation was observed (see sections 3.1 and 3.3) raise the issue of how to reconcile intermittent dynamics with ballistic motion. A simple explanation would be to assume that the dynamics is due to a series of individual rearrangements and that the particle motion—in a given region of the sample—resulting from distinct rearrangements is highly correlated (uncorrelated motion would lead to a diffusive-like behavior). The model proposed by Bouchaud and Pitard for the slow dynamics of colloidal fractal gels is indeed based on this idea [85].

An important point in the TRC experiments reported above is that the technique allows one to probe directly temporal heterogeneity, not spatial heterogeneity, because each CCD pixel receives light issued from the whole scattering volume. However, the very existence of large temporal fluctuations of  $c_I(t, \tau)$  demonstrates—albeit indirectly—that the dynamics is spatially correlated over large distances. More precisely, in order to observe intermittent dynamics the number  $N_d$  of dynamically independent regions contained in the scattering volume has to be limited, because for  $N_d \rightarrow \infty$  many rearrangement events would occur in the sample at any given time, leading to small, Gaussian fluctuations of  $c_I(t, \tau)$ . Similar arguments have been invoked in recent simulation and theoretical works to explain non-Gaussian fluctuations in systems with extended spatial or temporal correlations (see for example references [130, 137, 162, 164, 165, 166, 167, 168]). In particular, the probability density function (PDF) of  $c_I$  at fixed  $\tau$  is in many cases strongly reminiscent of the “universal” Gumbel distribution [164, 165] or of a generalized Gumbel-like PDF [137]. These distributions

are characterized by an asymmetric shape, with an (asymptotically) exponential tail. We note however that the detailed shape of the PDF of  $c_I$  depends sensitively on the lag  $\tau$  [169], a feature also found in theoretical work [162].

In the TRC experiments discussed above, individual rearrangement events can be identified and the probability distribution of the time interval,  $t_e$ , between such events can be calculated. For the flocculated suspension studied in reference [158] Sarcia and Hébraud find a power law distribution  $t_e \sim t^{-2}$ . Interestingly, this behavior agrees with theoretical predictions derived in the framework of the trap model for glassy systems, in the regime where a limited number of dynamically independent regions are observed [162]. For other experimental systems, individual rearrangement events may not be distinguishable, because the drop of  $c_I$  associated with one single event may be negligible. In this case, a measurable loss of correlation is always due to the cumulative effect of many events, even for the smallest delays  $\tau$  accessible experimentally. Deviations from temporally homogeneous dynamics are still detectable, however. An example is provided by the dynamics of a shaving cream foam [163]:  $c_I(t, \tau)$  is found to exhibit large fluctuations on a time scale much longer than the average relaxation time of the intensity autocorrelation function. As a consequence, the two-time correlation function decays smoothly at any time (no step-like relaxation such as that in figure 4b is observed), but its relaxation time slowly fluctuates with time  $t$ . These fluctuations are quantified by introducing the variance of  $c_I$ , defined by  $\chi(\tau) = \langle c_I(t, \tau)^2 \rangle_t - \langle c_I(t, \tau) \rangle_t^2$ .  $\chi(\tau)$  is the analogous for TRC experiments of the generalized dynamical susceptibility  $\chi_4$  introduced in theoretical and numerical works on spin systems, hard spheres, and molecular glass formers [163, 170, 171]. Note that  $\chi_4$  is proportional to the volume integral of the so-called four-point density correlation function, which compares the change of the local configuration around the position  $\mathbf{r}_1$  during a time interval  $\tau$  to the corresponding quantity for position  $\mathbf{r}_2$  [163, 171]. Because  $\chi_4$  is related to the spatial correlations of the dynamics, this parameter provides a quantitative link between temporal and spatial dynamical heterogeneity. For the foam,  $\chi(\tau)$  has a peaked shape, the largest fluctuations of the dynamics being observed on a time scale comparable to  $\tau_s$ , the average relaxation time of the system. This feature is strongly reminiscent of the behavior of the systems investigated numerically and theoretically in references [162, 163, 171].

In simulations of glass formers, the height of the peak of  $\chi_4$  increases when approaching the glass transition [171]. This behavior has been interpreted as due to the increase of the size of dynamically correlated regions. The foam and the Ising spin models studied in reference [163] provide a means to test this hypothesis on systems for which there is a natural characteristic length that increases with time, due to coarsening (this length is the bubble size and the size of parallel spin domains for the foam and the Ising models, respectively). Indeed, for both systems the same dynamic scaling of fluctuations with domain size is observed:  $\chi(\tau/\tau_s) \sim N^{-1}$ , where  $\tau_s$  is the average relaxation time of the correlation function and  $N$  is the number of bubbles (or spin domains) contained in the system. Similar TRC experiments have been performed on a

very polydisperse colloidal paste by Ballesta and coworkers [172]. They find that  $\chi(\tau)$  has a peaked shape, similarly to the systems reported above. Moreover, the height  $\chi^*$  of the peak evolves in a very surprising way: initially  $\chi^*$  increases with increasing volume fraction  $\phi$ , similarly to the growth of the peak in supercooled molecular systems upon cooling [171]. In contrast with molecular systems, however,  $\chi^*$  reaches a maximum value at intermediate volume fractions and is drastically reduced at the highest  $\phi$  experimentally achievable [173]. More experiments on different systems will be needed to test the generality of this behavior. In particular, model systems such as hard spheres suspensions are an attracting choice, since detailed predictions on the behavior of  $\chi(\tau)$  in the framework of the MCT are now available [139].

### *5.3. Other experiments and concluding remarks on dynamical heterogeneity*

Dynamical heterogeneity has been measured also by other techniques and in different systems. Strongly intermittent behavior has been observed in the dielectric signal for a Laponite glass [128], as already mentioned in section 4.2. As a result, the PDF of the voltage signal measured in these experiments exhibits a non-Gaussian behavior, with roughly exponential tails similar to those reported in reference [130]. The microscopic origin of these events is still unclear. Attempts to measure intermittent behavior in the rheological response of the same Laponite system using the “zero-shear” rheometer [129] mentioned in section 4.2 were, to date, not successful.

Interestingly, heterogeneous dynamics has been reported for a variety of granular systems, using different techniques. Intermittency has been measured by TRC in granular systems gently vibrated [99, 159, 160]. These experiments show that the evolution of the system configuration is not continuous, but rather occurs through a series of discrete rearrangement events, similar to those reported in references [33, 78, 158] for colloidal systems. On a more microscopic level, Marty and Dauchot [174] and Pouliquen and coworkers [175] have tracked the motion of individual “grains” in two-dimensional and three-dimensional granular systems submitted to a cyclic shear. They find that the grain motion is strongly reminiscent of that of colloidal glasses: a cage effect is observed and deviations from a Gaussian behavior in the PDF of the grain displacement are reported, similarly to the results of the experiments discussed in section 5.1. Collectively, these analogies support and extend to a microscopic level the unifying picture underlying the concept of jamming proposed by Liu and Nagel [2].

As a final remark, we note that intriguing analogies exist also between the heterogeneity of the spontaneous dynamics of soft glasses and the behavior of many complex fluids under shear. Indeed, for concentrated colloidal suspensions and surfactant systems the macroscopic rheological response to an applied constant strain or stress has been shown to exhibit large temporal fluctuations [176, 177, 178, 179]. On the other hand, simulations and experiments have shown that the stress relaxation and the flow of foams, ultrasoft glasses and concentrated surfactant systems are both temporally and spatially heterogeneous (see e.g. references [178, 180, 181, 182, 183, 184]).



Although this heterogeneous behavior is usually associated to the existence of different microstructures (e.g. disordered/ordered onion phases in [180]), simulations of a simple model of an (athermal) generic yield stress fluid suggest that heterogeneity may exist even in structurally homogeneous fluids [185]. In these simulations, the flow of a yield stress fluid sheared at a constant rate is shown to be due to discrete rearrangement events, whose characteristic size diverges for a vanishing shear rate. The basic ingredients of this model (localized plastic events due to a microscopic yield stress and elastic propagation of the local stress relaxation) are certainly relevant for many soft glasses. In particular, close analogies may be drawn between slowly sheared yield stress systems and elastic glassy materials—such as colloidal gels—where internal stresses are progressively built up and induce particle rearrangements. More work will be needed to explore in depth these analogies and to fully assess their relevance and generality.

## 6. Conclusion

In this paper, we have reviewed the experimental work of the last few years on the slow dynamics in soft matter. In particular, research in four areas has been discussed: the existence of two different glass states (attractive and repulsive), the dynamics and the aging of systems far from equilibrium, the effect of an external perturbation on glassy materials, and dynamical heterogeneity. As it was pointed out in many occasions in the preceding sections, these topics are closely related and indeed the same systems have been often studied in the context of two or more of these areas. At the end of each section we have listed what are, in our opinion, the most relevant questions that are still open: here, we limit ourselves to some brief final considerations.

A great effort has been directed to developing unified approaches that may account for the similarities in the slow dynamics of many soft materials and for the fascinating analogies with hard condensed matter glasses and granular media. The most successful theory is probably the MCT: initially, it was restricted to hard sphere suspensions, but it has now been extended to include attractive systems at moderate to high volume fractions. However, it should be noted that the deep physical reasons of its success are still somehow unclear; for example, dynamical heterogeneity, now recognized as a key feature of the slow dynamics of most glassy systems, is not included in standard formulations of the MCT. Very recent theoretical work shows that quantitative predictions on dynamical heterogeneity can be made in the framework of the MCT: experiments that test these predictions would certainly shed new light on the limits to the validity of the MCT.

An alternative unifying approach is the jamming scenario, which is however a conceptual tool rather than a fully-developed quantitative theory. Its appeal resides in the large variety of systems whose fluid-to-solid transition may be rationalized in a unified picture, ranging from colloidal suspensions to molecular glasses and granular materials. The analogies in the local dynamics between glass formers and granular media that have been rapidly reviewed in this paper (cage effect, dynamical heterogeneity)

provide additional support to the jamming scenario. Another intriguing similarity hinted to by recent work is the increase of heterogeneity in unperturbed glassy systems when temperature or packing fraction approaches a critical value, which is paralleled by the growth of spatial and temporal heterogeneity in yield-stress fluids when the shear rate vanishes. This analogy is particularly suggestive in the framework of jamming, because of the similar role that is attributed to temperature (or interparticle potential and volume fraction) and stress in driving the fluid-to-solid transition.

While the MCT and the jamming scenario provide some guidance in describing systems that approach the non-ergodicity transition from the fluid phase, our understanding of materials deeply quenched in an out-of-equilibrium phase is less advanced. Although some common features are observed (dynamical heterogeneity and a general trend for the dynamics to slow down with sample age being two of the most prominent), a large palette of different behaviors is observed, which remains largely unexplained (see, e.g., the various aging regimes discussed in this review). The concept of effective temperature may prove useful to describe quantitatively out-of-equilibrium soft materials and their aging; however, current experimental determinations of  $T_{\text{eff}}$  are still too scarce and yield contradictory results. In particular, simultaneous measurements of the effective temperature for various observables and in a wider variety of systems will be necessary. Finally, we observe that stress relaxation appears to be an important ingredient of the slow dynamics of many soft glasses; in spite of that, it has been generally neglected in theoretical approaches, with the exception of the model for colloidal gels cited in section 3.1.

Recent advances in the investigation of slow dynamics in glassy soft matter have been made possible by close interactions between theory, simulation and experiments. On the experimental side, new methods and techniques have been developed to extend measurements to out-of-equilibrium and very slowly relaxing systems. A great effort is currently done to obtain spatially- and time-resolved information on the dynamics, and to identify the most insightful quantities to be extracted from the raw data in order to characterize heterogeneous behavior. Future advances will likely include the combined (and possibly simultaneous) use of these methods, in order to achieve a more complete understanding of the various physical mechanisms that drive the relaxation of glassy soft matter, as well as of their interplay. Conceptually, the focus will be in identifying and explaining the “universal” features of the slow dynamics in vastly different systems.

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