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Colloidal gels—low-density disordered solid-like states

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Abstract

The analogies between colloidal glasses and gels have stimulated an increased effort in recent years to unify the description of the transitions to these disordered solid-like states within a single conceptual framework. Mode coupling theory, which successfully describes the hard sphere colloidal glass transition, has been extended to describe the effect of weak attractions at large volume fractions. By comparison, diffusion limited cluster aggregation models successfully describe the behavior for the other limit, irreversibly aggregated, fractal gels formed at low volume fractions and very large interaction potentials. A theoretical picture, which unifies these two limits, is still the subject of research. In this review, we summarize some of the results obtained to date, aiming to give an overview of our current understanding.

Keywords: Colloidal gel; Colloidal glass; Non-equilibrium fluid-solid transitions; Mode coupling theory; Jamming

1. Introduction

Colloidal particles can form disordered solids in several seemingly disparate ways. At very high volume fractions, crowding of non-interacting, or hard-sphere particles results in a colloidal glass, whose solid-like properties originate from the permanent trapping of particles within cages formed by nearest neighbors [1–3]. By contrast, at very low volume fractions, inducing strong attraction between the particles results in the formation of fractal clusters, which ultimately form space-filling networks, whose connectivity determines the solid-like properties of the system [4–6]. At volume fractions intermediate between these two extremes, colloidal particles can still form disordered solids, with a transition from liquid-like to solid-like behavior that depends on both the strength of the interparticle attraction, U, and the volume fraction of particles, . A continuous boundary describing the onset of disordered solid states connects the high-density repulsive glasses to the low-density space-spanning systems with highly attractive potentials. Fig. 1 shows a schematic of such a state diagram, based on results obtained for systems with short-range potentials [7–9••,10•]. The two extremes of the state diagram are the hard sphere colloidal glasses at high and low U, and the strongly attractive colloidal gels at low and high U. All disordered solid states described within this state diagram are defined by their arrested dynamics and elasticity. A central question of recent research in colloidal science has been whether colloidal glasses and gels can be described within a single framework. Two quite different frameworks have been invoked. One approach is mode coupling theory (MCT), which focuses on density fluctuations and the formation of cages leading to structural arrest [11]. A second approach, which to date is still only conceptual, is jamming, which infers stress-bearing networks underlying the solid-like properties in a variety of disordered solids [12].

The aim of this paper is to summarize some of the recent results concerning both the existence of a continuous boundary and the investigation of the nature of the fluid to solid transition. Our focus is on the dynamic arrest and the onset of elasticity at the transition, rather than on specific forms of the correlation functions describing the dynamics.

2. Transitions at high densities and low interaction potentials

The colloidal hard sphere glass transition has been extensively studied in the past and MCT has been used

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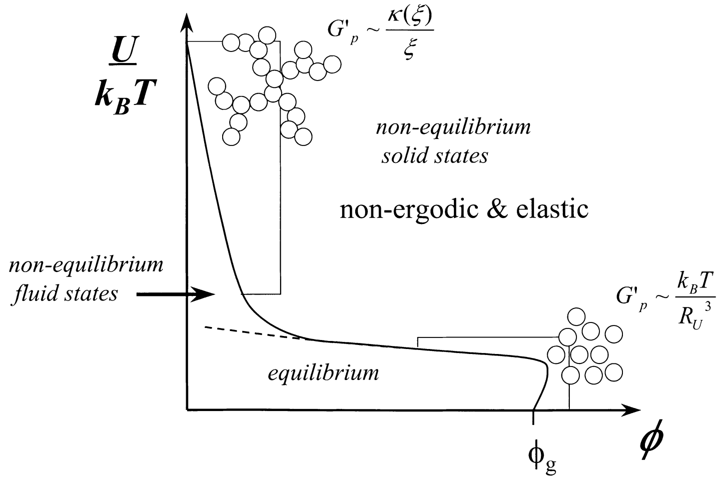

Fig. 1. Schematic state diagram of colloidal particles with short-range potentials, based on results given in ref [7–9••,10•]. The solid line represents the boundary of disordered solids, the dashed line the boundary between equilibrium and non-equilibrium behavior. The grey area at low volume fractions and large interaction potentials denotes the region, where gels are typically formed. The elasticity is determined by connectivity and can be best understood as the ratio of a characteristic spring constant, $\kappa(\xi)$, to the characteristic elastic correlation length of the system, ξ. The grey area at large volume fractions and low interaction potentials denotes the region where glasses are typically formed. The elasticity is determined by the constraint of the particle, which is unable to move out of a cage formed by its nearest neighbors; this is due to crowding and bonding. The elasticity here is of entropic origin and is best understood as the ratio of energy to a characteristic volume, which is the volume of the characteristic structural length of the system, R_U; at large volume fractions, this is the particle size.

successfully to describe the main features of this transition [3,13,14]. As the transition is approached, the increase in the volume fraction of particles leads to caging, which gives rise to an intermediate plateau in both the frequency dependence of the storage modulus $G'(\omega)$ [15] and the time dependence of the correlation function measured by dynamic light scattering $f(q,t)$ [3,16,17]. At the glass transition ($\;_g=0.58$), the α-relaxation time, which describes the long-time structural relaxation process, diverges, and the system exhibits non-ergodicity in addition to a plateau modulus at low frequencies. Both, the ergodic–non-ergodic transition and the rheological fluid–solid transition coincide, clearly indicating that the structural arrest is the cause of the elasticity. The low frequency plateau modulus G'_p is finite at the transition and is predicted to increase as $G'_p \sim A + B(\; - \;_g)^\nu$ with $\nu = 0.5$ [11].

More recently, the effect of introducing short-range attractions in glasses has been studied theoretically [18–20••] and experimentally [9••,21•,22••,23•]. At volume fractions slightly above $\;_g$, weak attractive interactions lead to a melting of the glass, which is due to an increase in the free volume available for particle motion resulting from the attraction-induced decrease in the local particle–particle separation. Increasing the attraction still further increases the lifetime of the particle bonds [20••] resulting in a transition to a solid, which is termed an attractive glass. This reentrant behavior is indicated schematically in the diagram of Fig. 1; the precise experimental diagram can be found in Ref. [9••]. Because of the higher constraint in the particle motion due to bonding, the elasticity is predicted to be much larger in the attractive glass than in the repulsive glass [20••,24••]. A direct transition from repulsive to attractive glasses, which should occur when an attraction is introduced at even larger volume fractions, is predicted to display a sharp or even discontinuous increase in the elasticity of the system, depending on the range of the potential [20••,24••].

3. Transitions at low densities and large interaction potentials

Attractive interactions between colloidal particles can be controlled in many different ways. A widely used way is given by depletion interactions [25,26], which are present when a small entity, such as a polymer, micelle or particle, is added to an otherwise stable suspension of large colloids. Because the center of mass of the smaller species S cannot exist within a shell around the colloid C, there is a net gain in the free volume available to the smaller species when the colloids approach each other such that their excluded volumes overlap; this results in a net osmotic force exerted on the large particles by the small ones, and leads to an effective attraction between the large particles. The advantage of such depletion-induced attractions is that both the range and the depth of the potential can be easily adjusted by, respectively, the size ratio S/C and the free volume concentration of S. Because of this excellent means of control, many of the studies on equilibrium and non-equilibrium behavior of attractive colloids have used depletion attraction as a model system [7–9••,10•,22••,27–29•,30•,31•,32•,33•,34•], with a notable example being sterically stabilized polymethylmethacrylate (PMMA) particles, suspended in organic media using polystyrene (PS) as depleting agent.

In their pioneering work on the non-equilibrium behavior of PMMA/PS-systems, P.N. Pusey, W.C.K. Poon and collaborators [7,27] reported the existence of a systematic $-U$ boundary between fluid-like and space-spanning solid-like systems. However, because of the density mismatch between the particles and the medium, the continuous space-spanning solids persisted only for a limited time before they collapsed and settled due to gravity; this behavior lead the authors to term these solids as transient gels. Below the boundary describing the onset of transient gelation, they found non-equilibrium states for a wide range of and U, which do not exhibit solid-like properties. The approximate position of the boundary delimiting the equilibrium phases from the non-equilibrium states is shown by the dashed line in Fig. 1.

Remarkably, a recent extension of MCT describing the behavior of depletion systems at low volume fractions, captures this onset to non-equilibrium, rather than the fluid–solid-transitions occurring at larger U [24••]. Considering that MCT treats the dynamic arrest at the particle level and does not incorporate the contributions of any space-spanning structures, which typically result from classical aggregation-gelation theories [35–41•], this result appears to be rather significant. For the non-equilibrium fluid states, the formation of either compact or fractal clusters have been reported, depending on the strength of the interaction potential [7,29•,30•,31•]. The cluster itself is likely to be an elastic solid; the particles within the clusters are trapped in local cages, and their motion within the frame of the cluster is constrained so that their local dynamics are arrested. Thus, we can consider the particles within the cluster to be in a glassy state, which is correctly captured by MCT. However, this leads neither to a measurable bulk elasticity nor to a measurable non-ergodicity since the clusters themselves continue to freely diffuse.

Segre et al. [30•] investigated the dynamics of a nearly density-matched PMMA/PS-system, where was varied while U was held fixed at a value large enough to allow the rising branch of the state boundary to be crossed. These systems typically exhibit a small-angle peak in the scattered intensity, indicating that the clusters formed are uniform in size [7,29•]. Using dynamic light scattering to probe the dynamics at q-values near the peak reveals the development of a second relaxation process, whose characteristic time diverges at some critical volume fraction $_c$; this is reminiscent of the colloidal glass transition. Moreover, the q-dependence of the correlation functions which probe the dynamics on the length-scale of the clusters exhibits a scaling behavior similar to the one found for systems near the hard sphere glass transition, where the q-range over which scaling is exhibited corresponds to length-scales where the motion of single particles is explored [42]. This led the authors to postulate that the gelation transition is caused by the trapping of clusters in cages of neighboring clusters, implying the existence of a glass of clusters. Within this picture, the ergodic–non-ergodic transition observed in the low particle-density limit is a result of an increased effective volume fraction, caused by the growth of space-filling clusters.

The rheological behavior of depletion systems similar to the one used by Segre et al. [30•] was investigated by Prasad et al. [10•]. They found an onset and increase of the elasticity, which was reasonably well described by a critical-like function $G'_p = B(\ - \ _c)^\nu$, where ν was found to depend on the range of the potential, varying from $\nu \sim 2.1$ to $\nu \sim 3.3$ as the range of the depletion attraction decreased. The critical-like onset of the plateau modulus observed by a number of authors [10•,43–45] is reminiscent of rigidity percolation, where sets the probability of the formation of a bond which contributes to the elasticity. The differences in the exponents reflect differences in the stress-bearing properties of the network. As the range of the potential decreases, the network switches from one that resists only bond-stretching [46] to one that also resists bond-bending [47]. Within this percolation picture, we expect at $_c$ a connected elastic network with a correlation length $\xi = \infty$. Clearly, the characteristic lengths determining the ergodic-nonergodic transition and the rheological fluid–solid transition differ significantly from each other. The finite cluster size determines the non-ergodic transition, while the infinite elastic correlation length determines the rheological transition. The characteristic cluster size is reflected by the peak in the static structure factor, whereas by contrast, there is no manifestation of the elasticity correlation length in any structural probe. Rheologically, however, it is this tenuous, yet structurally invisible, underlying network which determines the elastic properties of the low-density systems; particles which are not part of the stress-bearing network act here as mere spectators to the elasticity [48••]. Interestingly, the critical volume fraction for the non-ergodicity transition, determined from dynamic light scattering measurements, is found to be lower than the critical volume fraction for elasticity, determined from rheological measurements [10•]. This suggests that the glassy arrest of the clusters is not sufficient to provide a measurable elasticity; the formation of a true elastic network is necessary for the system to bear stress. The reason for the lack of elasticity at the non-ergodicity transition may be a consequence of the open and floppy characteristics of clusters, which allows for both interpenetration [49] and internal energy dissipation [5]. An alternate explanation is that the magnitude of the modulus at the ergodic–nonergodic transition is too small to be measured, because of the increased size of the unit that is actually arrested, R_U. The elasticity obtained by glassy arrest is of entropic origin, where the configuration of the particles or, respectively, the clusters resists deformation out of its most probable configuration. By analogy to the entropic elasticity of glasses, the plateau modulus is proportional to energy over a characteristic volume, $k_B T/R_U^3$, where R_U is the size of the cluster at low and the size of the particle at large . Thus, as the cluster size increases with decreasing , the modulus at the non-ergodic transition becomes too small to be measured. Instead, the only measurable modulus is that of a connected stress-bearing network, and the critical-like onset for this occurs at a higher value of .

For very strong attractions, we recover the behavior expected for irreversible aggregation, where the kinetics leads to the formation of fractal colloidal gels. The plateau modulus is found [50] to increase as $G'_p = B\ \ ^{3.2}$ as expected for kinetic aggregation, where $_c \sim 0$. The dynamics of these systems as measured with dynamic light scattering typically exhibit subdiffusive behavior at short times and arrested dynamics at longer times [5,6,51]. This behavior can be accurately described by a hierarchy of internal elastic modes within the fractal clusters, where the largest fluctuation is quantitatively related to the elastic modulus of the system [5,6]. Elasticity and non-ergodic dynamics of strongly attractive systems are clearly related to their underlying network. Moreover, the cluster size of these systems corresponds directly to the correlation length relevant for elasticity, $R_U = \xi$.

Thus we are left with a rather intriguing scenario. Mode coupling theory seems to accurately capture the onset of the local trapping of the particles over the entire range of , thereby describing the onset to non-equilibrium behavior [24••]. At large enough volume fractions, the cages physically overlap, leading to the scenario of measurable non-ergodicity and elasticity of hard sphere glasses. As shown by recent simulations [52•,53•], mode coupling theory correctly describes non-ergodicity transitions for volume fractions as low as $= 0.4$. However, as the volume fraction is decreased further, local trapping is no longer sufficient to macroscopically arrest the system dynamics, as the number of cages becomes too small to fill space. Instead, finite clusters are formed, where within each cluster, the particles themselves are arrested. Macroscopic non-ergodicity arises only when the effective volume fraction of the clusters is sufficiently high. As U increases, larger clusters are formed and a smaller particle-volume fraction is required to achieve an effective volume fraction sufficiently high to cause macroscopic non-ergodicity. Because of the increased size of the unit, which gets arrested at low , the magnitude of G'_p becomes immeasurably small. The clusters have to connect, and a percolated elastic network has to form, for the system to exhibit any measurable elasticity.

From these observations, we can infer the schematic state diagram shown in Fig. 2. Boundary I (solid line) is due to the local arrest of the particles. Boundary II (dashed line) is due to crowding of the relevant unit of the system and corresponds to the macroscopic non-ergodic transition over the entire range of . This boundary merges naturally with boundary I as R_U becomes equivalent to the particle size at large .

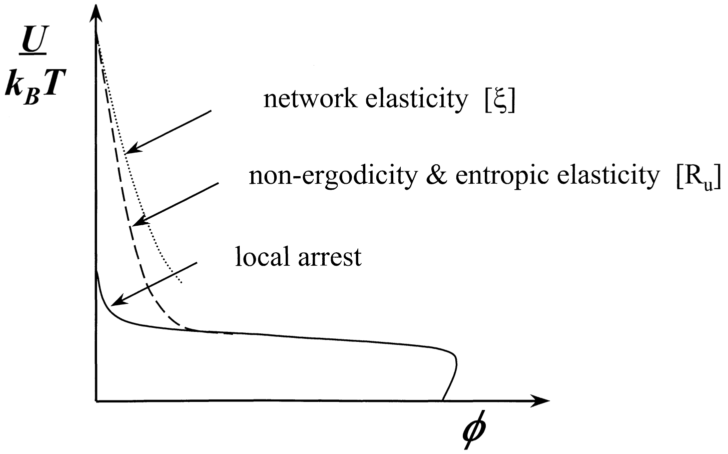

Fig. 2. Schematic diagram denoting the different boundaries that we may expect for systems with short range potential. Boundary I (solid line) represents the onset of the arrest of individual particle motion, due to trapping in cages of nearest neighbors [24••]. At low volume fractions, this condition is necessary, but not sufficient, for the system to arrest macroscopically. The dashed line represents boundary II, where the effective volume fraction of the space-filling unit of size R_U becomes sufficiently high to prevent long range motion within the system. This boundary naturally merges with the boundary of local arrest, as R_U approaches the particle size at large volume fractions. The dotted line represents boundary III, where a percolating stress-bearing path through the system is observed for the first time, the elastic relevant correlation length ξ is infinite at the boundary. How this boundary extends to larger volume fractions is not yet clear.

Boundary III (dotted line) is due to the formation of a percolated stress bearing network and corresponds to the onset of a measurable elasticity at low and larger U. How this boundary extends to large volume fractions is not clear. At large enough interaction potentials the bonds between particles will necessarily become resistant to stretching or even bending and any percolating path of bonds will, therefore contribute to the elasticity through typical network elasticity, which is characterized by the ratio of the characteristic spring constant $\kappa(\xi)$ to the elastic correlation length ξ. Whether the onset of this contribution can be detected for systems at higher , which already exhibit entropic elasticity, must still be resolved by experiments. For intermediate particle volume fractions, transitions through boundary III should in principle be noticeable, as the network elasticity seems to increase with distinctly higher exponents than any predicted for the increase of entropic elasticity [11,54•]. Moreover, the short-time dynamics should reflect contributions from the elastic modes, similar to those observed in both strongly and weakly attractive systems at particle volume fractions below 10% [5,6,51,55].

It is evident that any meaningful attempt to describe the fluid–solid transitions at low volume fractions must include conditions, which lead to space-filling structures. In models that describe irreversible aggregation, it is the kinetics that determines the mechanism of formation of space-filling structures [37,40,41•]. Here, we restrict the use of the word ‘kinetics’ to processes, which occur in time, such as nucleation and growth and diffusion limited cluster aggregation, and we use the word ‘dynamics’ exclusively for processes describing motion, such as diffusion and thermal fluctuations. Starting from a fully dispersed system, and assuming that there is no repulsive barrier that add stability to the particles, any aggregation process will be determined by two competing time scales, the life-time of the bonds and the time for two particles to encounter one another. If the life-time of the bond is much greater than the collision time, it is the kinetics which governs the arrest. The system gradually quenches deeper and deeper into a non-equilibrium state as time proceeds, due to aggregation being much faster than any process driving the system to equilibrium. The particles are arrested within the growing clusters; the clusters grow until they connect, whereupon their growth is arrested; this leads to a ‘kinetic arrest’ of the structure, which generally is fractal and thus space filling. The kinetics observed for such irreversible aggregation [36] is strikingly similar to those observed for aggregation when the attractive interaction is much weaker [7,29•]. However, for the weakly aggregated systems at low , it seems that the growth can become arrested before the clusters become connected to each other, which lead to phases that consist of disconnected, ‘fluid’ clusters. The transition to connected clusters occurs at finite values of ; the underlying origin of this remains unclear. For fractal growth one can, in principle, expect space-spanning networks at any volume fractions. The critical-like onset and increase of the elasticity with increasing observed at intermediate U, indicates that the correlation length of the stress-bearing network decreases as $\xi\sim(\quad-\quad{}_c)^{-1}$; this is similar to DLCA-systems where $R_U\sim\quad{}^{-1/(3-d_f)}$ with $d_f\sim2$ the fractal dimension, except there ${}_c=0$ and $\xi=R_U$. The origin of this behavior seems to stem from the same limitation that causes the limited growth of the clusters in the non-equilibrium fluid state. The most likely explanation for the existence of ${}_c$ is that there may be a bond-breaking and bond-forming rate, which limits the growth of the clusters and subsequently determines the growth of the stress-bearing network. However, conclusive evidence for the validity of this scenario has yet to be found.

4. Conclusion

Our understanding of the implications and consequences of a continuous boundary that describes the onset of formation of disordered solids as U or are varied is certainly far from complete. Further parameters controlling the position of the boundary, and thus the dynamics and rheology of a given system, include the range of the potential, the time elapsed after the quench to the initial non-equilibrium state and the load applied on the system; these are all topics of current, and surely also future research. The importance of new aspects of the transition, such as the spatial and temporal heterogeneities observed in the dynamics of systems near the glass transition [56,57], are becoming increasingly recognized and are being explored within the context of a general understanding of transitions to disordered solids [58•].

Besides the scientific interest in understanding the nature and control of these transitions, unifying schemes to describe them are likely to have considerable impact for industry, where the applications of colloidal systems rely to a large extent on their rheological properties. These are precisely the properties affected by the fluid–solid transitions; thus growth laws that predict the increase of viscosity upon approach to the transition, and the increase of the plateau modulus or yield stress above the transition, would provide a powerful tool for the design of material properties. In addition, a unified description of the glass transition and gelation would impact the more general description of such transition in terms of jamming or other evolving concepts.

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● of special interest
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