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Are particle gels “glasses”?

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Abstract We propose an analogy between a new type of glass, recently found within the mode coupling theory framework, and a particle gel, experimentally observed in colloidal suspensions where the particles have attractive interactions. We report the study of a colloidal system model, made of particles with hard core interacting via an attractive square-well potential. The well-width has a range much shorter than the particle diameter. We find new phenomena in the temperature-composition plane related to the width of the attractive interactions, namely a re-entrant behaviour in the ‘phase’ diagram and a coexistence line between two types of glasses. One has been identified as the commonly studied colloidal glass and the

other as a new type, the ‘attractive’ glass, that can be viewed as a particle gel. The coexistence line terminates at an end-point, named A_3 , after which the gel and the colloidal glass become indistinguishable. We also show characteristic features of the normalised density correlators, for the gel at a relatively low density and close to this singularity point, where the gel and the colloidal glass start to coexist. For the latter it is remarkable to note that the density correlators show a logarithmic time decay.

Key words Colloidal systems · Square-well potential Glass transition · Particle gels · Nonergodic systems

Introduction

Systems of colloidal particles have long been of both practical and scientific importance, and there has been a considerable growth of knowledge in recent years in the area of dense colloidal systems. However, particle gels and the process of gelation itself have not been much studied at a very fundamental level, despite the practical importance of this part of the field. The reason is probably that there are few theoretical approaches within which to rationalise the information. We present here a new way of viewing these systems, based on developments already well established in glass theory.

For colloidal particle systems with short-range attractions, it was quite natural to argue by analogy to all

of the phenomena present for molecules. Thus, we expect to find liquids, gases, and crystals, and perhaps some sort of dense but imperfectly packed or glassy state. This perspective, whilst quite reasonable in many regards, does not take into account the great difference in energy scales and length scales between molecules and colloidal particles. The hard core of a colloidal particle might be on the scale of a micron, and the attraction, tunable using a variety of solvents and other additives, might have a range of only a few percent of this [1, 2, 3]. Typically, though not always, the repulsion is very hard and short-ranged, being mainly derived from the material properties of the particle itself. In addition, the flexibility in the use of solvents and additives may lead to very strong effective attractions, and this combined with the large

mass of the particle means that attractive interactions might easily overcome the tendency of the particles to disperse, even if the true entropic interaction balance is more favourable to a dispersion. So, far from being a rare occurrence, much effort is devoted to preventing colloidal particles from “collapsing” into a condensed phase, a precipitate, or a “gel”, the result usually considered to be poorly characterised, or characterisable. Thus, whilst there are clear analogies between molecular behaviour and colloidal systems, we may also need to look again more carefully at the nature and prominence of all the phenomena, and we may expect new features to emerge and a change in the relative importance of existing phenomena. In fact, as we will show, the result of such a reexamination may well lead us to be able to systematise colloidal phenomena long considered to be inconvenient, rather than scientifically interesting.

We chose as a model of attractive colloidal particles the square-well potential. Such a choice was driven by two reasons: firstly, the square-well potential is a good approximation for many colloidal systems (i.e. colloids with depletion interaction, grafted colloids, etc. and, secondly, it possesses many relevant characteristics of a vast range of potentials i.e. hard-core repulsion and short-range interaction). This model has been widely used to describe interacting colloidal solutions and, to some extent, phenomena such as depletion interaction and grafted colloids are well represented by it [3–7].

Our idea is that the glass theoretical framework, in particular the mode-coupling theory (MCT) [8], that has been introduced and extensively used to describe the glass transition for both simple liquids and colloidal systems, can also be extended to describe other nonergodic states of matter, such as particle gels. The new results recently found for a Yukawa [9, 10] and a square-well potential [11] for an ‘attractive glass’, that will be discussed later in detail led us to propose an analogy between this nonergodic state and a gel. In brief, we propose that the ergodic state (fluid) can be considered to be a sol phase, the “repulsive” glass, also discussed later, is the commonly studied colloidal glass (hard-sphere type), and the “attractive” glass is a particle gel. Thus, what follows will be discussed in these terms.

Mode-coupling theory

We have already alluded to the fact that we use glass theory to study the square-well potential. The reason is that we shall be looking for transitions to a nonergodic state that could represent the process of gelation. The most practical theory to use in this respect is MCT, which has previously been shown to describe colloidal glasses driven by packing forces or pure repulsive interactions and, indeed, has been found to be in very good agreement with experiments [12]. The theory is, in outline, as follows.

The MCT equations of motions for the normalised density correlators, $\Phi_q(t) = \langle \rho_q^*(t) \rho_q \rangle / \langle |\rho_q|^2 \rangle$, for a colloidal system [13] are

$$\tau_q \phi_q(t) + \phi_q(t) + \int_0^t m_q(t-t') \phi_q(t') dt' = 0, \quad (1)$$

where $\tau_q = vS(q)/(vq)^2$, with $S(q)$ being the static structure factor, v the thermal velocity, and the approximation of the instantaneous friction is the constant v . The kernel m_{t_q} is given as $m_q(t) = \mathcal{F}_q(\{\Phi_k(t)\})$, where the mode-coupling functional \mathcal{F}_q is,

$$\mathcal{F}_q(\{f_k\}) = \frac{1}{2} \int \frac{d^3k}{(2\pi)^3} V_{\vec{q},\vec{k}} f_{\vec{k}} f_{|\vec{q}-\vec{k}|}, \quad (2)$$

$$V_{\vec{q},\vec{k}} \equiv S_q S_k S_{|\vec{q}-\vec{k}|} \frac{n}{q^4} [\vec{q} \cdot \vec{k} c_k + \vec{q} \cdot (\vec{q} - \vec{k}) c_{|\vec{q}-\vec{k}|}]^2, \quad (3)$$

where $c_q = (1 - S_q^{-1})/\rho$ is the Fourier-transformed direct correlation function. In order to locate and characterise the gel phase we define the nonergodicity parameter (or Edwards–Anderson parameter) as the long-time limit of the density–density correlation function, $f_q = \lim_{t \rightarrow \infty} \Phi_q(t)$. It is clear that if the system is ergodic the correlation function will decay to zero after a certain time; in contrast when the system is in a nonergodic regime, the density fluctuations will not be able to relax and, consequently, the function f_q will have a finite value. Indeed, the fact that from dynamic light scattering $\Phi_q(\infty)$ is nonzero, is a frequent observation as the gel transition is crossed. We numerically solved Eq. (1) on a grid of 2000 equally spaced q values extending up to $q\sigma = 72$; f_q is obtained by an iterative solution of the bifurcation equation,

$$\frac{f_q}{1 - f_q} = \mathcal{F}_q(\{f_k\}), \quad (4)$$

that corresponds to the long time limit of Eq. (1). From Eq. (4) is evident that $f_q = 0$ is always a solution but it is not always a stable one: at the transition a new solution $f_q \neq 0$ emerges owing to the formation of a nonergodic phase. The most striking feature of MCT is the fact that it can produce dynamics using as an input only static quantities (i.e. static structure factor and number density). Therefore it is possible, by only providing the structure factor of the system, to locate the ergodic–nonergodic transitions. This brief exploration of the MCT results is not by any means exhaustive and for greater insight we suggest the reader explore the literature [8, 14].

Results

For the interaction of the colloidal particles we have chose a square-well potential,

$$\beta V(r) = \begin{cases} \infty & 0 < r < \sigma \\ \beta u_0 & \sigma < r < \sigma + \Delta \\ 0 & \sigma + \Delta < r \end{cases}, \quad (5)$$

where $\beta = (k_B T)^{-1}$, where k_B is Boltzmann's constant. In order to obtain the structure factors we solved the Percus–Yevick equation for this model; details of this procedure can be found in Ref. [11]. In contrast to the hard-sphere case, where the volume fraction, ϕ , is the only control parameter, the ratio $u_0/k_B T$ between the well depth and the temperature and the well width, $\Delta\phi$, are important control parameters as well. In what follows will make use, in order to characterise the width of the attraction, of the adimensional parameter $\epsilon = \Delta/(\Delta + \sigma)$. We remind the reader that for polymer-induced depletion interactions the well width is controlled by the size of the polymer and the well depth increases with polymer concentration.

The “phase” diagram for the case $\epsilon = 0.03$ in the thermodynamic plane (ϕ , T) is represented in Figs. 1 and 2; the lower density region is reproduced in Fig. 1, whereas the high density regime is shown in Fig. 2. In Fig. 1 we present the sol–gel (fluid–attractive glass) transition line together with the underlying gas–liquid spinodal. It is remarkable to note that the gel transition line in this region lies above the coexistence curve. This type of behaviour may indeed have been observed experimentally for effective potentials with a very narrow range of attractions [1, 5]. We believe that in this region the attractive gel is a space-spanning structure of particles strongly attached to each other; however, we caution the reader that on the left-hand side of the critical point and in its vicinity, we cannot accept blindly the MCT results. Further work is necessary to elucidate this region. Some of these concerns have been addressed in

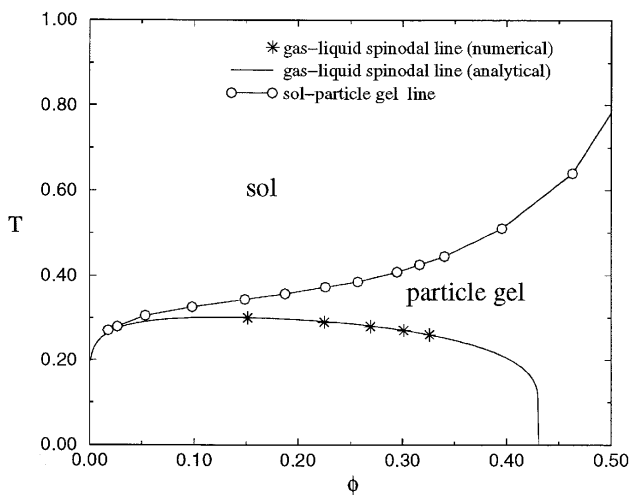


Fig. 1 Sol–gel transition line at low packing fraction for $\epsilon = 3\%$

Ref. [15] while discussing the number of bonds present in these gel states.

In Fig. 2 firstly we note that for $T \rightarrow \infty$ we recover the glass-transition packing fraction, already found in MCT, for hard spheres (i.e. $\phi_g \simeq 0.516$). In this case the kinetic arrest is understandable in terms of a cage effect, i.e. each particle is trapped in a cage formed by its near neighbours and consequently the system is frozen. This is what we call “repulsive” glass, commonly manifested as the typical colloidal glass [12]. By decreasing the temperature, the attractions start to be relevant and the packing fraction at which the system freezes becomes larger than the hard-sphere one. This unusual reentrant behaviour continues up to a certain temperature where the line joins another branch of the transition line. The latter line extends towards lower densities and along it the arrest is due to the attraction, i.e. at low temperatures the transition is driven by the fact that the particles tend to stick together. We have named this second state the “attractive” glass or particle gel. The process of the arrest, glass or gel formation, is then driven by repulsion along the “vertical” line and by attraction on the “horizontal” one. The vertical repulsive line is explained by the fact that glassification is driven by the hard core, which lacks any energy scale, whilst the attractive line, being fairly horizontal, implies that there is a single, fairly well characterized energy scale that drives the gel formation. These simple observations essentially determine much of the shape of the phase diagram as a vertical line at roughly $\phi \simeq 0.52\%$ and a horizontal line at the characteristic energy (temperature) scale of gelation. An interesting feature to emphasise is the presence of a characteristic reentrant behaviour, corresponding to the presence of a liquid phase between the two glassy phases.

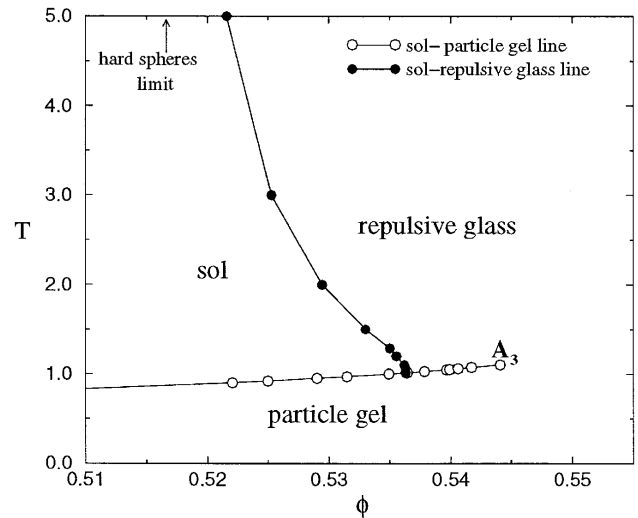


Fig. 2 Same as Fig. 1 for high packing fraction. A_3 is the endpoint of the gel–repulsive glass transition line

This behaviour is encountered in MCT calculations for different kinds of attractive potentials and was shown to be strictly related to the choice of a very narrow well width [9, 16, 11].

Another important feature emerging from Fig. 2 is the presence of a transition line between the two nonergodic states. Crossing it, the system passes from a repulsive glass to a gel abruptly, as the nonergodicity parameter shows a discontinuous behaviour. Thus, this line corresponds to the remarkable phenomenon of a gel–repulsive glass coexistence. It would be interesting to have unambiguous confirmation of this phenomenon, in the light of the current predictions [6].

The “order parameter” of the transition is the nonergodicity parameter. It shows very different behaviour in the two types of arrested states. For a repulsive glass, it remains almost unchanged with temperature, whereas for a gel it varies consistently, and in particular its range increases by decreasing the temperature. The range of f_q is related to the localisation length of the particles [17]. Thus, while for a repulsive glass this length (i.e. the size of the cage) remains almost the same with varying temperature, for the attractive gel the particles become more and more localised, strengthening the attractions between them. The latter phenomenon is the indication that in the gel the particle arrest is due to the formation of bonds between particles at close distance. Indeed, the bond formation has been seen as an important issue for colloidal aggregation and it has been studied within MCT [9, 10, 15]. It is important to note that the glass–glass transition line presents an end

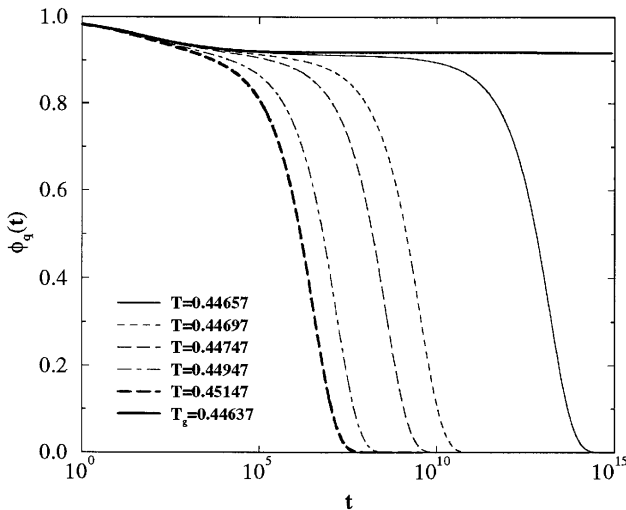


Fig. 3 Correlators $\Phi_q(t)$ for $q=10.0$ at constant packing fraction $\Phi=0.340349$ for various temperatures, close to and at the sol–particle gel transition. A typical two-step relaxation is developed the closer the system is to the transition temperature, T_g , finally approaching a nonzero plateau at T_g itself

point (labeled A_3 in MCT notation) after which the two gels become indistinguishable (i.e. f_q varies continuously).

The behaviour of the phase diagram on varying the range of the attractions has been studied in Ref. [11]. Here, we limit ourselves to report the most important features of that study. Firstly, the typical reentrant behaviour that have discussed for $\epsilon=3\%$ tends to vanish, increasing the attractive range. A second and more important feature is related to the behaviour of the gel–repulsive glass transition line. For values of ϵ roughly between 3 and 4% this line shrinks and eventually, for a certain value (i.e. $\epsilon \simeq 4.11\%$), the end point A_3 touches the sol–gel transition line, giving origin to a very peculiar point, corresponding to a higher-order singularity in MCT and is thus referred as the A_4 point [11].

The importance of finding these singularities A_3 and A_4 lies in the fact that in the proximity of them MCT predicts for the intermediate scattering function, $\Phi_q(t)$, instead of the typical two-step relaxation scenario [8] a very peculiar logarithmic decay.

For $\epsilon \geq 4.11\%$ the A_4 singularity disappears and the transition between the gel and a repulsive glass becomes continuous along the transition curve.

The behaviour of $\Phi_q(t)$ at the constant packing fraction value $\Phi=0.340349$ is shown in Fig. 3. The data correspond to the wave vector $q=10.0$, with the temperature being varied as indicated in the figure. In the phase diagram (Fig. 1), the case represented can be found to be far both from the underlying critical point for the gas–liquid transition and from the singularity A_3 .

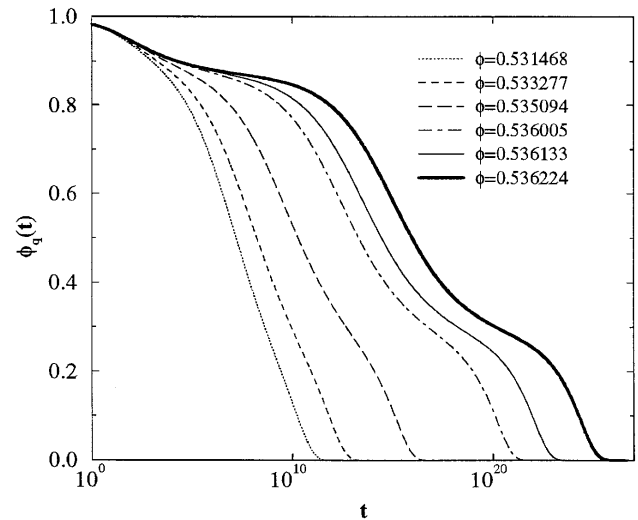


Fig. 4 Correlators $\Phi_q(t)$ for $q=10.0$ at constant temperature $T=1.0132$ for various packing fractions, close to and at the matching point between the sol–particle gel line and the sol–repulsive glass line. A logarithmic decay is observed for various decades in time, and approaching the transition ($\Phi_g=0.536270$), the presence of the two different types of arrested states is also evident

Thus, it represents a typical two-step relaxation function, as predicted from MCT [8], for a sol–particle gel transition which is more evident the closer the system is to the transition temperature $T_g = 0.44637$.

In contrast to the previous case, we show the behaviour of the intermediate scattering function close to the singularity A_3 (Fig. 2). To see the relaxation dynamics, we approach from the fluid side at constant temperature $T = 1.0132$, corresponding to the crossing point of the sol–repulsive glass line with the sol–particle gel one. Here, we vary the packing fraction, as reported in the figure, and we always refer to the wave vector $q = 10.0$. It is possible to observe a logarithmic decay of $\Phi_q(t)$ over a number of decades in time (e.g. at $\Phi = 0.531468$ it holds for about 5 decades). There may be an early indication of such behaviour in recent work [18]. Then, going closer and closer to the transition, the presence of two different types of arrested states starts to become evident, as the correlators seem to develop a double-plateau structure.

Conclusions

We have sought to introduce the reader to the broad developments that are taking place in connecting the traditional science of nonergodic systems, as glasses, to the world of disordered soft matter, and in particular particle gels. It would appear that the methods used in glass theory are also applicable to soft interactions where attractions dominate the loss of ergodicity. If this proposition turns out to be correct, it seems likely that we can interpret particle gels as glasses of a novel type, the so-called attractive glass. The ramifications of this connection are extensive and most have yet to be appreciated. At the most simplistic level, we now have the machinery to calculate the “phase” or state diagrams of the system, their dynamics and transport coefficients and other properties. Also, we can expect to find in experiments all of the traditional phenomena of the two-step relaxation as we approach gelation, as illustrated in Fig. 3 and, possibly, of the peculiar logarithmic decay predicted within our theoretical model (Fig. 4).

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