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The glass paradigm for colloidal glasses, gels, and other arrested states driven by attractive interactions

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Abstract

For some time, there has existed the idea that dense colloidal systems with repulsive interactions can be interpreted using certain approaches to glass theory. Recent advances in understanding the role of short-ranged attractive interactions in driving another type of 'glass-transition' have considerably extended the range of potential applications for such systems. Within this framework, particle gels are now regarded as 'attractive' glasses, and for some concentration regimes the details of the density correlation as we approach gellation for a broad range of experimental systems seem to be well described by glass-transition ideas and laws. Initial suggestions that this might be so came from theory, but the close collaboration between theory, simulation, and experimental science has been mutually stimulating. New advances in the theory are now to be expected, and novel systems where the ideas might be applicable are emerging. The exploration of these ideas is still at the beginning, but there is a reasonable expectation that the glass paradigm will be more generally useful in many areas of soft matter and colloid science, perhaps gathering apparently disparate phenomena of particle gellation, polymer gellation, aggregation, and other aspects of 'solidification' into a common interpretive scheme. © 2002 Elsevier Scienc Ltd. All rights reserved.

Keywords: Glass transitions; Non-ergodic; Colloidal suspensions; Complex fluids; Phase transitions; Crystallisation; Gellation; Proteins

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1. Introduction

Under a wide variety of conditions, colloidal and soft matter systems 'solidify' for reasons that appear to be quite unrelated to each other, and which do not involve the formation of crystalline order. Phrases such as 'freezing', gellation, coagulation, dynamical arrest, ergodic-non-ergodic transition and glassification have all been used to loosely describe these phenomena which are understood to lead to long-lived but non-equilibrium states of the system. We shall typically use the phrases dynamical arrest, or non-ergodic transition to describe these phenomena where they apply to colloidal systems. The resulting amorphous soft materials are of profound practical importance, being relevant in the food, medical and numerous other industries, but the lack of a fundamental coherent picture of these phenomena means that they are often dealt with on an ad hoc basis. On the other hand, the formation of these amorphous soft materials, rather than ordered structures, is sometimes also an undesirable and severe practical limitation. Thus, in widely varied applications such as protein crystallisation, the fabrication of ordered crystalline arrays of colloidal crystal for applications in photonics, and other arenas, it is the difficulty of forming a crystal of high quality that is the crucial limitation, and it would be of considerable interest to understand how this might be achieved. Therefore, sometimes we wish to form the disordered structure, and sometimes the crystal, but have lacked a clear understanding of the control parameters. Here, the role of an encompassing interpretive framework could be of the greatest importance. So far, only the first steps of an integrated picture are emerging, but the perspective is promising [1••]. It is fortunate that in other areas of condensed matter science, glasses, and the transition to them from the liquid (exemplified by common window glass, but manifested in a very wide range of

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different materials) has been studied from a fundamental perspective [2,3,57,4–7]. This has led to promising progress in developing theoretical tools, and perhaps more important, general motifs embedded in a powerful descriptive language on which detailed experimental studies in molecular glasses have been progressed.

It is worth commenting that there are two known regimes of glassy behaviour. The 'ideal' glass transition, described by mode coupling theory [8–10], and other simplified treatments [11–13] involves a time scale for density correlations that grows as a power law in density or temperature as we approach the transition. This behaviour, whilst it is often observed for a limited density or temperature regime for molecular glasses, eventually crosses over so that the time scale has an exponential dependence on (temperature or density) distance from the transition. So far, most of what has been observed in colloidal glasses appears to be purely ideal, an issue that is discussed in ref. [13]. One final point, by way of introduction: much of what we will say concerns new insights indicating that glass-like arrested states can arise due to attractive forces that have a short range compared to the size of the repulsive core. That there are new phenomena to be found here is a reflection that this limit is not too significant in molecular liquids, and has therefore been little explored. It is really in more complex colloidal systems, where the particles are themselves large, and the interactions remain of microscopic scale that this limit becomes dominant. This observation is at the heart of the emerging alliance between glass theory, and the broader range of colloidal and soft matter science.

2. Colloidal systems with repulsive interactions and the glass transition

It is natural to ask if these fundamental ideas on more familiar glasses, themselves developing in a very rapid and exciting manner, are relevant to soft amorphous systems. This potential has, explicitly or implicitly been addressed by many previous authors, some in the pages of this journal [14••,15••]. However, so far, the most explicit connections have undoubtedly been made in dense dispersions that have the properties of hard sphere fluids [12,13,16••,17•,18•, 19•,20••,58•]. The phenomena there are well known. At volume fractions of less than 49% we find only the fluid. Between 49 and 55% the equilibrium state is two-phase co-existence of a fluid and an FCC crystal. However, in preparing these dispersions it is observed that the system is dynamically much slowed near volume fractions of 58%, and beyond these concentrations it spends extended periods (dependent on the particle size and other system details) 'arrested' in an amorphous state, rather than relaxing into a crystal. Detailed study indicates that the system exhibits many of the properties of an 'ideal' glass transition as one approaches this volume fraction [20••]. In fact, dynamical light scattering data, plotted against the logarithm of time, exhibits the well-known plateau on approach to the transition [14••] and the data have been shown to be quite well described by MCT [20••]. There is, therefore, precedent for conceiving of the arrest of the simplest dense colloidal systems, as 'glass' transitions of some sort.

Recently, the idea of applying glass concepts and theories to soft matter and colloidal systems appears to be attracting a great deal of renewed attention. Much of this interest seems to stem from the recent studies of a very simple system, the hard sphere, to which there is added a short-ranged attraction, and the interpretation of the phenomena observed there in terms of non-ergodic ideas derived from glass theory [21••]. We will describe the findings emerging there shortly, but let us first note that although a rather narrow range of problems have been addressed so far, there is some justification for the emerging interest in this field. The first point is that, in this problem of short-ranged attraction, a new paradigm has emerged. Thus, whilst repulsive hard sphere particles stop moving at 58% volume fractions (to form a 'repulsive glass') simply because they run out of space, attractive particles can also lose ergodicity because they 'stick'. This is important because the range of applicability of the idea of applying the glass paradigm now becomes much greater, for many of the interesting and important problems of soft matter and colloidal science where there is loss of ergodicity involve a very significant aspect of attraction. Indeed, an early experimental report on colloidal particles with depletion-induced attractions [22••] commented that it might be possible to treat the particle gellation phenomenon in terms of glass theory, initiating the modern interest in this approach. The first calculations were made mainly on the Baxter model [23••,24••], but it was realised that this was not a well-behaved numerical limit for the non-ergodic transition [25•]. Subsequent calculations have focused on the square-well [21••], or hard-core Yukawa potential [26••], leading to an understanding of how the arrest evolves with the range of the potential. We will now turn to the details of the findings of the theoretical calculations that have emerged in last few years.

3. New glass phenomena driven by short-ranged attractions; theoretical perspective

The original study of the square well and hard core

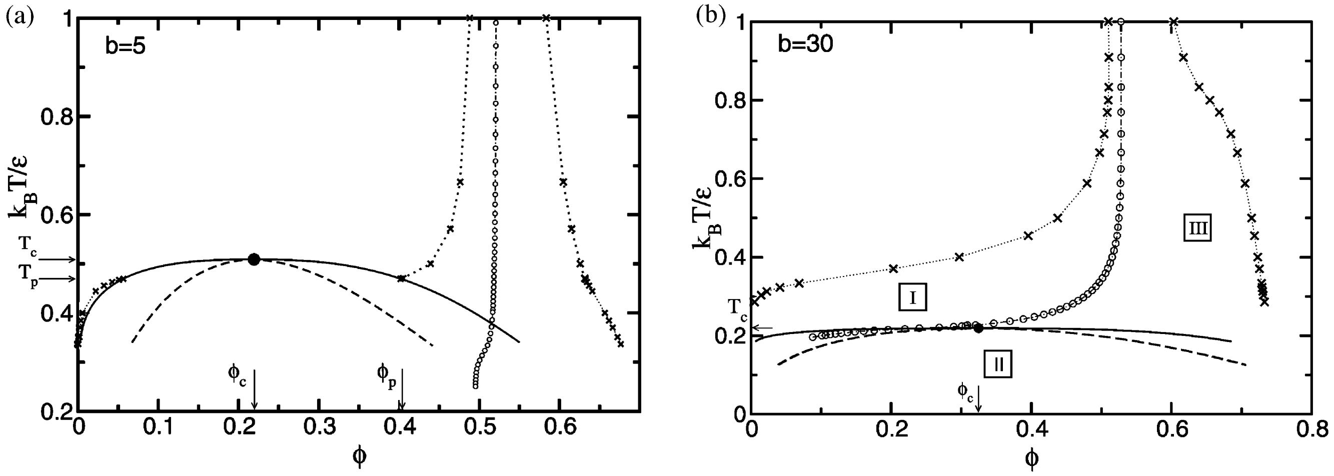

Fig. 1. See reference [1] for a numerically accurate version of this phase-diagram, and futher discussion. (a) The phase (and arrested state) diagram for a hard-core Yukawa potential with screening parameter $b = 5$ in units of the radius of the core. The equilibrium phases, crystal (FCC), liquid, and gas are in their conventional arrangements on the phase diagram for a simple substance. For colloidal systems the liquid and gas are equivalent to (respectively) more- and less- dense colloidal dispersions. The broken curve is the dynamical arrest curve (from MCT), To the left (or above) the arrest curve the equilibrium phases form normally. Attempts to form phases beneath the arrest curve (or to its right) experience competition from one or more dynamically arrested state. The value of b illustrated here may be considered to be a fairly wide well-width, leading to a phase (and state) diagram that is closer to, though still somewhat shifted from, the typical van der Waals scenario. (b) As for (a), the phase (and state) diagram but for $b = 30$. The liquid-gas bimodal is the solid curve, and the broken curve underneath is the spinodal. The common point (black circle) is the critical point of the liquid gas coexistence, which is itself metastable) Here the liquid phase is entirely submerged by the fluid-crystal curve (x), as well as the dynamical arrest curve (circles), due to the narrow well-width. Indeed, the glass is dominated by attractions for low volume fractions, and this is now viewed as equivalent to the particle gel. The solid-liquid coexistence region now becomes quite strongly distorted as attractive interactions play a stronger role. The three regions where potentially different crystallisation kinetics are expected are marked (I)–(III). At low volume fractions part of the fluid-crystal coexistence region lies outside the dynamical arrest curve(region I), and nucleation of crystals in this region may lead to better crystals, as discussed in Section 6 of this article in relation to the question of protein crystallisation. Region I may be related to the so-called 'crystallisation slot' discussed in reference I, and references to the protein crystallisation literature referred to therein.

Yukawa potential [21••] has subsequently been extended, and more complete phase- and state-diagrams worked out for closely related potentials [1••,27,28••], as well as mechanical [29•] and viscoelastic properties near the arrest [30,31]. One important observation is that the essential elements of the story are the same for a wide variety of potential shapes, in the limit of a short range [32]. Results for the regime where the attraction is short ranged may be summarised as follows. We observe that for such systems there are two important length-scales, the range of the hard core, and the range of the attractive well. For the square well these are well defined, otherwise one must take steps to establish a reasonable definition. It transpires that the ratio of the attractive to the repulsive range is the important parameter. When this ratio is large, we expect typical behaviour of a van-der Waals fluid with the solid, liquid and gas of a simple substance (solid, more-and less-concentrated phases in colloidal dispersions). However, when the range of the attraction narrows, the dynamical arrest that was found at 58% volume fraction becomes temperature dependent, and moves to lower density. In fact, it transpires that a separate and distinct glass, driven by the strong short ranged attractions emerges [1••,21••], and under certain circumstances this state exhibits non-equilibrium co-existence with the repulsive glass alluded to above. We return to the details of this co-existence later, and focus now on the nature of the attractive glass, which we identify as the gel state (Fig. 1a,b).

The idea of an attractive glass is simple enough, and it is natural that it should compete with the liquid when the range of the attraction decreases. However, in reading what follows, it should be borne in mind that the energy-entropy competition we refer to is local, rather than true thermodynamic equilibrium. There is no sense in which these gels (glasses) are thermodynamically stable. Entropy due to very local motions within the cage formed by neighbouring particles is present in both a liquid and a solid at comparable density. The distinguishing feature is that longer-ranged diffusive motions in the liquid confer additional (configurational) entropy, and this is lost when a colloidal glass is formed, thereby rendering the glass a non-equilibrium, though stable trapped state. The breathing movements of the cage, coupled to the longer ranged rearrangements are central to diffusion. Particles in the short-ranged attractive fluid benefit from the attractive interaction only whilst they remain within each other's attractive well. Evidently, when the range of that attraction is sufficiently small, those cage rearrangements required for liberating a caged particle result in particles moving outside each others attractive range, and the loss of that attractive energy, this loss being more than the gain from configurational energy gained from longer ranged motions. The system solidifies into an 'attractive' glass. This argument may be viewed as a sort of generalisation of the Lindemann criterion in more conventional systems. It is unsurprising, therefore, that the primary control parameter determining glassification in attractive systems should be the range of the attraction. However, the simplicity of the argument, and its generality, suggests that this should be a general phenomenon. Thus, we may expect the energy of short-ranged attractions to compete directly with the configurational part of the entropy, leading often to solidification, 'gellation', coagulation and the other typical processes observed in soft matter systems.

4. Origins of re-entrance and novel dynamical behaviour near glass coexistence

From the general point of view of the glass paradigm, outlined in the introduction to this article, there is a group of phenomena that lead to clear, but unusual, predictions and are therefore highly suitable for an interesting dialogue between theory and experiment, and potentially validation of key elements of the overall picture. Here we outline the phenomena, and later, in Section 5 give a description of the current experimental situation.

Apparently independent of the detailed nature of the shape of the interaction potential, there is a regime of attractive potential well widths where the attractive and repulsive glasses co-exist. Also, the coexistence curve terminates within the glass regime in a 'higher order' dynamical behaviour (A3) at which the attractive and repulsive glass become equivalent [21••]. This phenomenon is reminiscent of the critical point, relevant for equilibrium phases, where two phases merge to become one with an accompanying singular behaviour of the thermodynamic derivatives. Here instead the two phases are dynamically arrested, and merge in a novel (logarithmic) dynamic singularity that should be observable in dynamical scattering experiments on approach from the fluid. One may continue this idea of looking at special points by identifying that particular well-width for a particular potential at which the coexistence curve of attractive and repulsive glasses shrinks to zero length, merging with the fluid-glass curve itself and resulting in a single fluid-glass curve. In both cases, there results a logarithmic singularity in time where dynamical correlations are extremely long-lived, and without a natural definition of elementary time-scale accompanying the process.

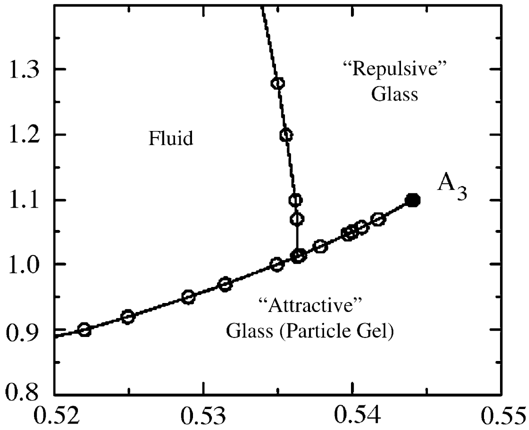

Fig. 2. The typical arrangement of liquid and dynamically arrested (glassy) states for narrow well-widths. This particular diagram is appropriate for the square well (the ratio of attractive well to core diameter is 0.03), but it is now known that the overall picture is unchanged for a number of quite different well-shapes (square well, Yukawa and others). Note that considerably larger screening parameters would be required to see this phenomenon than b = 30 exhibited in Fig. 1. Prominent features to note are as follows. Firstly the presence, and co-existence, for a range of temperatures and densities of two different arrested states ('glasses'), one dominated by repulsions, and the other by the attractive glasses. These, within the theory, are differentiated only by the long term limit of the density correlation function (so called Edwards-Anderson order parameter) which parameterises the degree of freedom of movement in the glass, after long time periods. The long-time average structure is however identical since the structure factor is identical in the two phases for any point on the glass-glass coexistence curve. These two states were subsequently named respectively the repulsive and attractive glass. The glass–glass 'coexistence' curve terminates in the A3 singularity at which the glasses become identical. Note that for a range of densities one can begin in a glass (attractive) at low temperature, pass to a liquid, and then re-enter another glass state (repulsive)at higher temperature. This re-entrance behaviour may also be viewed as an anomalous destabilisation of the glasses at high density, the liquid occupying a small strip of parameter space that would normally have been viewed as solid. This is attributed to the cancellation of the leading effects of attractions and repulsion's in this restricted regime. Approach to the vicinity of the A3 singularity within this re-entrant regime leads to a logarithmic decay of the density correlations, a unique and distinctive signature of existence, and proximity to that singularity (see text).

It is important to note that all these phenomena, re-entrance of the liquid near glass-glass coexistence and logarithmic relaxation of dynamics in the fluid, on approach to the A3 singularity, are a result of the same underlying mechanism of competition between attractions and repulsions in the regime where they nearly balance each other. We should expect to see all these phenomena occurring together in experiment (Fig. 2) (see ref. [29•]).

Finally, whilst these predictions began with theoretical calculations [21••], molecular dynamics has now begun to confirm theory in detail. That particle gellation is related to the dynamical arrest and new evidence for logarithmic decay of correlation in the vicinity where gellation and hard sphere arrest compete has recently been reported [28••]. Hard sphere molecular dynamics calculations have been carried out to make direct comparisons between theory and simulation and the re-entrance phenomenon observed [33•]. In the most recent calculations, a high degree of agreement between most details of the theory and simulation has been reported, again for the square well [34••].

The basic conceptual framework therefore now seems to be taking shape, and the agreement between different models, theoretical techniques and simulations for the spherical potentials is reassuring.

5. Reservations and open questions in relation to conceptual framework

It should not be thought that the broader conceptual framework outlined here is without problems, and can be accepted without reservation. There are problems, but it is as yet too early for these to be well reflected in the literature. For example, the idea of a glass, driven by attractive interactions should encompass particle gels formed at low and intermediate volume fractions. On the other hand, such gels are apparently often quite weak, decomposing quite rapidly, an aspect not described by current glass theory. Also, the presence of attractive interactions means that for intermediate densities spinodal decomposition and phase-separation kinetics intermingle with arrest. These issues are not well described by mode coupling theory, although devices for slowing the phase separation in order to study the low-density glass have been presented [28••]. On the other hand, we consider this limitation of the theory to be a somewhat understood and temporary limitation, and as one learns how to express ideas of glass ageing in such colloidal systems, these issues will be resolved [35,36].

At present there are deeper questions that are still open. For example, we have noted that hard core colloidal systems seem to be well described by MCT, and other model systems [12]. However, we know that the this same theory gives an incomplete description of most true glasses, where characteristic time-scales grow exponentially on approach to the arrest, rather than the typical power law dependence of ideal glass transitions described by mode coupling theory. We may wonder whether MCT is also quantitatively satisfactory for more complex soft matter systems, or whether these also have non-ideal behaviour. Reflections on these open questions are just beginning to emerge [13].

6. Short-ranged attractions and the consequences for model experimental systems

In a certain sense in Section 3 and Section 4 we have merely given a theoretical rationale for systems that have been well-known to gel, glassify, or otherwise solidify into an amorphous state for many years, and our comments on the experimental literature must be seen in that light. However, the new experimental interest is partly driven by the fact that the new conceptual framework that has arisen makes many detailed and quite subtle predictions for these phenomena that had not been appreciated before, and renders more detailed study of interest.

We have already alluded to earlier studies of spherical silicium oxide coated with stearyl alcohol, dispersed in benzene [22••]. Here a broad understanding of the particle gel state has been displayed, in particular the relationship of the dynamical arrest to the more dense-less dense colloidal phase-separation was discussed. However, even earlier [37•], there were puzzling indications that a dispersion of microgel particles, then considered to be in the good solvent regime, might possess non-standard dynamical behaviour. In a rather elegant conclusion to this story, these authors have pointed out that the original system involved also some unseparated dissolved free polymer leading to effective depletion forces and short ranged attraction, thereby enabling the earlier experiments to be explained. Further studies [38••] have indicated that indeed the addition of free polystyrene to cross-linked polystyrene microparticles leads to reentrance, and (their figure 4), a reasonably large window (roughly two orders of magnitude) where the characteristic logarithmic decay of correlations pertains.

Another interesting and related type of system involves (for example PMMA) colloidal particles in the presence of free polymer. A long record of study of this type of system has been developed [39–41•,42], and it is upon this that many ideas on the role of short ranged attractions in colloidal systems have been built. With the emergence of the glass paradigm this strand of activity has culminated in a synthesis of experiment, simulation and theory that, combined, provides compelling evidence for the re-entrant scenario, associated with logarithmic correlations [43••].

In an interesting series of reports on Pluronic L64 copolymer micelles in solution, extensive evidence is displayed for the effects of an attractive potential between the micelles, including the presence of a lower consulate point, and percolation transition.

These experiments have the potential disadvantage that the L64 system is more complex than some of the microgel or colloidal particle studies, but they provide access to an interesting particle size range, and are intriguing in that they provide evidence that the paradigm will be applicable to a broader range of systems. For this system, studies using dynamical light scattering yield a reasonably large time-window where anomalous dynamical relaxation is observed [44••]. A well-defined logarithmic decay was detected over two decades in time, along with a power-law decay of the von Schweidler type, both signatures of the A3 type singularity described earlier. In the most recent article [45••], the same system has been studied using neutron scattering and the first attempts have been made to carry out a quantitative connection of phase diagram, dynamical arrest curves (figure 14 of [45••]) and scattering data to the theory, based on the square well. The authors also give very preliminary evidence of the appearance of a glass–glass transition.

There are, therefore, three systems in the experimental literature where claims have been made that the re-entrant phase diagram, logarithmic density correlations, and other expected attendant features of the glass paradigm, have been observed. The first steps in establishing the paradigm experimentally have been taken.

7. The glass paradigm applied to more complex colloidal and soft-matter systems

It should not be thought that the simple particulate dispersions or micellar systems discussed above are the only potential candidates to see this type of behaviour. Indeed, systems such as polystyrene–polyisoprene or styrene–isoprene copolymer micelles in the presence of free homopolymer melts offer potentially useful alternative systems for this type of study [46–49]. Apart from the new range of rheological and other techniques that can be applied to such systems they are of interest in extending the paradigm into more complex systems. Other very recent observations on star polymers have indicated that some aspects of the paradigm may extend even to softer and longer ranged potentials [50]. Thus, addition of free polymer is seen to drive what is apparently a star-polymer repulsive glass back into the fluid as the repulsions are weakened by depletion interactions. It is too early to tell if this is indeed the correct interpretation of these interesting results, and if there is some accompanying higher order dynamical singularity associated with this system.

There has also been, for some time, a stream of thought that globular proteins possess a short-ranged potential in comparison to their size [1••,41•, 51••,59••]. This raises the rather interesting and important question of whether simple models from colloidal science such as those discussed above can be helpful in understanding just why such proteins take so long to crystallise, and having done so, often possess a low degree of crystallinity. This approach seems to be somewhat promising, though far from complete. Very full studies, predating much of what is discussed here, have lead to a clear picture of the equilibrium phase diagram for short-ranged potentials, including the first report that there appear to be two crystalline states present, one stabilised by repulsions and the other by attractions, and a transition between them [52•,53••,60•]. Building on this work, and the glass paradigm, an overall picture has been built of the origin of the 'gel' curve in protein crystallisation, and its possible role in producing crystals of low quality [1••,54•,55,56•]. It seems, at the present time, that the interplay between theory, simulation, and experiments on model colloidal systems may lead to a deeper understanding of the challenges currently experienced in producing good quality crystals.

8. Conclusions

The era of application of equilibrium statistical mechanics to colloidal and soft matter systems has been highly successful. Hints from many scientists have now combined to indicate that non-equilibrium, non-ergodic systems may now be treated within another framework of dynamical arrest or glass transitions, albeit themselves under development. In fact, as the picture evolves, colloidal science may well play a leading role in that development.

Admittedly, our ideas are as yet based on relatively few examples of systems that have been studied theoretically, with simulation, and with simple model colloidal systems. However, based on these and relying on our growing knowledge of more simple molecular glasses, certain expectations of considerable generality have begun to emerge. Thus, there is reason to suppose that many of the complex systems familiar to colloidal and soft matter science that are 'arrested' may ultimately be interpretable within this paradigm. The development of a community extending across the relevant disciplines and experience is in itself, a promising event, and bodes well for future explorations. It is pleasing to note that colloidal and soft matter science may play a leading role in the development of our fundamental understanding of one of the most challenging arenas of condensed matter science.

Acknowledgements

I acknowledge with pleasure the close and most stimulating interactions with Professors F. Sciortino, P. Tartaglia and colleagues from the INFM Centre for Excellence in Complexity and Glasses in University of Rome, La Sapienza who introduced me to these problems. I also acknowledge with pleasure associations with our post-graduate students G. Foffi, P. De Gregorio, A. Lawlor, G. McCullagh, E. Zaccarelli with whom, and from whom, I have learned and am learning about the glass transition. Also, I acknowledge with pleasure the many colleagues in this field who have explained their work to me, and sent me preprints, and provided the collegial atmosphere and inspiration for this work. Manuscript preparation was assisted by C. Brown, A. Farrell, and A. Lawlor whom I thank.

References and recommended reading

● of special interest
●● of outstanding interest

[1] ●● Foffi G, McCullagh G, Lawlor A et al. Phase equilibria and glass transition in colloidal systems with short-ranged attractive interactions: Application to protein crystallisation. Phys Rev E 2002;65:031407–031417.

A complete study of the hard core Yukawa, and limited comparison of the square well potential, both for short-ranged limit of the potential. Here quantitatively accurate theories of liquid state are used, the crystal free energy accurately calculated, and the dynamical arrest computed according to MCT, using accurate input structure factors. This paper sums up the overall picture gained from previous works [21●●,41●,51●●,52●,53●●,54●,59●●,60●].

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[5] Kivelson D, Tarjus G. The Kauzmann paradox interpreted via the theory of frustration-limited domains. J Chem Phys 1998; 109:5481–5486.

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Collectively references [2–7,57] give an impression of how the broader field of glass theory is developing. They include different techniques, and different perspectives, and the reader should conclude that the nature of the true glass transition is currently of great interest, but far from settled.

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[9] Gotze W. The mode-coupling theory of liquid-to-glass transitions. J Phys Condens Matter 1990;2:SA201–SA205. Suppl. A

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References [8,9] detail the foundations of the mode coupling theory of dynamical arrest. This theory describes only the 'ideal' glass transition where, for example, diffusion constants are typically power laws in distance (temperature or density) from the arrest. This theory does not describe real molecular glasses fully, since very close to the transition the dynamical law crosses over to an exponential. However for colloidal systems it has been highly successful, and there is no evidence as yet of any colloidal system that does not arrest according to 'ideal' dynamics. Therefore, colloidal systems seem to be well described by MCT. An alternative derivation of MCT is given in [10].

[11] Biroli G, Mezard M. Lattice glass models. Phys Rev Lett 2002;88:025501–025504.

[12] Lawlor A, McCullagh GD, DeGregorio P, Tartaglia P, Dawson KA. Insights from a lattice glass model. 2002.

[13] Lawlor A, McCullagh GD, DeGregorio P, Tartaglia P, Dawson KA. The nature of the lattice glass transition for short-ranged attractions, 2002.

Reference [11] contains a novel way of representing, in a highly simplified manner, essential features of the hard sphere fluid as a lattice model. A dynamical arrest transition is found, by simulation, to be precisely of ideal type possibly providing the beginnings of insights into why the present colloidal systems obey MCT. References [12,13] are studies of this model that shows how the lattice model can describe all of the observable generic phenomena currently observed at ideal dynamical arrest. These papers also attempt to provide a view of 'holes' or 'available volume' as the key to understanding the ideal glass transition, and propose a method of extending this view to short-ranged attractive systems.

[14] ●● Hartl W. Colloidal glasses. Curr Opin Colloid Interface Sci 2001;6:479–483.

Reference [14●●] is a useful preliminary for reading this article. References are also made to the author's previous work representing some of the first attempts to give detailed interpretation of collodial experimental data using MCT. The idea (propounded by these authors in that article) of studying a wider range of potentials to see how their dynamics arrests is an arena that could now usefully be revisited.

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The second of these two articles seems to be the first attempt to use three-dimensional imaging data of colloidal particles to study a collodial system.

[18] ● Weeks ER, Crocker JC, Levitt AC, Schofield A, Weitz DA. Three-dimensional direct imaging of structural relaxation near the colloidal glass transition. Science 2000;287:627–631.
Cipelletti L, Segre PN, Prasad V, Schofield AB, Weitz DA. Phys Rev Lett 2001;86:6042. Trappe A, Prasad V, Cipelletti L, Segte PN, Weitz DA. Jamming phase-diagram for attractive particles. Nature 2001;411:772. Lin AJ, Nagel SR. Nonlinear dynamics: Jamming is just not cool anymore. Nature 1998;396:21.

The first of these articles is an elegant exploration of 3-D configurations what had been considered to be pure hard-core repulsive colloidal particles. Subsequent studies may be leading to the conclusion that the potential is slightly more complex. The other articles are relevant to attractive 'glassy' discussions, the topic of this article. The authors interpret the observations on the mechanical properties of particle 'gels' in terms of a model of 'jamming'. A schematic is sketched of the jamming phase diagram, and the gel state identified within it. These articles are well worth consulting since they represent an alternative view of how these arrested states might be described, besides the glass paradigm. The theory of the 'glass transition', though yet in its infancy is relatively well-developed, as outlined in references [2–9,57], and it possible to begin the process of fitting theory to experiment. There is as yet no quantitative theory for jamming, and it is possible that the two views will merge in the future. Such a prospect is outlined in references [12] and [13].

[19] • Torquato S. Glass transition-Hard knock for thermodynamics. Nature 2000;405:6786.

A thoughtful article, worth reflecting on in development of a general view of the true glass transition, in contrast to dynamical arrest.

[20] •• Van Megen W, Underwood SM. Glass Transition in colloidal hard-spheres-measurement and mode-coupling theory analysis of the coherent intermediate scattering function. Phys Rev E. 1994;49:4206–4220.

One of the papers on which the modern idea of colloidal freezing as some sort of ideal glass transition is founded.

[21] •• Dawson KA, Foffi G, Fuchs M et al. Higher-order glass-transition singularities in colloidal systems with attractive interactions. Phys Rev E 2000;63:011401–011417. This paper represents the most complete mathematical understanding of the phenomenon.

The first paper in which the A3 and A4 scenario is correctly deduced from calculations on the square well and Yukawa potentials. The essential features of attractive glass and repulsive glass are noted. The explicit nature of the logarithmic singularities of A3 and A4 type, are identified in the vicinity of the re-entrant portion of the dynamical arrest diagram are studied.

[21a] •• Recently this singularity has been clarified in detail in the Ref. below: Goetze WE, Sperl M. Logarithmic relaxation in glass-forming systems. Phys Rev E 2002;66:0114xx.

This article represents the most complete analytical analysis of A3 and A4 behaviour.

[22] •• Verduin H, Dhont JKG. Phase diagram of a model adhesive hard-sphere dispersion. J Coll Int Sci 1995;172:425.

It would appear that this is the first paper where the idea of using glass theory to describe dynamical arrest leading to particle-gels is made. (However, see interesting comments made in introduction to Ref. [39].) The phase diagram, also amongst the first due to short-ranged potential has the, now typical, behaviour of submerged critical point and particle gel curve.

[23] •• Fabbian L, Götze W, Sciortino F, Tartaglia P, Thiery F. Ideal glass-glass transitions and logarithmic decay of correlations in a simple system. Phys Rev E 1999;59:R1347–R1350.

Interesting for historical reasons this paper on the Baxter model is the work where indications of the whole A3/A4 scenario, later to explored in detail, first began to emerge. In fact it transpired that this scenario was spurious for the Baxter model studied in this paper. The observed behaviour arising from a limited numerical cut-off. When the cut-off is dealt with correctly, the A3–A4 scenario vanishes (see reference [25•]). The Baxter model should not in future be used in interpreting dynamical arrest transitions in this way, and the correct picture is given in reference [21••].

[24] •• Bergenholtz J, Fuchs M. Non-ergodicity transitions in colloidal suspensions with attractive interactions. Phys Rev E 1999;59:5706–5715.

This paper gives results for the Baxter model and Yukawa models. As in Ref. [23] above the Baxter model results presented depend on a wavevector cut-off, but the Yukawa calculations are still valid. At this time the A3 and A4 scenario in the Yukawa system was not a focus of the paper. It was not until somewhat later that the existence of this scenario for the Yukawa potential was confirmed (private communication from J. Bergenholtz to present author). Nevertheless, Ref. [24] does contain a discussion of the attractive glass and its connection to gelation. Of localization lengths, and shear moduli, and makes the first attempt to fit light scattering results to experimental data due to Verduin and Dhont.

[25] • Foffi G, Zaccarelli E, Sciortino F, Tartaglia P, Dawson KA. Kinetic arrest originating in competition between attractive interaction and packing force. J Stat Phys 2000;100(1-2):363–376.

Interesting historically, in this paper it is realised that the Baxter model is unsuitable for MCT calculations, and that previous results on it (reported in reference [23•] and [24•]) are a result purely of the numerical cut-off. The outcome of this realisation was reference [21••].

[26] •• Bergenholtz J, Fuchs M. Gel transitions in colloidal suspensions. J Phys Condens Matter 1999;11:10171–10182.

A very nicely written article about the relationship of the attractive glass and gel.

[27] Bergenholtz J, Fuchs M, Voigtmann TH. Colloidal gelation and non-ergodicity transitions. J Phys Condens Matter 2000;12:6575–6583.

[28] •• Puertas AM, Fuchs M, Cates ME. Comparative simulation study of colloidal gels and glasses. Phys Rev Lett 2002;88:098301.

The first confirmation by molecular dynamics calculations of the overall picture offered in, for example, reference [21••]. Certain assumptions have been made to make the simulations straightforward, notably the choice of non-standard potential. However, in all likelihood the conclusions are unaffected by this choice, and the MCT view of attractive-driven dynamical arrest is confirmed. Also, evidence, is given of the existence of the logarithmic singularity. These results are an important departure because they imply that the conclusions are not a consequence of applying an approximation such as MCT.

[29] • Zaccarelli E, Foffi G, Dawson KA, Sciortino F, Tartaglia P. Mechanical properties of a model of attractive colloidal solutions. Phys Rev E 2001;63:031501–031511.

A useful indication of how the two arrested (glassy) phases may be distinguished using mechanical methods.

[30] Dawson KA, Foffi G, Sciortino F, Tartaglia P, Zaccarelli E. Mode-coupling theory of colloids with short-range attractions. J Phys Condens Matter 2001;13(41):9113–9126.

[31] Zaccarelli E, Foffi G, De Gregorio P, Sciortino F, Tartaglia P, Dawson KA. Dynamics of supercooled liquids: density fluctuations and mode coupling theory. J Phys Condens Matter 2002;14(9):2413–2437.

[32] Dawson K, Foffi G, McCullagh GD, Tartaglia P, Zaccarelli E. Ideal glass in attractive systems with different potentials'. J Phys Condens Matter 2002;14(9):2223–2235.

[33] • Foffi G, Dawson KA, Buldyrev SV, Sciortino F, Zaccarelli E, Tartaglia P. Evidence for Unusual Dynamical Arrest Scenario in Short Ranged Colloidal Systems. in press Phys Rev E, 2002, (cond-mat/0201372).

First clear evidence from molecular dynamics simulation of the re-entrant nature of the phase diagram near the A3 and A4 singularity. These calculations are interesting also because a square well potential, has been studied, allowing direct comparison to the theory, rather than schematic comparisons.

[34] •• Foffi G, Dawson KA, Buldyrev SV, Sciortino F, Zaccarelli E, Tartaglia P. Molecular dynamics simulations of square well potential: comparison between theory and simulation of dynamical arrest scenario in short-ranged colloidal systems, 2002 (cond-mat/0206408).

A thorough study of the dynamical arrest transitions of the square well potential, with extensive calculations of the whole A3, A4 regime. The decay of the density correlations has been studied in detail, and a long dynamical window over which logarithmic correlations can be seen is presented. The implication is that the logarithmic singularity, discussed in [21••] is well validated beyond MCT. Detailed comparisons of other aspects of the dynamics are made, and compared to the theory of the square well.

[35] De Gregorio P, Sciortino F, Tartaglia P, Zaccarelli E, Dawson KA. Slowed Relaxational Dynamics Beyond the Fluctuation-Dissipation Theorem. Physica A 2002;307:15.

[36] Latz A. Universal properties of ageing in structural glasses. cond-mat/0106086.

[37] • Bartsch E, Antonietti M, Schupp W, Sillescu H. Dynamic light scattering study of concentrated microgel solutions as mesoscopic model of the glass transition in quasiatomic fluids. J Chem Phys 1992;97:3950.

Apparently the first experimental work in which anomalous dynamical (i.e. logarithimic decay) correlations are noted. At the time, it was not realised that attractive forces were present (due to dissolved free-polymer impurity), but the authors point out that this system appears to be exhibiting non-hard sphere arrest.

[38] •• Bartsch E, Eckert T, Pies C, Sillescu H. The effect of free polymer on the glass transition dynamics of microgel colloids. J Non-Cryst Solids 2002; in press.

One of the three modern claims in the experimental literature to have confirmed the logarithmic decay of correlations, and validation of the picture offered by theory. (others are in references [43,45]).

[39] Pusey PN, Pirie AD, Poon WCK. Dynamics of colloid polymer mixtures. Physica A 1993;201(1–3):322–332.

The introduction to this paper notes that there are suggestive parallels to the glass transition, a prescient comment.

[40] • Poon WCK, Pirie AD, Pusey PN. Gelation in colloid-polymer mixtures. Faraday Discussions 1995;101:65–76.

[41] • Poon WCK. Crystallisation of globular proteins. Phys Rev E 1997;55:3762–3764.

A foundation paper from which grew the idea that short-ranged ranged attractive interactions in colloidal system might model the essential features of globular protein solutions.

[42] Anderson VJ, de Hoog EHA, Lekkerkerker HNW. Mechanisms of phase separation and aggregation in colloid-polymer mixtures. Phys Rev E 2002;65:011403–011408.

[43] •• Pham KN, Puertas AM, Bergenholtz J et al. Multiple glassy states in a simple model system. Science 2002;296:104–106.

An elegant combination of theory, simulation, and experiment in the short ranged depletion interaction colloidal particle system. The paper is compelling partly because it synthesises information from the different approaches. One of the three experimental claims to observe the logarithmic decay of correlations. (others are in reference [38••,45••]).

[44] •• Mallamace F, Gambadauro P, Micali N, Tartaglia P, Liao C, Chen S-H.

Kinetic glass transition in a micellar system with short-range attractive interaction. Phys Rev Lett 2000;84:5431–5434.

[45] •• Chen WR, Chen SH, Mallamace F. Small-angle neutron scattering study of the temperature dependent attractive interaction in dense L64 co-polymer micellar solution and its relation to kinetic glass transition. Phys Rev E (in press).

This system is complex, and more difficult to interpret, this is the first attempt to fit the whole phase-diagram and dynamical-arrest diagram of a single system to the theory of the square well potential. Detailed neutron scattering results are also presented. The first claim of evidence of a glass-glass transition exhibited by an attractive system. This is one of three experimental claims (along with reference [44••]) to observe the logarithmic singularity. (others are in reference [38••,43••]).

[46] Gohr K, Pakula T, Tsutsumi K, Schärtl W. Dynamics of copolymer micelles in an entangled homopolymer matrix. Macromolecules 1999;32:7156–7165.

[47] Gohr K, Schärtl W. Dynamics of copolymer micelles in a homopolymer melt—Influence of the matrix molecular weight. Macromolecules 2000;33:2129–2135.

[48] Lindenblatt G, Schärtl W, Pakula T, Schmidt M. Synthesis of polystyrene grafted polyorganosiloxane-microgels and their compatibility with linear polystyrene chains. Macromolecules 2000;33:9340–9347.

[49] Lindenblatt G, Schärtl W, Pakula T, Schmidt M. Structure and dynamics of hairy spherical colloids in a matrix of nonentangled linear chains. Macromolecules 2001;34:1736.

[50] Stiakakis E, Vlassopoulos D, Likos CN, Roovers J, Meier G. Polymer-mediated melting in ultrasoft colloidal gels, unpublished.

References [46–50] give indications that dynamical arrest (or 'glassy') phenomena may be expressed in other, quite different, systems. They mainly point to the rich types of soft matter systems that can be studied in the present context.

[51] •• Piazza R. Interactions and phase transitions in protein solutions. Curr Opin Colloid Interface Sci 2000;5:38–43.

The first of these is one of the clearest summations of how short-ranged attractive potentials might be relevant to solutions of globular proteins, written by one of the leading proponents of that idea.

[52] • Hagen MHJ, Frenkel D. Determination of the phase diagrams for the hard-core attractive Yukawa system. J Chem Phys 1994;101:4093–4097.

Important reference for the phase diagrams of short ranged potentials, and basis of much of later work on the connection between the equilibrium and glassy behaviour.

[53] •• Bolhuis P, Frenkel D. Prediction of an expanded-to-condensed transition in colloidal crystals. Phys Rev Lett 1994;72:2211–2214. (Note the connection to an earlier work; Young DA, Alder BJ, J Chem Phys 1980;73:2430).

The discovery of the two-phase expanded and condensed crystal equilibrium of short ranged potential. This, and many other features of the short ranged potential systems were first explained by the authors, though the inclusion of the glass into the story came somewhat later; see reference [1••]

[54] • Noro MG, Kern N, Frenkel D. The role of long-range forces in the phase behaviour of and Colloidal Proteins. Europhys Lett 1999;48:332–338.

An intriguing paper. A direction yet to be explored in detail.

[55] Costa D, Caccamo C, Abramo MC. Phase behaviour of model fluids interacting through short-range forces. J Phys Condens Matter 2002;14(9):2181–2191.

[56] • Costa D, Ballone P, Caccamo C. Kinetics of phase transformations in a model with metastable fluid–fluid separation: A molecular dynamics study. J Chem Phys 2002;116(8): 3327–3338.

Both references [55,56•] are thorough and interesting studies of the short-ranged potential, including some systematic view of the kinetic phenomena. This type of work is bound to become a more important focus in future.

[57] Sastry S. The relationship between fragility, configurational entropy and the potential energy landscape of glass-forming liquids. Nature 2001;409:164–167.

[58] • van Blaaderen A, Wiltzus P. Real-space structure of colloidal hard-sphere glasses. Science 1995;270:1177–1179.

The second of these two articles seems to be the first attempt to use three-dimensional imaging data of colloidal particles to study a collodial system.

[59] Malfois M, Bonnete F, Belloni L, Tardieu A. A model of
•• attractive interactions to account for fluid–fluid phase separation of protein solutions. J. Chem. Phys. 1996;105: 3290–3300.

This paper begins a stream of research by these authors, and their colleagues, that ultimately lead to a rather full description of the inter-protein potential for a variety of different globular proteins.

[60] Dijkstra M, Brader J, Evans R. Phase behaviour and struc-
• ture of model colloid–polymer mixtures. J Phys Condens Matter 1999;11:10079–10106.

Important reference for the phase diagrams of short ranged potentials, and basis of much of later work on the connection between the equilibrium and glassy behaviour.