Routes to colloidal gel formation

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Abstract

We discuss features of simple inter-particle potentials which are able to generate low-packing fraction arrested states, i.e. gels, in the absence of a macroscopic phase separation phenomenon. We suggest that the ratio between surface and bulk free energy is crucial in favoring *ideal* gel states. Two possible models for gels, one based on the competition of short range attraction and long range repulsions and the other on local constraints disfavoring packed local structures are discussed.
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1. Introduction

In recent years, a significant effort has been devoted to the study of colloidal dispersions at large packing fraction, approaching the line of dynamical arrest. Particles interacting via an effective potential resembling the hard sphere limit have been shown to undergo a glass transition around packing fraction

$\phi \approx 0.58$ [1,2]. Dynamics close to the hard-sphere glass transition is well described by Mode Coupling Theory [3] and explained by the onset of a localization length of the order of a tenth of the particle diameter. When the hard core repulsion is complemented by a very short range attraction—very short as compared to the particle size—an arrest phenomenon has also been predicted and experimentally observed at large packing fraction [4–9]. In this last case, the localization length at the glass transition is not only controlled by packing but mostly by the range of interaction. Decay of density correlation functions close

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to dynamical arrest shows a peculiar logarithmic decay, as opposed to the standard stretched exponential form [10]. The attraction-controlled arrested state, commonly named attractive glass, has been recently experimentally studied in polymer–colloid mixtures, inducing the short range attraction via polymer depletion mechanisms [8].

Colloidal dispersions also form disordered arrested states at low packing fractions (down to a few percent). These states are commonly named colloidal gels [11,12]. Despite the important application of colloidal gels in food, cosmetic and detergent industries, processes leading to gel formation are not fully understood. Difficulties arise due to the several distinct routes which transform a solution capable of flowing into a highly viscous substance and, eventually into an arrested system capable of sustaining shear stresses. Interrupted phase separation, percolation, irreversible diffusion limited aggregation, attractive glass transition, have been suggested as possible mechanisms leading to physical gels in colloidal systems. Understanding the gel formation in this class of materials would also significantly advance our understanding of the protein crystallization problem, where the possibility of generating crystal structures is hampered by the formation of a viscous gel state. In this manuscript, we review some of our recent work on the possible routes to gelation in colloidal systems [13–16], focusing in particular on the basic ingredients required to model physical gelation, in its most pure way.

2. Gelation as a result of phase separation interrupted by an attractive glass transition

Studies of the phase diagram of short-ranged (uncharged) attractive colloidal systems show that these systems are characterized by fluid and crystal phases and by an almost flat metastable liquid–gas spinodal which extends to considerably low values of ϕ. The thermodynamic phase diagram of simple models for short-range attraction has been evaluated theoretically and successfully compared with experimental data [17–20]. When the attraction range is a few percent of the particle size, the equilibrium phase diagram is composed only of a fluid-phase and a crystalline phase. The liquid–gas coexistence locus
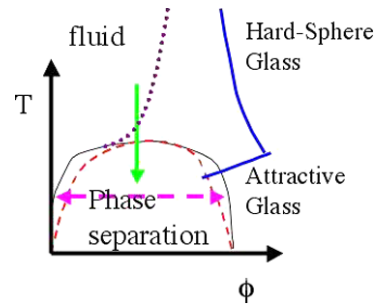

Fig. 1. Schematic representation of the phase diagram of short-range attractive potential, including the percolation (dotted), coexistence (thin), spinodal (dashed) and glass lines (thick). Under conditions of deep quench (arrow) the packing fraction in the dense phase reaches, during coarsening, the values at which an attractive glass transition is expected and the vanishing mobility effectively stops the separation process. Kinetically arrested states at overall small packing fraction can thus be generated by this mechanism.

is hidden within the region of fluid–crystal coexistence.

A percolation line, defined as the locus in the $\phi–T$ phase diagram where an infinite cluster of bonded particles appears, intersect the liquid–gas coexistence on the left of the critical point. It appears that, even at the temperature at which the coexistence curve is located, the lifetime of the interparticle bonding is short and that the lifetime of the short-range attraction bonding is not sufficient to generate a spanning network capable of sustaining stresses in the fluid phase.

For square well short-range attractive potentials the relation between the gel locus and the percolation and liquid–gas spinoidal lines has been recently calculated [13,21]. It has been shown that gel phases result only from an interrupted liquid–gas phase separation, interrupted by the glass transition which takes place in the dense regions created during the spinodal decomposition kinetics [13,22,23]. This scenario is shown schematically in Fig. 1. The attractive glass line meets the phase separation line on the high ϕ branch. For deep quenches, the density in the high packing fraction region is well within the attractive glass region. The spinodal decomposition and coarsening process arrests due to the slowing down of the particle mobility in the dense phase.

The morphology of the low ϕ arrested state is thus dictated by the phase separation kinetics. At very small ϕ, in the nucleation region, beads of the glass phase could be formed [24] and generate cluster

phases, as opposed to the percolating spinodal decomposition pattern, dominant for larger ϕ.

3. The quest for the ideal (thermoreversible) gel model

The previous section provides an example of gelation resulting from kinetic arrested following a phase separation process at finite temperature. In the same class of gel-formation mechanisms, one can also include diffusion limited cluster aggregation, which can be considered as the $T \to 0$ limit of this phenomenon.

Conceptually, it would be interesting to ask oneself how it would be possible to generate low packing fraction arrested states without the intermediate irreversible phase separation step. If this were possible, one could in principle approach the gel-line from the non-gelling side from equilibrium conditions and provide precise information on the dynamics close to the gel transition and on the morphology of the gel state.

In principle, the attractive glass line could be located above the phase separation curve [5]. If this were the case, on cooling, the system would arrest before meeting the phase transition line. For short-range attractive potential, this scenario is ruled out by numerical simulations, showing that for any small value of the attractive range, from few percent down to the infinite short-range Baxter limit, the scenario of Fig. 1 is found [21].

The basic reason why the formation of low packing fraction arrested states requires a phase separation process can be understood according to the following arguments. A low packing fraction arrested state requires a structure held together by inter-particle bonds. In physical gel conditions, bonds are not permanent and hence have a finite lifetime. A gel can be seen as a state in which the bond lifetime has grown so much that a connected percolating structure able to sustain stress survives for time longer than the experimental probe characteristic time. To increase the lifetime of an inter-particle bond (in conditions where excluded volume does not favor caging) it is needed to work at low temperature conditions, i.e. for $kT \ll u_0$, where u_0 is the characteristic energy of the attractive potential.

The low T condition favors not only the long bond lifetime, but also the phase separation process, since configurations in which particles are surrounded by many neighbors (up to twelve for spherical potentials) significantly decrease the energy of the system. In this respect, long bond lifetime and phase separation are strongly coupled.

In order to generate low packing fraction arrested states in the absence of phase separation one has to find out the features of the potential disfavoring condensation of the liquid phase, so that a single phase is stable, in equilibrium, at low T. A guide to answer this question is offered by the work on physical clusters developed by Hill [25,26]. The free energy F_N of a cluster of N particles can be written as contribution of a bulk and a surface term, respectively proportional to N and to $N^{2/3}$. The free energy per particle is thus

$$\frac{F_N}{N} = f_{\text{bulk}} + \frac{\gamma}{N^{1/3}} \tag{1}$$

where $\gamma \sim f_{\text{surface}} - f_{\text{bulk}}$ plays the role of surface tension. Here f_{bulk} (f_{surface}) is the free energy per particle in bulk (surface) conditions. If $\gamma > 0$, then F_N/N is minimized as $N \to \infty$ and hence a condensed liquid phase is expected. In this framework, to destabilize the liquid–gas phase separation is equivalent to finding which features of the inter-particle potential can generate conditions such that $f_{\text{surface}} \approx f_{\text{bulk}}$ or even $f_{\text{surface}} < f_{\text{bulk}}$ so that $\gamma \leqslant 0$ and no driving force for liquid condensation is present. At sufficiently low T, the condition $f_{\text{surface}} \lesssim f_{\text{bulk}}$ reduces to $e_{\text{surface}} \lesssim e_{\text{bulk}}$, where e_{surface} and e_{bulk} are respectively the energy of a particle in the interior of a cluster and the energy of a particle on the surface of a cluster. This provides a hint on how to model an inter-particle potential in which low T states can be reached without intervening phase separation processes.

4. Competition between short-range attraction and long-range repulsion

A way to establish the condition $\gamma < 0$ is offered by long range repulsive interactions [27], which in colloidal systems are usually of screened electrostatic origin. In the absence of any attractive component in the potential, the liquid phase is missing and the phase diagram shows, even at low ϕ, only a crystal and possibly a glass phase of monomers caged by the long-range repulsive interaction. When the weak long-range repulsion is complemented by a strong short-range attraction (which in colloidal systems can be of van der
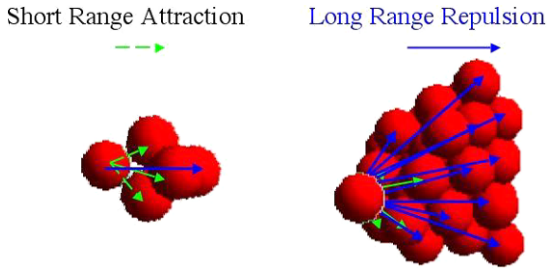
Fig. 2. Cartoon showing the different number of repulsive vs. short-range attractive interactions characterizing clusters of different sizes. The number of attractive interactions is indeed bounded by the surface geometry while the number of repulsive interactions is essentially limited by the cluster size.
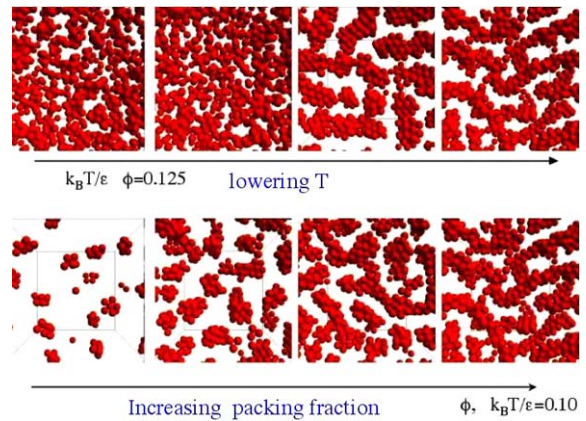

Fig. 3. Snapshots of a system of particles interacting via a spherical short-range attractive potential and a screened electrostatic repulsive potential, at fixed $\phi = 0.125$ as a function of T and at fixed $k_B T/u_0 = 0.10$ as a function of ϕ. The structure of the system is composed of clusters, whose size progressively increases on lowering T or increasing ϕ, reaching an arrested low-density state, corresponding to the last snapshot [14]. A slab of width of a few particle diameters is shown.

Waals or depletion origin) then at sufficiently low T clusters will start to form [14,28–31].

As shown in Fig. 2, for small cluster sizes, the decrease of energy due to the bounding of an additional particle to the surface wins over the additional limited number of repulsive interactions established. However, when the cluster has grown over a certain size, the fixed gain in "attractive" energy on adding one further monomer is compensated by an equivalent amount of "repulsive" energy, which becomes more and more relevant due to the long range of the attraction.

The size dependence of the ground state cluster energy has been recently studied for this class of potentials [14,15]. It has been found that for certain parameter conditions, at low T, stable cluster phases can be generated. In these states, the system behaves as a liquid, whose particles are made by large clusters of optimal size, which can undergo a cluster glass transition (see Fig. 3). For other choices of the resulting potential the cluster shape is predominantly one-dimensional [15]. Branching of these $\gamma \approx 0$ clusters favors the formation of large, but very stable in time, aggregates which turn into macroscopically percolating systems on increasing ϕ.

5. Maximum valency models

A different way to establish the condition $\gamma \approx 0$ is offered by a modification of the potential, via the introduction of many body forces or non-spherical potentials [32,33], creating already at the level of nearest neighbor interaction, an energetically unfavorable

condition for dense local configurations. An efficient way to model this condition is to impose a constraint on the maximum number N_{max} of particles interacting via a short range potential (see Fig. 4). When $N_{max} < 6$, new particles sticking on the surface of the cluster may gain an energy essentially equivalent to particles sitting in the bulk of the cluster, again reducing the driving force for phase separation.

These types of models, in which the short range attraction is described by a square well (SW) potential, for different values of N_{max} have been recently studied [16,34]. It has been shown that the part of the phase diagram in which phase separation occurs significantly reduces on decreasing N_{max}. For $N_{max} < 6$ a window of packing fractions values opens up in which it is possible to reach very low temperature (and hence states with extremely long bond lifetime) without encountering the phase separation.

The T-evolution of the structure at $\phi = 0.20$ for $N_{max} = 3$ is shown in Fig. 5. In this conditions, percolation takes place around $T/u_0 = 0.3$. On lowering T, the number of bond increases, as well as the spacial correlation between particles, favoring the establishment of a spanning network of long-living bonds, i.e. a gel.
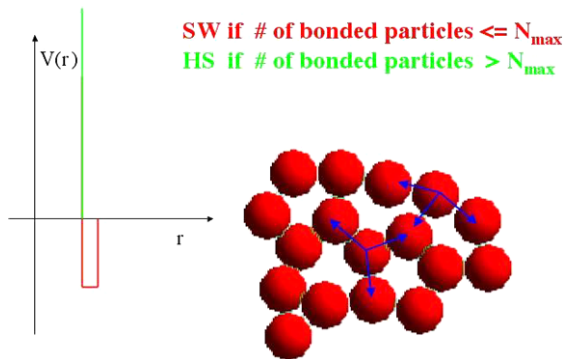
Fig. 4. Cartoon of a maximum valency model, in which the short range attraction is modelled by a square well (SW) potential. If N_{max} particles are already bonded, the incoming particles feels a hard sphere repulsive potential. In this simple way, the local energy does not grow when the number of neighbors increases beyond N_{max}. Particles in the bulk of the cluster have the same energy as particles at the surface of the cluster.
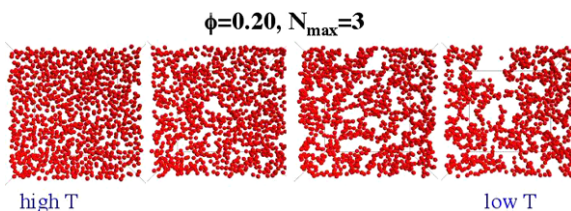

Fig. 5. Snapshots a system of particles interacting via a spherical short range square well attractive potential with a constraint on the maximum number N_{max} of bonded interactions [16]. Here $N_{max} = 3$, $\phi = 0.20$ and reduced $T/u_0 = 0.9, 0.3, 0.12, 0.03$. A slab of width of three particle diameters is shown.

6. Conclusions

In this manuscript, we have discussed the basic features of an inter-particle potential which can give rise to ideal gel states, i.e. those that can be approached, in principle arbitrarily close, from the equilibrium sol state. An ideal gel cannot result from an interrupted phase separation, which implies a discontinuous transition from the sol to the gel state.

Gel states are favored by conditions in which the cluster surface free energy is close to the cluster bulk free energy. We have shown two possibilities of reaching this condition: by an interplaying of short range attractive and long range repulsive interactions, and by designing a non-spherical and/or non-additive attractive potential disfavoring configurations with large number of neighbors. In the case of colloidal suspen-sions, particles with a reduced number of sticky points are the best candidates for ideal gel formation.

The tuning of off-lattice models in which phase separation is essentially inhibited offers the possibility of studying the nature of the gel transition, the differences/analogies between gels and glasses and the relation between gelation and percolation in physical (as opposed to irreversible bond chemical) gelation [16, 35]. Work in this direction is in progress.

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