Percolation, gelation and dynamical behaviour in colloids

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Abstract

We review some results on the dynamics of gelation phenomena, obtained via a lattice model and via molecular dynamics using a DLVO potential. This study allowed us to make a connection between classical gelation and the phenomenology of colloidal systems, suggesting that gelation phenomena in attractive colloids at low temperature and low volume fraction can be described in terms of a two-line scenario.

1. Introduction

The gelation transition transforms a viscous liquid into an elastic disordered solid. In polymer systems, this is due to chemical bonding, that can be induced in different ways [1, 3], producing a polymerization process. As first recognized by Flory, the change in the viscoelastic properties is directly related to the constitution inside the sol of a macroscopic polymeric structure, that characterizes the gel phase. In experiments [2] the viscosity coefficient grows as a power law as a function of the relative difference from the critical polymer concentration with a critical exponent k. The onset of the elastic response in the system, as a function of the same control parameter, displays a power law increase of the elastic modulus with a critical exponent f. As implicitly suggested in the work of Flory and Stockmayer [1], the percolation model is considered as the basic model for the chemical gelation transition and the macromolecular stress-bearing structure in these systems is a percolating network [3–5]. In experiments the gelling solution typically displays slow dynamics: the relaxation functions present a long time stretched exponential decay $\sim e^{-(t/\tau_0)^\beta}$ as the gelation threshold is approached. In particular at the gel point the relaxation process becomes critically slow, and the onset of a power law decay is observed [6].
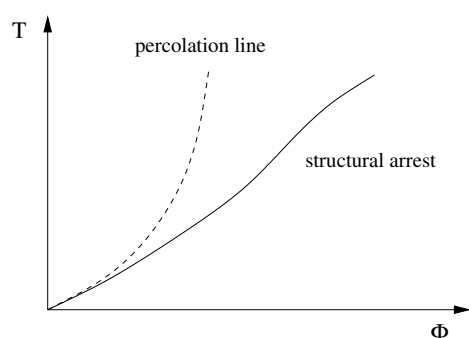
Figure 1. A schematic phase diagram for attractive colloids.

In many other physical systems where aggregation processes and structure formation take place, gelation phenomena can be observed. Typically, these are colloidal systems, i.e. suspensions of mesoscopic particles interacting via short range attraction. Such systems are intensively investigated due to their relevance in many research fields (from protein studies to the food industry). Due to the possibility in experiments of opportunely tuning the features of the interactions, they also play the role of model systems. A rich phenomenology is found in the temperature–volume fraction plane [7–12]. At high temperature a hard sphere glass transition occurs at a volume fraction, $\phi \simeq 0.57$. By decreasing the temperature, at high volume fraction, the effect of the short range attraction produces an attractive glass line with a re-entrant line well described in the framework of the mode coupling theory [13, 14], and confirmed by experiments. At low temperature and low volume fraction a much more complex situation arises [9, 16, 17], characterized by a cluster phase followed by a kinetic arrest. Viscoelastic properties very similar to those found in polymer gelation suggest that also in this case gelation corresponds to the formation of spanning structure, which makes the system able to bear stresses.

At low temperature particles are linked due to the presence of the attractive interaction. However, the bonds are not permanent as in chemical gelation. In any case one expects that at very low temperature the lifetime of the bonds is extremely high and the onset of a spanning network might produce a phenomenon closely related to standard irreversible gelation. At higher temperature the lifetime of the bonds decreases and the macroscopic relaxation time or viscosity might exhibit only an apparent divergence close to the onset of a spanning cluster. The apparent divergence, corresponding to an interrupted gel, is due to the bond breaking which limits the lifetime of the long living clusters. However, as the volume fraction increases the long living clusters might eventually give rise to a structural arrest. This picture could give a coherent interpretation for the features experimentally observed in structural arrest phenomena in colloidal systems, as reported in [9]. It has been initially developed on the basis of the study of a lattice model for gelation phenomena [19], where finite lifetime bonds were introduced[6].

These considerations suggest the presence of two lines in colloidal systems, as shown in the schematic phase diagram of figure 1: an interrupted gel which occurs close to the percolation line and, at higher volume fraction, a second line corresponding to structural arrest. At high temperatures the first line becomes less and less observable, as the clusters are not long living enough and are not detectable, while the second line tends, as the temperature increases, to the hard sphere glass transition. At very low temperature, the interrupted gel line and the structural

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[6] The effect of permanent bonds versus non-permanent ones on the structural arrest in colloidal systems has also been investigated in [20].

arrest line will come close to each other, until they merge and become indistinguishable. In this region structural arrest is expected therefore to combine many features of gelation and glass transition.

Molecular dynamics simulations of colloidal particles interacting via a DLVO potential [26] have allowed us to test this two-line scenario in a more realistic frame for colloidal systems [23]: in systems with only short range attraction these two lines usually interfere at low temperature with the liquid–gas coexistence curve. On the other hand the presence of charges due to the screening effect may produce an effective repulsion in the potential which tends to prevent the liquid–gas phase separation and stabilize the size of the clusters [15, 18].

In the following we will review the main results obtained in a lattice model [19] with finite bond lifetime, and we will present molecular dynamics simulations of particles interacting via a DLVO potential [23]. The first case corresponds to the high temperature region of the schematic phase diagram plotted in figure 1, and to that system where, depending on the details of the potential, the two lines may be detected even at relative high temperature, as found in some experimental works [21, 22]: in the model studied here an interrupted gel, with an abrupt increase of the relaxation time (i.e. the viscosity), is observed close to the percolation line, and a structural arrest line at higher density where a glass transition is found. The second case corresponds to the low temperature region of the phase diagram plotted in figure 1 and to systems where the presence of charges due to screening effect may produce an effective repulsion in the potential which tends to prevent the liquid–gas phase separation: in this case a structural arrest with gel features is found at low density and low temperature very close to the percolation line.

2. Lattice model for polymer and colloidal gelation

The lattice model studied in [19] corresponds to a solution of monomers diffusing on a cubic lattice. As in most experimental polymer gels, we choose the monomers to be tetrafunctional. Each monomer occupies a lattice elementary cell, and therefore eight vertices on the lattice. To take into account the excluded volume interaction, two monomers cannot occupy nearest neighbour and next nearest neighbour cells on the lattice, i.e. nearest neighbour monomers cannot have common sites. At $t = 0$ we fix the fraction ϕ of monomers present with respect to the maximum number allowed on the lattice, and randomly quench bonds between them. This actually corresponds to the typical chemical gelation process that can be obtained by irradiating the monomeric solution. We form at most four bonds per monomer, randomly selected along lattice directions and between monomers that are nearest neighbours and next nearest neighbours (namely bond lengths $l = 2, 3$). Once formed, the bonds are permanent. For each value of ϕ there is an average value $N_b(\phi)$ of the fraction of formed bonds with respect to all the possible ones, obtained by averaging over different initial configurations.

Varying ϕ the system presents a percolation transition at $\phi_c = 0.718 \pm 0.005$ [24]. The critical exponents found at the transition agree with the random percolation predictions [4] (e.g. for the mean cluster size $\gamma \simeq 1.8 \pm 0.05$ and for the correlation length $\nu \simeq 0.89 \pm 0.01$ in 3d [24]).

The monomers diffuse on the lattice via random local movements and the bond length may vary but not be larger than l_0 according to bond-fluctuation dynamics (BFD), where the value of l_0 is determined by the self-avoiding walk condition. On the cubic lattice we have $l_0 = \sqrt{10}$ in lattice spacing units and the allowed bond lengths are $l = 2, \sqrt{5}, \sqrt{6}, 3, \sqrt{10}$ [25].

We let the monomers diffuse to reach the stationary state and then study the system for different values of the monomer concentration.
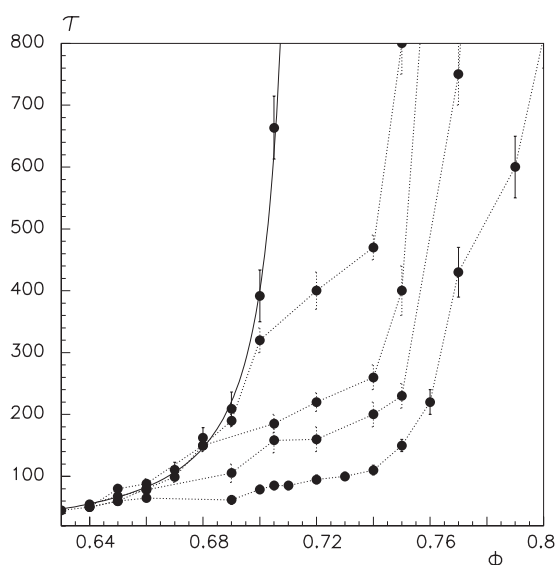
Figure 2. The average relaxation time as a function of the density; from left to right: the data for the permanent bond case diverge at the percolation threshold with a power law (the full curve); the other data refer to finite $\tau_b = 3000, 1000, 400, 100$ MC step/particle decreasing from left to right (the dotted lines are a guide to the eye).

This lattice model with permanent bonds has been introduced to study the critical behaviour of the viscoelastic properties at the gelation transition [24]. The relaxation time is found to diverge at the percolation threshold ϕ_c with a power law behaviour [24]. The elastic response in the gel phase has been studied by means of the fluctuations in the free energy and goes to zero at ϕ_c with a power law behaviour as well [24].

We introduce a novel ingredient in the previous model by considering a finite bond lifetime τ_b and study the effect on the dynamics.

The features of this model with finite τ_b can be realized in a microscopic model: a solution of monomers interacting via an attraction of strength $-E$ and excluded volume repulsion. Due to monomer diffusion the aggregation process eventually takes place. The finite bond lifetime τ_b is related to the attractive interaction of strength $-E$, as $\tau_b \sim e^{E/KT}$.

We start with the same configurations of the previous case, with a fixed ϕ where the bonds have been randomly quenched as described above. During the monomer diffusion with BFD at every time step we attempt to break each bond with a frequency $1/\tau_b$. Between monomers separated by a distance less than l_0 bonds are then formed with a frequency f_b. In order to obtain monomer configurations that are similar to the ones with permanent bonds, for each value of τ_b we fix f_b so that the fraction of present bonds coincides with its average value in the case of permanent bonds, $N_b(\phi)$ (see footnote 1).

With respect to the case of permanent bonds we notice that, as the finite bond lifetime τ_b corresponds to an attractive interaction of range l_0, it actually introduces a correlation in the bond formation and may eventually lead to a phase separation between a low density and a high density phase. For the choices of τ_b and f_b considered here, together with the constraint given by the tetrafunctionality, there is no phase separation.

In figure 2 the relaxation time, τ (obtained from the equilibrium autocorrelation functions of the density fluctuations), is plotted as a function of the monomer concentration, ϕ, for the

permanent bond and for the finite lifetime bond cases at different values of τ_b. In the figure one finds the data for the permanent bond case on the left, and then from left to right the data for decreasing values of bond lifetime, τ_b. In the case of permanent bonds (chemical gelation), $\tau(\phi)$ displays a power law divergence at the percolation threshold ϕ_c. For finite bond lifetime the relaxation time instead increases following the permanent bond case up to some value ϕ^*, and then deviates from it. The longer the bond lifetime the higher ϕ^* is. For higher ϕ the further increase of the relaxation time corresponds to the onset of the glassy regime in the relaxation behaviour discussed in [19]. This truncated critical behaviour followed by a glassy-like transition has been actually detected in some colloidal systems in the viscosity behaviour [21, 22].

In both cases of permanent bonds and finite lifetime bonds, clusters of different sizes are present in the system. In the permanent bond case, a cluster of radius R diffuses in the medium formed by the other percolation clusters with a characteristic relaxation time $\tau(R)$. At the percolation threshold the connectedness length critically grows in the system and so does the overall relaxation time. In the case of a finite bond lifetime τ_b, there will exist a cluster size R^* so that $\tau_b < \tau(R^*)$. That is, clusters of size $R \geqslant R^*$ will break and lose their identity on a time-scale shorter than $\tau(R)$ and their full size will not contribute to the enhancement of the relaxation time in the system. We can say that the finite bond lifetime actually introduces an effective cluster size distribution with a cut-off and keeps the macroscopic viscosity finite in the system. At high concentrations the system approaches a glassy regime and the relaxation time increases.

3. Molecular dynamics simulations of colloidal systems

The results shown in section 2 corresponds to the high temperature region of the schematic phase diagram plotted in figure 1, and to that system where, depending on the details of the potential, the two lines may be detected even at relatively high temperature, as found in some experimental works [21, 22]. In the present section we consider a more realistic situation, molecular dynamics simulations of a system of $N = 1000$ particles interacting via a DLVO potential [26]. The results obtained in this case correspond to the low temperature region of the phase diagram plotted in figure 1 and to systems where the presence of charges due to the screening effect may produce an effective repulsion in the potential which tends to prevent the liquid–gas phase separation. The DLVO potential [26] in fact contains a van der Waals type interaction plus an effective repulsion[7] due to the presence of charges:

$$V(r) = \epsilon \left[a_1 \left(\frac{\sigma}{r} \right)^{36} - a_2 \left(\frac{\sigma}{r} \right)^6 + a_3 \exp\left(-\lambda \left(\frac{r}{\sigma} - 1 \right) \right) \right], \tag{1}$$

where $a_1 = 2.3$, $a_2 = 6$, $a_3 = 3.5$, and $\lambda = 2.5$. With these parameters (see figure 3) the repulsion term dominates the van der Waals attraction at long range, providing a short range attraction and a long range repulsive barrier. Because of the periodic boundary conditions, the potential is cut off at a distance of 5σ. To mimic the colloidal dynamics, we performed molecular dynamics simulations at constant temperature. Equations of motion were then solved in the canonical ensemble (with a Nosé–Hoover thermostat) using a leap-frog Verlet algorithm [27] with a time step of $0.001t_0$ (where $t_0 = \sqrt{\frac{m\sigma^2}{\epsilon}}$ and m is the mass of the particles). At a given value of the volume fraction, ϕ, the system, first equilibrated at high temperature, is quenched at $k_B T = 0.2\epsilon$. In order to investigate the relation between gelation and the

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[7] In equation (1) the effective repulsion is chosen as $\exp(-\lambda(\frac{r}{\sigma} - 1))$, and the power law decay r^{-1} typically present in the DLVO potential is in a first approximation neglected. However, varying suitably the parameters in equation (1), qualitatively similar potentials are obtained.
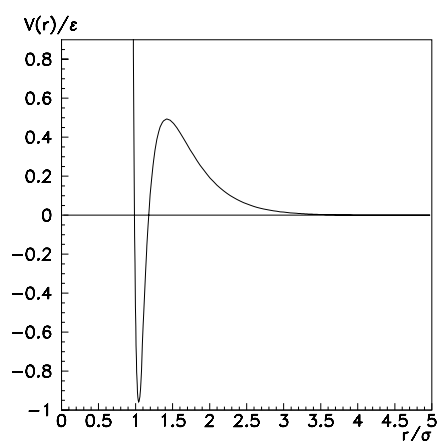
**Figure 3.** The DLVO potential (see equation (1)) as a function of the radial distance, r/σ.
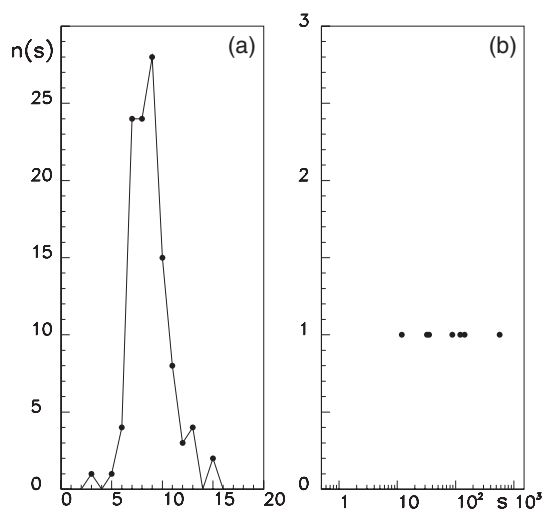
Figure 4. The cluster size distribution for $k_B T = 0.2\epsilon$ and volume fraction: (a) $\phi = 0.10$, where a peaked distribution is observed (the continuous curve is a guide for the eyes), and (b) $\phi = 0.17$, in the percolation region.

physical clusters observed in colloidal systems [10], we use the Hill criterion to define self-bound clusters [28]: two particles are linked if their relative kinetic energy is lower than the negative of their interaction energy. After the quench, in the asymptotic regime reached at long time, we calculated the cluster size distributions, $n(s)$ ($n(s)$ refers to a single configuration of the system, and $N = \sum_s n(s)s$). In figure 4, the cluster size distribution for $k_B T = 0.2\epsilon$ is reported at volume fraction, ϕ, just below (a) and just above (b) the percolation transition. As we can see in figure 4, at low volume fraction (a) a peaked cluster size distribution is observed, before the percolation threshold estimated at a volume fraction, $\phi_p = 0.14 \pm 0.01$. In figure 5 typical snapshots are shown: a configuration at $\phi = 0.10$ with finite size clusters (a), and a configuration at $\phi = 0.17$ with a spanning cluster containing more than half of the particles (b). The behaviour here observed is clearly due to the presence of the repulsive barrier, which favours clusters around the same finite size.
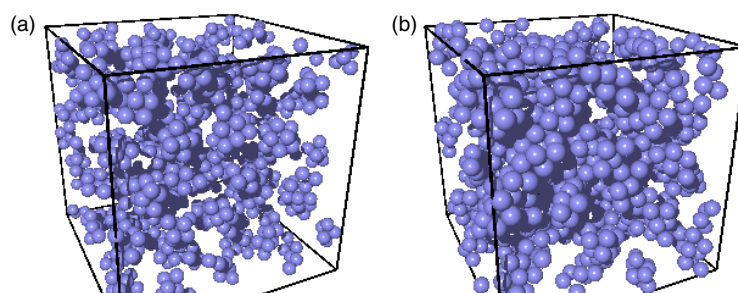
Figure 5. Two snapshots of the system made up of 1000 particles for $k_B T = 0.2\epsilon$: (a) a configuration at $\phi = 0.10$, where finite clusters are formed, and (b) at $\phi = 0.17$, where a spanning cluster made up of 570 particles is present.

(This figure is in colour only in the electronic version)
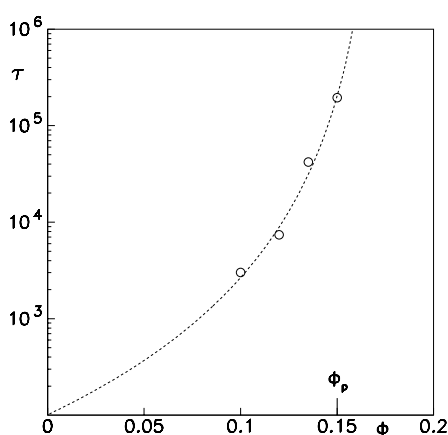
Figure 6. The relaxation time, τ (in units of MD steps), as a function of the volume fraction, ϕ, respectively for $k_B T = 0.2\epsilon$ (empty circles). The dashed curve is a power law, $(\phi_c - \phi)^{-b}$, with $\phi_c = 0.174 \pm 0.050$ and $b = 3.82 \pm 0.10$. The percolation threshold is $\phi_p \simeq 0.14$.

In figure 6 the relaxation time, τ, is plotted as a function of ϕ. The data are well fitted by a power law, $(\phi_c - \phi)^{-b}$, with $\phi_c = 0.174 \pm 0.050$ and $b = 3.82 \pm 0.10$. The critical value of the volume fraction obtained in this way is very close to the percolation threshold, $\phi_p = 0.14 \pm 0.01$.

At low temperature a fluid cluster phase [9] is observed at low volume fraction ($\phi = 0.10$), where the cluster size distribution displays a peak around a typical finite size, and the intermediate self-scattering function presents a fluid-like behaviour [23]. At a higher volume fraction structural arrest is observed just a little above the percolation threshold and dynamical properties are found in part to be reminiscent of those of polymer gelation [23]. This point, close to the percolation threshold, where structural arrest occurs is interpreted as the onset of colloidal gelation [8].

4. Discussion and conclusions

We have studied a model for gelling systems both in the case of permanent bonds and finite bond lifetime. The study of the dynamics shows that when bonds are permanent (chemical

gelation) the divergence of the relaxation time is due to the formation of a macroscopic critical cluster and the decay of the relaxation functions is related to the relaxation of such a cluster. In the case of finite τ_b there is an effective cluster size distribution, with a size cut-off. Note that the clusters cannot be easily defined, as in the case of chemical gelation: the effective clusters do not coincide with pairwise bonded particles. A cluster can be identified in a statistical sense as a group of monomers which keeps its identity (i.e. the bonds are unbroken) when diffusing a distance of the order of its diameter. The formation of effective clusters leads to an apparent divergence of the relaxation time which is characterized by exponents corresponding to the case of random permanent bonds (random percolation). As the monomer density increases the presence of effective clusters further slows down the dynamics, until a glass transition is reached. In the case $\tau_b \to \infty$, starting with a random configuration of unbonded monomers one obtains an out of equilibrium state as in cluster–cluster aggregation models, which can be representative of colloidal gelation. Ideally this out of equilibrium system is connected to the two lines described above, the percolation line and the glassy line. The percolation line can be detected in the dynamics if the effective cluster size is large enough and it is quite distinct from the glassy line. However, both lines interfere at low densities and low temperatures with the phase coexistence curve. We have tested this scenario within a more realistic frame for colloidal systems: we have performed molecular dynamics simulations of colloidal particles interacting via a DLVO potential. At high temperature the system does not display any dynamical anomalies at the percolation threshold [23]. At low temperature, a fluid-like cluster-phase is observed and at the percolation threshold the system is dynamically arrested. These results support the 'two-line' scenario. At low volume fraction and low temperature the formation of long living large clusters strongly influences the dynamical behaviour of the system. Therefore structural arrest exhibits gel-like and glass-like features. This is in agreement with many experimental observations [8, 11, 10, 9] and gives a possible interpretation of these phenomena. Depending on how far separated the two points are, the structural arrest will be more gel-like or glass-like. This would explain the change in the viscoelastic properties which is experimentally observed in structural arrest of colloidal systems as the temperature and the volume fraction increases [11]. For higher volume fraction we expect that in general the arrest is more and more glassy as the two lines depart, as found in the lattice model with finite bond lifetime. Further studies on the DLVO potential at high temperature and volume fractioon are in progress.

Acknowledgments

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