Clusters in attractive colloids

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Abstract

We discuss how the anomalous increase of the viscosity in colloidal systems with short-range attraction can be related to the formation of long-living clusters. Based on molecular dynamics and Monte Carlo numerical simulations of different models, we propose a similar picture for colloidal gelation at low and intermediate volume fractions. On this basis, we analyze the distinct role played by the formation of long-living bonds and the crowding of the particles in the slow dynamics of attractive colloidal systems.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Colloidal suspensions include systems that can be very different and complex at a chemical level, from proteins to blood, milk, paints, or different types of microemulsions [1–3]. In spite of this diversity, in the experiments where the volume fraction and the strength of the attraction between the particles can be controlled and varied, similar phenomena of slow dynamics are observed [4, 5, 7, 6, 8]. Hence these studies become a fundamental tool to investigate slow dynamics and structural arrest in complex fluids within a general framework, a research field where the work of Chen, using neutron and light scattering, has made an outstanding contribution over the years [9].

Interestingly, in recent years, a fruitful interplay has developed between experiments and modelling studies [10] due to the possibility of using simple mesoscopic models to investigate the slow dynamics via numerical simulations. In the following, we will briefly review some

recent contributions to the understanding of the phenomena of slow dynamics in attractive colloidal systems at low and intermediate volume fractions obtained by the group in Naples.

Firstly, it is interesting to remark that in attractive colloidal suspensions a strong short-range attraction between particles is able to produce irreversible aggregation phenomena, leading to a permanent gel at extremely low volume fractions, due to aggregation limited by the diffusion of particles or clusters [11]. On the other hand, it is well known that, at high volume fraction and in the presence of a weak interparticle attraction, these systems display a glassy behaviour and have been investigated intensively as the prototype of hard sphere glasses [4]. At intermediate volume fractions and strengths of the attraction, i.e. far from both this glassy regime and the irreversible aggregation regime, unexplained slow dynamics is observed, accompanied by structure formation and a significant change in the viscoelastic behavior, in close analogy to gel formation [8, 12]. This picture, supported by experimental and numerical studies, has led to the proposal of a unifying description for these phenomena [13]. It underlines the fact that, in the slow dynamics, a relevant number of particles must stop moving all together, and might therefore suggest that gelation phenomena in colloidal systems at lower volume fractions could also be related to a glassy structural arrest. In this case, different mechanisms have been proposed [14] for the trapping of particles in the well of the attractive potential, in analogy to the caging mechanism invoked for the glass transition, or a glassy structural arrest of clusters.

In order to further understand this point, it is worth considering the nature of gelation transition [15]. Gel formation is the transition from a viscous liquid (a polymer solution or a particle dispersion...) into an elastic disordered solid, which is the gel phase. This means that the viscoelastic response of the system changes, with the viscosity coefficient strongly increasing in the liquid phase and the onset of a low-frequency elastic modulus that characterizes the gel phase. That is, the high-frequency elastic response of the material moves towards lower and lower frequencies. In polymer gels, such a dramatic change of the viscoelastic response is typically associated with the formation of a spanning interconnected network, which is often well described in terms of a random percolating network [16]. Of course, the random percolating structure here is not considered at all in the sense of a geometric instantaneous percolation, which could not be responsible for the change in the viscoelastic response, but in the sense of the formation of a permanent interconnected structure. In spite of many differences in the details of the network formed in colloidal irreversible gels, whose structures tend to be more open and similar to those obtained with DLCA models [11], the change in the viscoelastic properties is qualitatively the same.

On the basis of these considerations, we have proposed [17] that two different mechanisms could be responsible for the slow dynamics in attractive colloidal systems, that is, the formation of permanent or long-living structures at low volume fractions in the presence of a significant attraction strength, and crowding of the particles at high volume fractions. Depending on the details of the system, at different volume fractions the typical energy, time and length scales might produce a different interplay between these two mechanisms and qualitatively diverse slow dynamics.

2. A minimal model for gelation phenomena

We have first investigated the role of permanent or long-living structures in the dynamics by means of a minimal model for gelation phenomena, studied via lattice Monte Carlo simulations [17]. We consider a solution of tetrafunctional monomers with excluded volume interactions on a cubic lattice of size L. At $t = 0$, the volume fraction ϕ is fixed, and bonds between monomers are randomly quenched. The four possible bonds per monomers, randomly
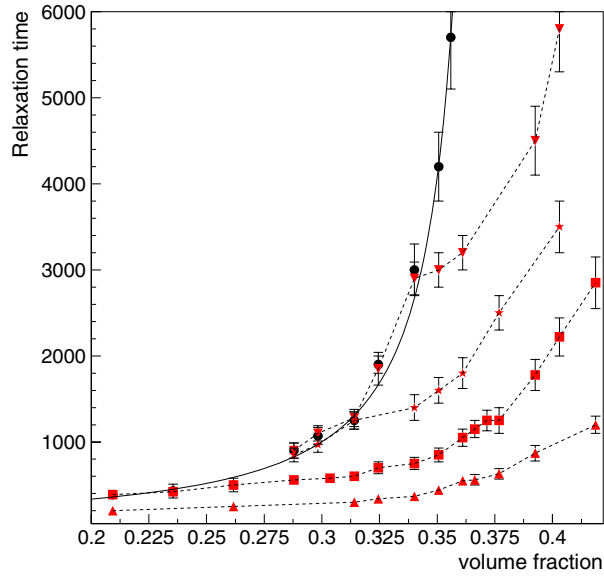
Figure 1. The relaxation time τ (in MCstep/particle) as a function of the volume fraction ϕ, calculated from the incoherent scattering function at wavevector $q = \pi/8$ in lattice unit length. From left to right: the data for the permanent bond case diverge at the percolation threshold with a power law (continuous line); see text. The other data refer to finite $\tau_b = 10^4, 5 \times 10^3, 10^3, 10^2$ MCstep/particle, decreasing from left to right (the dashed lines are guides to the eye). (Data obtained using the model from [20].)

selected, are formed along lattice directions between monomers that are nearest neighbors and next nearest neighbors. We consider two different cases: permanent bonds and bonds with a finite lifetime τ_b. In the case of permanent bonds, the monomers diffuse according to the bond-fluctuation dynamics (BFD) [18]. The system has a percolation transition at $\phi_c = 0.376 \pm 0.003$ and, after the monomers have reached the stationary state by diffusing on the lattice, we study the system for different values of concentration. In the case of a finite bond lifetime τ_b, we start with the same configurations as the previous case, with a fixed ϕ where the bonds have been randomly quenched. During monomer diffusion with BFD, at each time step we attempt to break each bond with a frequency $1/\tau_b$. Between monomers separated by a distance of less than l_0, bonds are then formed with a frequency $1/\tau_u$.

These two parameters of the model can be generally related to the case where bond formation implies the overcoming of an entropic barrier. The bond lifetime τ_b can be related to the height of such an entropic barrier S_b, i.e. $\tau_b \sim e^{S_b}$ (in units of Boltzmann's constant). The characteristic time τ_u for bond formation is $\tau_u \sim e^{S_u}$, where S_u is the entropic barrier to be overcome in order to go from the un-bonded state to a bonded state. Therefore the probability p_b for two close monomers to be bonded is given by

$$p_b = \frac{e^{S_b}}{e^{S_b} + e^{S_u}}.$$

Such a bond probability can be much smaller than 1, depending on the value of S_u. As a consequence, in this case percolation can occur at quite a high volume fraction compared to other colloidal systems [8, 13], as is in fact observed, for example, in micellar systems [19].

From the time autocorrelation function, $f_q(t)$, of equilibrium density fluctuations for the smallest wavevector $q_0 = \frac{2\pi}{L}$, we calculate the relaxation time τ as the time such that $f_q(\tau) \sim 0.1$. In figure 1, the relaxation time, τ, is plotted as a function of the volume

fraction, ϕ, for the permanent bonds and for the case of finite lifetime bonds at different values of τ_b. The data refer to a lattice size $L = 16$ and $q_0 = \pi/8$ in lattice unit length [19]. In the figure, on the left one finds the data for the permanent bond case, and from left to right one finds the data for finite bond lifetime, for decreasing values of τ_b. In the case of permanent bonds, $\tau(\phi)$ displays a power-law divergence, $(\phi_c - \phi)^{-k}$, at the percolation threshold. For finite bond lifetime τ_b, the relaxation time instead increases following the permanent bond case, up to some value ϕ^*, and then deviates from it. For higher ϕ, the increase in the relaxation time corresponds to the onset of the glassy regime in the relaxation behavior discussed in [20]. This qualitative behavior has also been confirmed via molecular dynamics simulations in [25].

With the crude simplifications that are adopted, this can be considered to be a toy model for gelation phenomena. Nonetheless, it turns out to capture some essential physics of the problem. The results obtained show that, when the spanning structure is permanent (on the observation time scale), the relaxation time in the system is controlled by the structure formation and critically increases at the percolation threshold. When the spanning structure is not permanent and the bond lifetime is short enough compared to the relaxation time in the system, the dynamics is not affected by the percolation threshold and a more glassy slowing down, due to the crowding of the particles, can be observed only at higher volume fractions. Finally, when the bond lifetime is comparable to the relaxation time in the system, τ is affected by the formation of long-living structures of increasing size, but does not show a real critical increase, since a permanent structure of critically increasing linear size does not exist. In this case, a crossover from a gel-like to a glassy dynamic regime can be observed by increasing the volume fraction. This picture, first proposed in [17], has been recently receiving increasing attention.

3. Colloidal gelation in the presence of competing attraction and repulsion

We have further investigated this problem within a more realistic framework for colloidal systems, where structure formation is due to interparticle interaction: in colloids, recent experimental works highlighted the presence of a net charge on colloidal particles [3, 7] giving rise to a long-range electrostatic repulsion in addition to the depletion interaction. The competition between attractive and repulsive interactions produce a rich phenomenology and a complex behavior as far as structural and dynamical properties are concerned. Hence, for particular choices of the interaction parameters, the liquid–gas phase transition can be avoided and the cluster size can be stabilized at an optimum value [21]. Experimentally, such a cluster phase, made up of small equilibrium monodisperse clusters, is observed using confocal microscopy at low volume fraction and low temperature (or high attraction strength) [8, 7, 3]. Increasing the volume fraction, the system is transformed from an ergodic cluster phase to a nonergodic gel [8, 7], where structural arrest occurs. We consider a system of $N = 10000\,\phi$ particles, with $\phi = 0.08$–0.25, interacting via a DLVO-type potential [22], which contains a van der Waals type interaction plus an effective repulsion due to the presence of charges:

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

where $a_1 = 2.3$, $a_2 = 6$, $a_3 = 3.5$, and $\lambda = 2.5$.[7] With these parameters, the repulsion term dominates the van der Waals attraction at long range, providing a short-range attraction and a long-range repulsive barrier. The effective repulsion in the potential prevents the liquid–gas phase separation and stabilizes the size of the clusters, as expected [21]. To mimic the colloidal

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[7] The potential $V(r)$, equation (1), essentially coincides with a Lennard-Jones interaction plus a repulsive Yukawa potential $\epsilon \left[A_1 \left(\frac{\sigma}{r} \right)^{36} - A_2 \left(\frac{\sigma}{r} \right)^6 + a \frac{e^{-r/\xi}}{\frac{r}{\sigma}} \right]$, with $A_1 = 3.56$, $A_2 = 7.67$, $a = 36.79$ and $\xi = 0.49\sigma$.
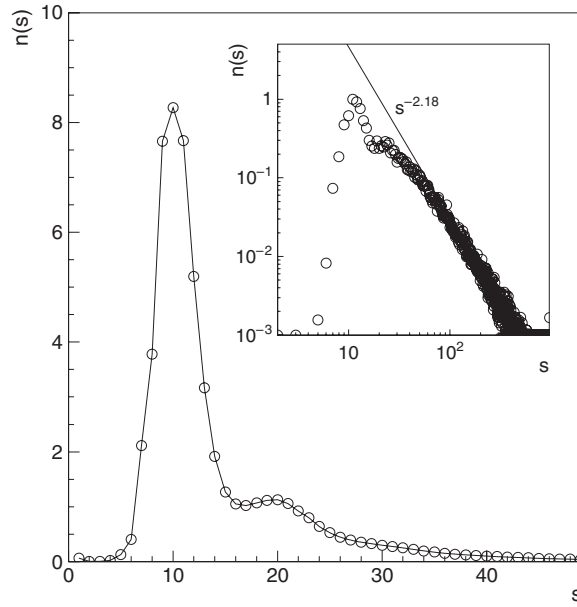
Figure 2. Main frame: the cluster size distribution, $n(s)$, at $k_B T = 0.2\epsilon$ and $\phi = 0.13$ displays a peak around an optimum cluster size. Inset: at $\phi = 0.16 \simeq \phi_p$, a power-law tail appears.

dynamics, we performed molecular dynamics simulations at constant temperature. Equations of motion were solved in the canonical ensemble (with a Nosé–Hoover thermostat) using a velocity Verlet algorithm [23] with a time step of $0.001 t_0$ (where $t_0 = \sqrt{\frac{m\sigma^2}{\epsilon}}$ and m is the mass of the particles). We equilibrate the system at temperatures $k_B T = 0.2, 0.23, 0.25\epsilon$ and ϕ increasing from 0.07 to 0.23. Here we review the main results of [17], analyzing the structure and the dynamics as the temperature and volume fraction are varied. We first calculate the static structure factor, $S(k)$, and the cluster size distribution, $n(s)$, where two particles are linked if their relative distance is smaller than the local maximum of the potential.

At low temperatures (i.e. when the kinetic energy becomes smaller than the repulsive barrier) and low volume fractions, the static structure factor, $S(k)$, displays a peak at around $k_0 \simeq 2$. This feature is due to the fact that the competing short-range attraction and long-range repulsion produce stable clusters of a typical size. The presence of a typical size clearly appears in the cluster size distribution, $n(s)$, plotted in figure 2 at $k_B T = 0.2\epsilon$ and $\phi = 0.13$. It is interesting to observe the secondary peak due to the fusion of two stable clusters. By increasing the volume fraction ϕ, a spanning cluster appears at $\phi = 0.16$ for $k_B T = 0.2\epsilon$, and the cluster size distribution typically displays a power-law decay with an exponent $\tau \simeq 2.18$, consistent with the random percolation model [24]. In figure 3, we show the dependence of the cluster size, s, on its radius, r, at ϕ_p: the data correspond to a compact structure for clusters of dimension $s \lesssim 10$ and radius $r \lesssim 1$, a fractal dimensionality $d_f \simeq 1.2$ on intermediate length scales, and a crossover to $d_f \simeq 2.5$ at larger length scales. These results suggest that, at low volume fraction, compact stable clusters form with typical size $s \simeq 10$ and radius $r \simeq 1$. By increasing the volume fraction, a residual attractive interaction between the clusters produces tube-like structures with fractal dimension $d_f \simeq 1.2$ up to a size $s \sim 60$. By further increasing the volume fraction, these structures coalesce to build a random percolating network. From the time autocorrelation functions of density fluctuations $f_q(t)$ and of the bonds $B(t)$, we calculate
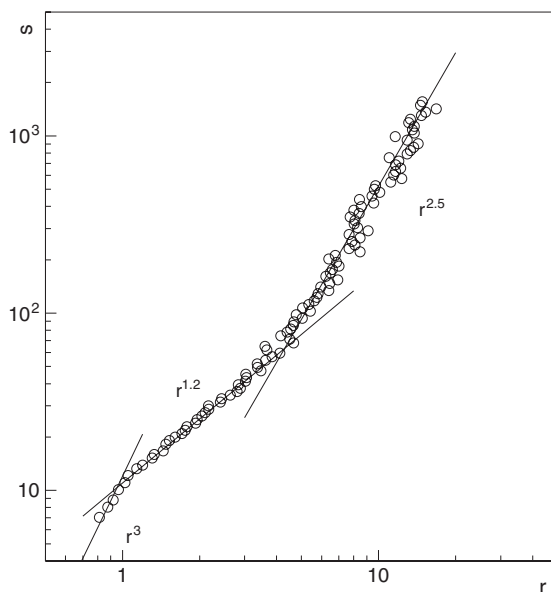
Figure 3. The cluster size, s, as a function of the radius, r, at $k_B T = 0.2\epsilon$ and $\phi = 0.16 \simeq \phi_p$: while at very small scales clusters are compact, on intermediate length scales the dependence suggests the presence of very thin and chain structures made up by clusters of typical size $s \lesssim 10$; it crosses over to a random percolation type of structure over larger length scales.
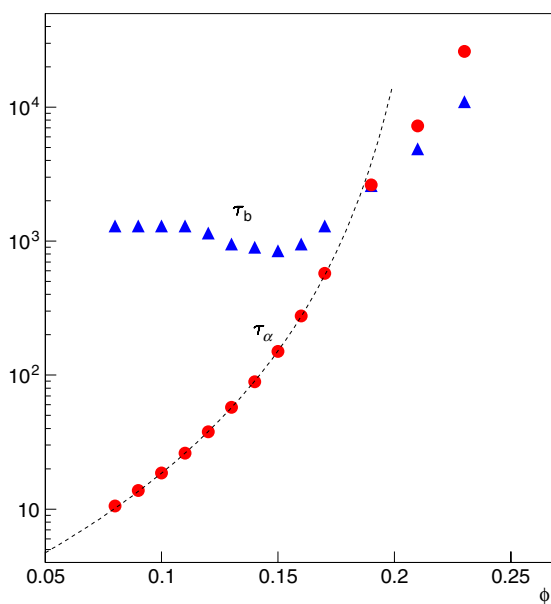

Figure 4. The bond lifetime, τ_b, and the relaxation time, τ_α (in units of MD steps) as a function of the volume fraction ϕ at $k_B T = 0.25\epsilon$. The curve in figure is a power-law fit, $(\phi_c - \phi)^{-\gamma}$, with $\phi_c \simeq 0.22$ and $\gamma \simeq 4.0$.

the relaxation time τ and the bond lifetime τ_b, which is not tuned as an external parameter in this case but results from the aggregation process. In figure 4, the relaxation time τ obtained for the

wavevector $q \simeq 2$ is plotted as function of the volume fraction together with the bond lifetime $\tau_b(\phi)$ at the low temperature $T = 0.25$. Over these length scales, at low volume fractions, i.e. below the percolation threshold, the bond lifetime is significantly larger than the relaxation time and the last one increases following a power law close to the percolation threshold. Close to the percolation threshold, on the timescale of the structural relaxation time, the bonds cannot be considered to be permanent anymore and we observe a crossover to a different dynamic regime. This interpretation is in agreement with the picture proposed above, supporting the idea that two different mechanisms—the formation of long-living structures and the crowding of the particles—may be responsible for the slow dynamics in attractive colloidal systems, producing different dynamical regimes at different volume fractions. It is also interesting to mention that, in colloidal systems with competing attractive and repulsive interactions, the formation of a long-living gel network may interfere with the formation of modulated structures and ordered phases, therefore producing a more complex scenario for the dynamics. Here we have focused on the fact that, at low volume fractions, the slow dynamics is crucially related to the formation of long-living clusters, providing evidence for the percolation nature of the colloidal gel transition at low temperatures. This scenario has been confirmed by recent experiments [7] and other molecular dynamics studies [25]. Finally, at higher temperatures, when the bond lifetime does not play any role, structural arrest will occur at higher volume fractions and will eventually be due to the hard sphere component of the potential, producing the crowding of the particles.

Acknowledgments

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