Model for Reversible Colloidal Gelation

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We report a numerical study, covering a wide range of packing fraction ϕ and temperature T, for a system of particles interacting via a square well potential supplemented by an additional constraint on the maximum number $n_{\max}$ of bonded interactions. We show that, when $n_{\max} < 6$, the liquid-gas coexistence region shrinks, giving access to regions of low ϕ where dynamics can be followed down to low T without an intervening phase separation. We characterize these arrested states at low densities (gel states) in terms of structure and dynamical slowing down, pointing out features which are very different from the standard glassy states observed at high ϕ values.

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Extensive investigations have recently focused on slow dynamics in colloidal systems, triggered by the experimental discovery of multiple mechanisms leading to a disordered arrested state. At high packing fraction ϕ, arrest takes place via a glass transition process, which can be driven by jamming, as in hard-sphere (HS) systems, or by attractive bonding between colloidal particles, generating the so-called "attractive glass" [1–3]. At low ϕ, arrest takes place via particle clustering [4] and formation of an amorphous state of matter—named a gel—able to support weak stresses [5]. Clustering and gelation have no counterpart in atomic or molecular systems, being induced by the presence of attractive interactions between particles, with a range of interaction much smaller than the particle size.

Recently, several studies have addressed the question of the routes to the gel state in colloidal systems [6–12]. In most models proposed so far, phase separation or microphase separation provides the initial step of the gelation process. For short-ranged attractive colloids, at low ϕ and temperature T, the phase diagram is characterized by a flat phase-coexistence curve (e.g., see Fig. 1). A quench inside the two-phase region induces, via spinodal decomposition, a separation into colloid rich (liquid) and colloid poor (gas) phases. However, in appropriate conditions, dynamical arrest in the denser region (of the attractive glass type) intervenes by freezing the pattern generated during the coarsening process. The time to arrest and the structure of the formed gel depends on ϕ and on the interaction strength. The connection between gelation and phase separation [13–17] is supported by the experimental observation of a peak in the scattered intensity at small wave vectors [4,18]. In the case of phase separation induced gelation, the slowing down of the dynamics associated with the formation of an arrested state cannot be continuously followed through equilibrium states, since gelation takes place only after a quench inside the coexistence region. This is different from the slowing down of the dynamics on approaching the glass transition at high densities, for which the ϕ and the T dependence of the slow dynamics can be characterized in terms of (metastable) equilibrium states in a reproducible and reversible way.

In principle, gelation could also occur in the absence of any phase separation, if the liquid-gas separation is suppressed or if the gel line is encountered before the liquid-gas coexistence locus [6], preventing phase separation. In these cases, the approach to the gel state could be in principle followed in equilibrium and reversibly. Some experimental groups [18] do indeed favor this interpretation, explaining the increase in the scattered intensity as intrinsically due to the inhomogeneities associated with the gel structure, posing a challenge to theoreticians to develop a model where arrest at low ϕ is observed in the absence of a phase separation mechanism and in which reversible physical gelation can be studied in equilibrium.

In this Letter, we introduce and numerically study a simple model showing that dynamical arrest at low ϕ (as low as 0.2) can indeed be generated in the absence of phase

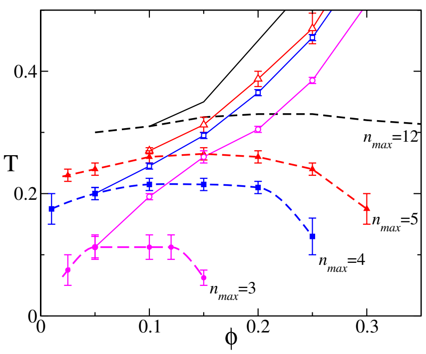

FIG. 1 (color online). Spinodal (dashed lines) and percolation (solid lines) loci (with reported error bars) for $n_{\max} = 3$ (circles), 4 (squares), 5 (triangles), and 12 (no symbols). Lines are a guide to the eye.

separation. We follow, via extensive simulations, the evolution in equilibrium of the density autocorrelation functions to point out the differences in the dynamics of a gel and of a glass, and to provide a way of discriminating between the two phenomena.

We study a modification of the short-range square well (SW) potential, by adding a constraint which limits the maximum number of bonds $n_{\max}$ that can be formed by the particles [19]. Without the constraint, each particle could in principle interact simultaneously with the maximum number of neighbors allowed by geometrical packing ($n_{\max} = 12$). The constraint switches off the attractive well potential when any of the two interacting particles has already $n_{\max}$ bonded neighbors. In this way, the energy difference between particles located in the interior of an aggregate and particles at the aggregate surface can be decreased and even suppressed. As a result, the surface tension decreases [20], the driving force for phase separation is significantly reduced, and open structures are favored. We find that, for $n_{\max} < 6$, the system can access the ϕ region usually dominated by phase separation and experience a dynamical slowing down by several orders of magnitude, thus entering the gel regime. Remarkably, the system undergoes the fluid-gel transition *in equilibrium*, so that the process is fully reversible.

We perform event-driven molecular dynamics (MD) simulations of particles interacting via a maximum valency model [21], i.e., a SW potential, where particles can form a maximum number of bonds $n_{\max}$. We fix the depth $u_0 = 1$ and the width $\Delta/(\sigma + \Delta) = 0.03$, with $\sigma = 1$ being the particle hard-core diameter. The square well form of the potential unambiguously defines bonded particles when particle centers lie within a distance $\sigma < r < \sigma + \Delta$ from each other. When a particle is already bonded to $n_{\max}$ neighbors, the well interaction with other particles is switched off, leaving only the HS potential. We simulate a large system containing $N = 10^4$ particles of mass $m = 1$ to minimize finite size effects. Temperature is measured in units of u_0, and time t in units of $\sigma(m/u_0)^{1/2}$. For all simulated state points, we first equilibrate the system at constant T until the potential energy and pressure P of the system have reached a steady state, and particles have diffused several σ's on average. Then, a production run is performed at constant energy. An average over typically 100 different realizations is done to gather statistics. We focus on the cases $n_{\max} = 3$, 4, and 5, since $n_{\max} = 6$ behaves similarly to the unconstrained case as far as liquid-gas phase separation is concerned. We perform MD simulations to efficiently propagate the system in time, even if Brownian dynamics (BD) would give a more realistic description of the short time dynamics. As far as slow dynamics is concerned, MD and BD are equivalent [22,23].

We report in Fig. 1 the evolution of the spinodal line for different $n_{\max}$ in the (ϕ, T) plane. We estimate the spinodal line by bracketing it with the last stable state point and the first phase separating state point along each isochore. The last stable state is characterized by a value of the structure factor at low q of the order of 10. We confirm the location of the spinodal by detecting the vanishing of the derivative of $P(V)$ along isotherms. The unstable area in the (ϕ, T) plane shrinks on decreasing $n_{\max}$, showing that the additional constraint opens up a significant portion of phase space, where the system can be studied in equilibrium one-phase conditions. The ϕ at which phase separation is not present, at all T, can be as low as $\phi \approx 0.20$ for $n_{\max} = 3$ [24], $\phi \approx 0.30$ for $n_{\max} = 4$, and $\phi \approx 0.35$ for $n_{\max} = 5$. Figure 1 also shows the percolation lines, calculated as the loci where 50% of independent configurations are characterized by the presence of a spanning cluster of bonded particles. The percolation loci also shift to lower T on decreasing $n_{\max}$, always ending in the spinodal on the low ϕ side.

As shown by the data in Fig. 1, the addition of the constraint on the maximum number of bonds, by suppressing the phase separation, makes it possible to study the dynamics of the model at very low T, where the lifetime of the interparticle bond increases, stabilizing for longer and longer time intervals the percolating network [25]. When the bond lifetime becomes of the same order as the observation time, the system will behave as a disordered solid. It is worth stressing that in the present model there is no thermodynamic transition associated with the onset of a gel phase [26]. To quantify these propositions, we study in the following the dynamics for all T in the ϕ region where the system is in a single phase.

Figure 2 shows the T dependence of the bond lifetime τ_B, defined as the time at which the bond autocorrelation function decays to 0.1, along different isochores for $n_{\max} = 3$, 4, and 5. The bond lifetime follows an Arrhenius behavior at low T, with an activation energy slightly increasing with $n_{\max}$, of the order of the bond energy, suggesting that breaking of one single bond is the elementary process. We do not observe any significant ϕ dependence, suggesting

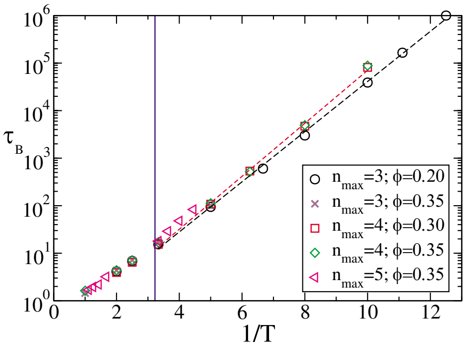

FIG. 2 (color online). Arrhenius plot of the bond lifetime τ_B for different values of $n_{\max}$ and ϕ. The vertical line indicates the lowest accessible T in the one-phase region for the unconstrained ($n_{\max} = 12$) case. Dashed lines are Arrhenius fits.

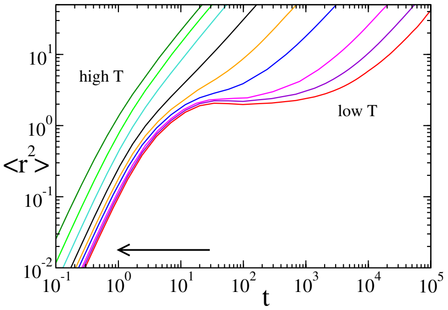

FIG. 3 (color online). $\langle r^2 \rangle$ for $n_{\max} = 3$ and $\phi = 0.20$ as a function of T. From left to right, T's are 1.0, 0.5, 0.3, 0.2, 0.15, 0.125, 0.1, 0.09, and 0.08. The arrow signals the typical plateau value for the HS glass.

that the bond breaking depends mostly on T [28] as well as on $n_{\max}$. All curves, for all reported $n_{\max}$ and ϕ, superimpose onto each other for high T, recovering the HS limit. The vertical line in Fig. 2 indicates the lowest T that can be reached before encountering the coexistence region for the unconstrained case. It is interesting to note that the introduction of a small $n_{\max}$ makes it possible to explore states with dynamics at least 4 orders of magnitude slower than without the constraint, allowing for an approach to arrested states from equilibrium conditions.

Figure 3 shows the T dependence of the mean squared displacement $\langle r^2 \rangle$. A T-independent plateau develops on cooling, indicating the presence of a localization length of order σ, much larger than the corresponding value typical of glass forming systems ($\langle r^2 \rangle \sim 0.01\sigma^2$). The localization length decreases on increasing ϕ. Caging in the gel is thus induced neither by the bond length (Δ) nor by the nearest-neighbor distance, and hence it is significantly different from the case of attractive and repulsive glasses [1,3]. This feature signals the crucial role of connectivity in the gel transition.

To quantify the dynamical slowing down on approaching the gel transition, we study the normalized density autocorrelation functions $\phi_q(t) \equiv \langle \rho_q(t)\rho_{-q}(0)\rangle / S(q)$. Figure 4 shows the behavior of $\phi_q(t)$ on decreasing T. A striking dependence on q is observed, a feature missing in the slow dynamics close to the glass transition. If we focus, as typically done in glass transition studies, on the q value of the first peak of $S(q)$, corresponding to the inverse average nearest-neighbor distance, we observe no sign of a plateau in $\phi_q(t)$, within the precision of our calculations (left panel of Fig. 4). However, at smaller q values, a clear plateau, named f_q, in analogy with its counterpart for the glass transition, where it is usually named the nonergodicity factor, emerges at a T that varies with q. This behavior is profoundly different from what is observed in a standard glass transition, but closely resembles what is observed at a percolation transition in the presence of chemical (infinite lifetime) bonds [12,29]. We find that the T dependence of the relaxation time τ_α [defined as the time at which $\phi_q(t)$ reaches the value 0.1] crosses over from $\tau_\alpha \sim 1/\sqrt{T}$ at nearest-neighbor distances to $\tau_\alpha \sim e^{1/T}$ at large length scales. For small q, τ_α is coupled to the bond lifetime, while at larger q, τ_α is controlled by the microscopic time scale (proportional to the thermal velocity). Figure 5 shows the T dependence of the plateau value f_q (calculated as the amplitude of a stretched exponential fit to the slow relaxation) for various q's (left panel), and compares its q dependence with f_q's typical of HS and attractive glasses [30] (right panel). While in the case of glasses (either HS or attractive) f_q is significantly different from zero at all physically relevant q values, in the present case f_q is significantly different from zero only at very small wave vectors. It is also interesting to observe that, while in the case of glasses f_q jumps from zero to a finite value at the glass transition, in the present case f_q appears to grow smoothly from zero.

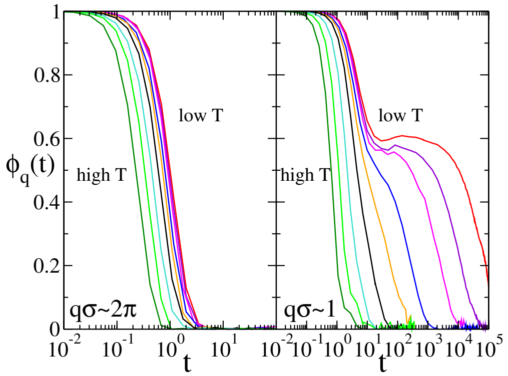

FIG. 4 (color online). Density autocorrelation functions $\phi_q(t)$ for $n_{\max} = 3$ and $\phi = 0.20$ as a function of T (sequence of values as in Fig. 3), respectively, for $q\sigma \sim 2\pi$ (left panel) and $q\sigma \sim 1$ (right panel). Note the difference in the T dependence of τ_α in the two cases.

In summary, we have proposed an off-lattice model which allows the study of dynamical arrest at low ϕ

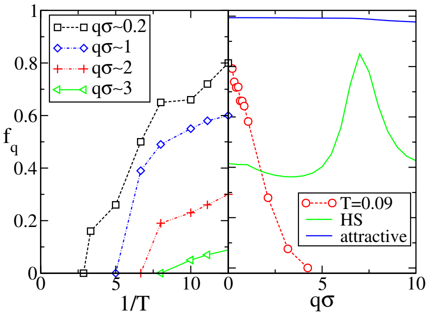

FIG. 5 (color online). Left panel: Plateau height f_q for $n_{\max} = 3$ and $\phi = 0.20$ as a function of T, for different values of $q\sigma$. At a given T, $f_q \neq 0$ at small q. At larger q, though $q\sigma$ is still smaller than 2π (nearest-neighbor length scale), $f_q = 0$ within the accuracy of the data. Right panel: f_q at $T = 0.09$, $\phi = 0.20$, $n_{\max} = 3$, compared with f_q of attractive and HS glass [30].

(physical gelation) in the absence of macrophase or microphase separation, effectively decoupling the effects of phase separation from the dynamical slowing down. The process of arrest can be followed in equilibrium. This condition offers the possibility of studying the behavior of the density correlators and of the mean squared displacement close to the gel transition, which is strongly coupled to the bond dynamics. We discover significant differences between glasses and gels in terms of the decay of the density correlation functions and of the localization length, which could be studied experimentally to discriminate between the phase separation route and the *single phase* reversible gelation case.

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[1] K. N. Pham *et al.*, Science **296**, 104 (2002); Phys. Rev. E **69**, 011503 (2004).

[2] T. Eckert and E. Bartsch, Phys. Rev. Lett. **89**, 125701 (2002).

[3] F. Sciortino, Nat. Mater. **1**, 145 (2002).

[4] P. N. Segrè *et al.*, Phys. Rev. Lett. **86**, 6042 (2001).

[5] N. A. M. Verhaegh, D. Asnaghi, and H. N. W. Lekkerkerker, Physica (Amsterdam) **264A**, 64 (1999).

[6] J. Bergenholtz and M. Fuchs, Phys. Rev. E **59**, 5706 (1999).

[7] J. Bergenholtz, W. C. K. Poon, and M. Fuchs, Langmuir **19**, 4493 (2003).

[8] K. Kroy, M. E. Cates, and W. C. K. Poon, Phys. Rev. Lett. **92**, 148302 (2004).

[9] F. Sciortino *et al.*, Phys. Rev. Lett. **93**, 055701 (2004).

[10] A. Coniglio *et al.*, J. Phys. Condens. Matter **16**, S4831 (2004); N. Sator *et al.*, cond-mat/0312591.

[11] A. M. Puertas, M. Fuchs, and M. E. Cates, Phys. Rev. Lett. **88**, 098301 (2002); Phys. Rev. E **67**, 031406 (2003).

[12] E. Del Gado *et al.*, Europhys. Lett. **63**, 1 (2003); Phys. Rev. E **69**, 051103 (2004).

[13] M. T. A. Bos and J. H. J. van Opheusden, Phys. Rev. E **53**, 5044 (1996).

[14] D. Sappelt and J. Jackle, Europhys. Lett. **37**, 13 (1997).

[15] J. F. M. Lodge and D. M. Heyes, J. Chem. Soc., Faraday Trans. **93**, 437 (1997); Phys. Chem. Chem. Phys. **1**, 2119 (1999).

[16] K. G. Soga, J. R. Melrose, and R. C. Ball, J. Chem. Phys. **110**, 2280 (1999).

[17] E. Zaccarelli *et al.*, *Unifying Concepts in Granular Media and Glasses* (Elsevier, Amsterdam, 2004), p. 181.

[18] S. A. Shah *et al.*, Langmuir **19**, 5128 (2003); J. Phys. Condens. Matter **15**, 4751 (2003).

[19] An experimental counterpart of this model can be found in particles with “sticky spots” [D. J. Pine (private communication)].

[20] T. L. Hill, *An Introduction to Statistical Thermodynamics* (Dover, New York, 1987).

[21] See, for example, R. J. Speedy and P. G. Debenedetti, Mol. Phys. **81**, 237 (1994); **88**, 1293 (1996). However, we do not impose any constraint on minimal bonded loops.

[22] T. Gleim, W. Kob, and K. Binder, Phys. Rev. Lett. **81**, 4404 (1998); G. Foffi *et al.*, Phys. Rev. Lett. **94**, 078301 (2005).

[23] We confirm that the T dependence of τ_B and the q dependence of f_q are independent from the microscopic dynamics by performing additional simulations for a system of 1000 colloidal particles and 10000 ghost particles. The ghost particles mimic the real solvent particles; see Y. Zhou, M. Karplus, J. M. Wichert, and C. K. Hall, J. Chem. Phys. **107**, 10 691 (1997).

[24] The T dependence of the static structure factor shows on cooling: (i) an increase of the intensity at small wave vectors, which saturates to a constant value when most of the bonds have been formed; (ii) a progressive structuring of peaks at $q\sigma \sim 2\pi$ and multiples thereof. The first feature indicates the presence of large inhomogeneities, characterizing the *equilibrium* structure, an echo of the nearby phase separation. The second indicates that particles progressively become more and more correlated.

[25] S. K. Kumar and J. F. Douglas, Phys. Rev. Lett. **87**, 188301 (2001).

[26] The important issue of the thermodynamic nature of the gel transition has been recently reviewed in Ref. [27]. In our model, the free energy can be calculated numerically with high precision from high T, where the system reduces to a HS fluid, down to very small T, where particles are fully connected into a single cluster. Indeed, the finite bond lifetime guarantees equilibrium even well within the geometric percolation region. The free energy and its derivatives are continuous in the entire T range, proving that across the gelation transition there is no thermodynamic transition. A locus of specific heat extrema, arising from the two-state origin of particle bonding, is present in the phase diagram around $T/u_0 \approx 0.25$. Our model strongly supports the view that gelation is a connectivity transition (see Fig. 3) with no thermodynamic character. Indeed, the cluster size distribution at the percolation transition is consistent with random bond percolation. We find the cluster size distribution $n_s \sim s^{-\tau}$, with $\tau = 2.20 \pm 0.05$, to be compared with the theoretical value $\tau = 2.18$.

[27] M. Rubinstein and A. V. Dobrynin, Curr. Opin. Colloid Interface Sci. **4**, 83 (1999).

[28] R. J. Speedy and P. G. Debenedetti, Mol. Phys. **86**, 1375 (1995).

[29] I. Saika-Voivod *et al.*, Phys. Rev. E **70**, 041401 (2004).

[30] The shown f_q's for the HS and attractive glass are results of the mode coupling theory solved within Percus-Yevick closure for the SW potential. See, for example, K. Dawson *et al.*, Phys. Rev. E **63**, 011401 (2001).