Equilibrium Route to Colloidal Gelation: Mixtures of Hard-Sphere-Like Colloids

Ph. Germain and S. Amokrane

Laboratoire de Physique des Liquides et Milieux Complexes, Faculté des Sciences et Technologie, Université Paris Est (Créteil),
61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France

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The binodals and the nonergodicity lines of a binary mixture of hard-sphere-like particles with a large size ratio are computed for studying the interplay between dynamic arrest and phase separation in depletion-driven colloidal mixtures. Contrary to the case of hard core plus short-range effective attraction, physical gelation without competition with the fluid-phase separation can occur in such mixtures. This behavior due to the oscillations in the depletion potential should concern all simple mixtures with a nonideal depletant, justifying further studies of their dynamic properties.

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The question of gelation in soft condensed matter systems has been the subject of a lively debate in the past few years [1–8]. On the one hand, following the extension of the conceptual framework developed for ordinary glasses [9,10], a broad picture of the arrest in soft matter ones has emerged from the recent literature [11]. In comparison with the ‘‘repulsive’’ glasses in which the arrest is driven mostly by repulsions (‘‘caging’’ mechanism), soft matter ones exhibit also a transition to different glassy states driven by short-range effective attractions (‘‘bonding’’ mechanism). At least in the effective fluid approach, such effective attractions, defined in a broad way, exist in a variety of colloidal suspensions, as, for example, globular proteins, colloidal silica or colloid-ideal polymer mixtures, etc. (see, for example, respectively [12–15]). Despite their quite different origins and shapes, these attractions could lead to attractive glasses—or gels at low density—provided that their range is short enough.

On the other hand, the interplay between such arrested states and the equilibrium phase transitions in colloidal systems is not completely established. The possibility for colloids with short-range attraction to form equilibrium physical gels—that is, reversible gels in the equilibrium fluid phase—has indeed been questioned, since this attraction plays also a role in the fluid-fluid phase separation. These questions have been analyzed theoretically mostly on the basis of generic model potentials (square well, Yukawa potential, etc.) that retained only what seemed the most significant feature of the effective interaction: the short range. For such simple models, increasing the attraction strength also favors the fluid-fluid transition. The question is then to know if gelation should occur outside the fluid-fluid coexistence domain, setting aside a possible crystallization. Early mode coupling theory (MCT) studies [9] answered positively for sufficiently short attraction ranges [8,11,16] (similar observations were also made on less asymmetric mixtures [17,18], for which a multicomponent view is, however, more suitable). Nevertheless, subsequent numerical simulations showed that the glass line intercepts in fact the fluid-fluid binodal for such short-range potentials (see [1] for a review). From the ensuing scaling with the attraction range of the dynamics and of the static transition lines, a new paradigm was developed according to which physical gelation—associated with short-range attraction—would be observed only through an arrested fluid-fluid phase separation [1–3]. It should apply to all of the systems for which this picture of the interactions—essentially, a hard core repulsion and a very short-range attraction—holds, as those mentioned above [12–15]. Very recent experiments seem to corroborate this paradigm [13,19,20], though some previous studies [6,7,21] are compatible with the opposite view. This motivated the search of a more complex interaction in order to favor equilibrium gelation (long-range electrostatic repulsion [22], ‘‘patches’’ [23], etc.).

The purpose of this Letter is to revisit this view focused on ‘‘short-range attractive colloids’’ and the resulting correlation between gelation and phase separation. We first show that the reduction of the effective interaction to a hard core plus a short-range attraction is in fact insufficient for discussing the interplay between dynamic arrest and phase instability in these systems. The simple example of an asymmetric binary mixture of hard spheres will show that the characteristics of the effective potential (range, depth, repulsive barriers, etc.) can affect differently the nonergodicity and phase transition lines: while preserving gelation, this may go up to suppressing the fluid-fluid coexistence and hence the very question of their competition. The behavior of real ‘‘depletion’’ mixtures can thus strongly depart from that observed when the depletion effect is reduced to the short-range attraction, as for the Asakura-Oosawa (AO) potential in colloid-*ideal* polymer mixtures. This considerably widens the scenarios for the interplay between the gelation and the equilibrium phase transition in colloids. We also show in this manner that simple binary mixtures of hard colloids might fulfil the conditions for equilibrium gelation, since the effective potential is there complex enough. Its oscillations at the scale of the small particles stabilize the physical bonds—due to the repulsive barrier close to contact—and remove the fluid condensation for some size ratios. While these well-known oscillations are often neglected in the literature, we predict situations in which they actually lead to equilibrium gelation.

The binodals and the nonergodicity transition lines have been computed for a model binary mixture, in the effective one-component fluid representation (see [24] for details). The thermodynamic variables are the big particle packing fraction η_b, the small particle density in the reservoir ρ_s^*, and the temperature T. The total effective potential between the colloids is the sum of the direct interaction potentials and the indirect one, computed at infinite dilution from the RHNC (reference hypernetted chain) integral equation. The RHNC and RHNC/variational perturbation free energies were used to compute the fluid-fluid and the fluid-solid binodals, respectively, in the (η_b, ρ_s^*) plane. The accuracy of this method has been established for the size ratios investigated here (see, e.g., [25–27]).

The nonergodicity transition line was computed from the MCT using the RHNC static structure factors. The one-component MCT for gelation in mixtures raises two different questions: first, that of its reliability in the vicinity of the fluid-fluid phase transition, due to the critical density fluctuations (see [8] for a discussion and [28] for simulations). This should not, however, constitute a problem here, since we precisely consider situations in which there is no fluid condensation. In the same situations, the question of cluster aggregation that occurs at very low density should also not arise. The second question concerns the reduction of the mixture to an effective one-component fluid. Qualitatively, the fluid of small spheres is expected to be ergodic in the free volume for the size ratios and the densities considered here ($\eta_s^* < 0.4$). The use of an effective potential in these situations is also substantiated by adiabaticity arguments [29]. More quantitatively, recent studies of star polymer mixtures [30] and simulations [31] partly support this view. Finally, due to the absence of fluid condensation in all of the situations we discuss here, a possible involvement of the small spheres in the arrest—above some packing fraction—should make gelation occur at an even lower packing fraction of the big ones than in the one-component representation. This would just reinforce our conclusions on gelation in these systems.

We first present the phase diagram of the hard-sphere (HS) mixture with diameter ratio $q = \sigma_2/\sigma_1 = 5$ (Fig. 1). A comparison with the AO model is also presented (inset) for the fluid-fluid transition and the nonergodicity lines. We observe for the HS mixture a quite distinct pattern, in comparison with the AO or other generic short-range potentials: first, in the HS mixture, the fluid-fluid binodal is absent (none is found at size ratios $q \leq 8$ [26,32]), and, second, the nonergodicity line is shifted to lower packing fractions (for $\rho_s^* = 0.8$, we find $\eta_g = 0.32$ and 0.19 for $q = 5$ and 8, respectively). Since the fluid-fluid instability is absent, one should thus observe gelation in the equilibrium homogenous fluid, provided that crystallization is prevented by a small amount of polydispersity [33]. This is in sharp contrast with the behavior found with the AO model, for which the metastable fluid-fluid binodal exists, and the nonergodicity transition is confined to the dense fluid region (the behavior observed with the present MCT for $\rho_s^* > 0.6$ should be taken with care, as it occurs just below the fluid-fluid transition [7,8]). These features are typical of usual models of attractive potentials with a moderate range [8,16]: while the fluid-fluid binodal is metastable with respect to the fluid-solid one due to the short range, this range is not short enough to induce low density gelation. In the HS mixture, on the contrary, gelation is observed, while the fluid condensation disappears.

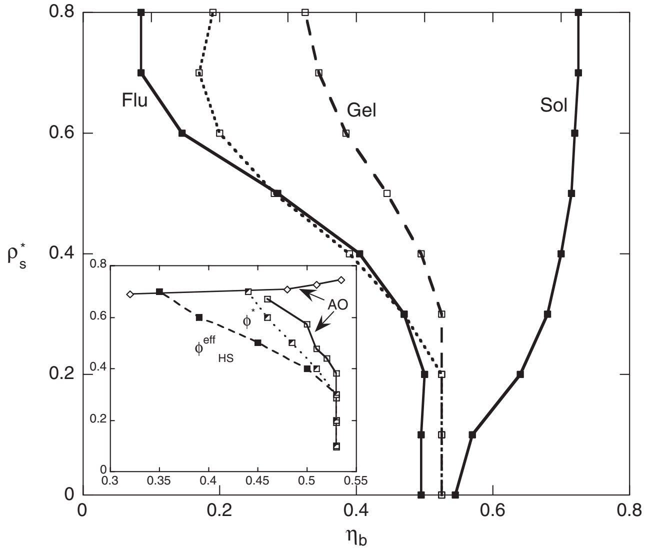

FIG. 1. Phase diagram of the effective fluid for $q = 5$. Solid lines: binodals; dashed line: nonergodicity line (dotted line: $q = 8$). Inset: Fluid-fluid binodal and nonergodicity lines for the Asakura-Oosawa (solid line), HS depletion potentials (long-dashed line), and truncated potential ϕ^* (short-dashed line). The fluid-fluid binodal (diamonds) is present only for the AO model.

This specific behavior of the mixture of hard colloids may now be correlated with the characteristics of the hard-sphere depletion potential. Here the repulsion between the small hard particles, ignored in AO model, leads to a more complex behavior of the HS depletion potential $\phi_{\mathrm{HS}}^{\mathrm{eff}}$. In place of a single well with range $1/q$, $\phi_{\mathrm{HS}}^{\mathrm{eff}}$ is oscillatory with repulsive barriers and wells varying in a complex way with q and ρ_s^*. Concerning the gelation line, one expects some influence of the repulsive barriers of $\phi_{\mathrm{HS}}^{\mathrm{eff}}$ (Fig. 2). The most important one is located right after the depletion well. Its magnitude $\Delta\varepsilon^{\mathrm{rep}}$ becomes comparable to the depletion well depth $\Delta\varepsilon^{\mathrm{att}}$ when ρ_s^* increases. The consequences on gelation are shown in the inset in Fig. 1, which compares the nonergodicity transition lines for the

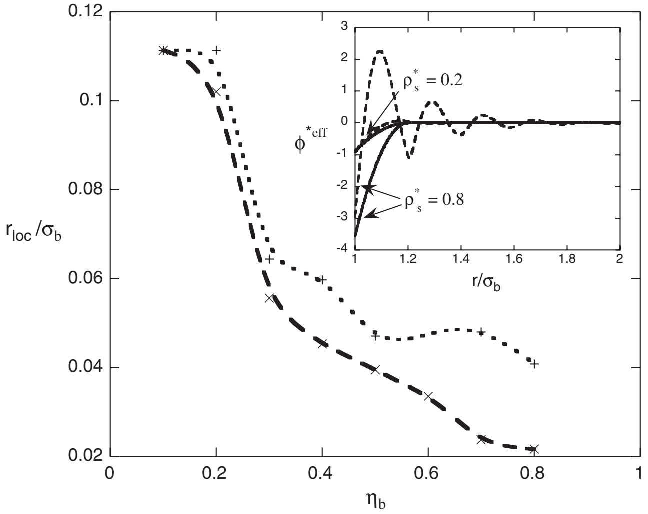

FIG. 2. Big particle localization length along the nonergodicity line for $q = 5$. Long-dashed line: HS mixture depletion potential; short-dashed line: truncated potential, ϕ^*. Inset: Effective potential (k_BT units) for the HS mixture (dashed line) and the Asakura-Oosawa one (solid line), for $\rho_s^* = 0.2$ and 0.8.

full depletion potential $\phi_{\rm HS}^{\rm eff}$ and for a truncated version ϕ^* (without barriers): $\phi^*(x \leq \delta) = \phi_{\rm HS}^{\rm eff}(x)$ and $\phi^*(x > \delta) = 0$, with $x = (r - \sigma_b)/\sigma_b$ the reduced distance and δ^* the reduced width of the attractive well. For ϕ^*, the nonergodic state is confined to the dense region, as for the AO potential. The repulsive barrier favors thus arrest at lower density. A simple interpretation of this observation is that the barrier stabilizes the "bonds" by making it more difficult for the particles to escape from the depletion well. For example, for $\rho_s^* = 0.8$, the energy $\Delta\varepsilon = \Delta\varepsilon^{\rm att}$. $\Delta\varepsilon^{\rm rep}$ associated to such a bond is $\Delta\varepsilon \approx 5.4k_BT$, instead of $\Delta\varepsilon \approx 3k_BT$ for ϕ^* (Fig. 2). This interpretation is substantiated by the behavior of the localization lengths $r_{\rm loc}$ of the two models [computed here from the simple Gaussian approximation $f_q \approx \exp(-q^2 r_{\rm loc}^2/6)$ of the nonergodicity factor [6]]: along the nonergodicity transition line, $r_{\rm loc}$ is indeed systematically smaller with $\phi_{\rm HS}^{\rm eff}$ than with ϕ^*.

Now, is the repulsive barrier the unique ingredient to stabilize equilibrium gelation? The role of barriers has indeed already been pointed out for this purpose. They are, for example, artificially introduced in numerical simulations for stabilizing homogenous gelation against fluid condensation [34]. Besides the fact that the barriers are here real, an important difference is that, in our case, they are irrelevant for the question of the fluid condensation, which is absent both with ϕ^* and with $\phi_{\rm HS}^{\rm eff}$. This absence is due to the reduction with ρ_s^* of the width of the attraction well (inset, Fig. 2): for $\rho_s^* = 0.8$, e.g., this width is about 4 times smaller than its low density limit $\delta^{(0)} \approx \frac{1}{q}$, the AO density independent value. This is why the fluid condensation is absent for $\phi_{\rm HS}^{\rm eff}$ and not for $\phi_{\rm AO}$. Homogenous gelation in the hard-sphere mixture results thus from a subtle mechanism: on the one hand, the repulsive barrier favors arrest at lower density by stabilizing the bonds, and, on the other hand, the fluid condensation is suppressed by the simultaneous reduction with ρ_s^* of the width of the attraction well.

Both in order to test the robustness of these conclusions and to anticipate the behavior of real suspensions, we have considered mixtures of hard spheres with a very short-range tail in the interaction potential between unlike ones: $\frac{V_{\rm sb}(r)}{k_BT} = \varepsilon^* \frac{\sigma_{\rm sb}}{r} \exp(-\frac{r-\sigma_{\rm sb}}{\xi_{\rm sb}})$. We took values typical of "residual" interactions in hard-sphere-like colloids (say, via the surface layers as in sterically stabilized ones or charge screening with very small range [35]): $\varepsilon^* = \pm 1.5$ and $\xi_{\rm sb} = \frac{\sigma_s}{100}$. With $q = 5$, this corresponds, for example, to $\sigma_s = 0.2\ \mu$m, $\sigma_b = 1\ \mu$m, and $\xi_{\rm sb} = 2$ nm [35]. Such *a priori* "small" interactions can have, in fact, important consequences on the binodals at high size asymmetry (see [35] for $q = 10$). We show in Fig. 3 the situation for $q = 5$. The fluid-fluid transition remains absent, as with pure hard spheres. The gel line is moderately shifted towards lower (greater) values of η_b according to the sign of $V_{\rm sb}$, a natural consequence of the enhancement or the reduction induced by solvation of the depletion mechanism. This does not modify qualitatively the picture relative to pure hard spheres, contrarily to the case $q = 10$. On this basis, it seems reasonable to predict that an equilibrium gel can form in mixtures of hard-sphere-like colloids with moderate asymmetry ($q \sim 5$), irrespective of the details of the residual interactions.

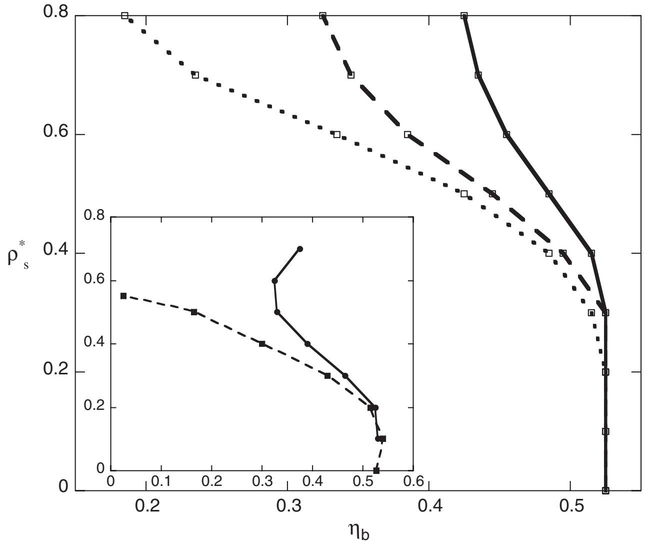

FIG. 3. Gelation lines of a mixture of hard-sphere-like particles for $q = 5$ and small-big particle Yukawa potential with range $\xi_{\rm sb} = \frac{\sigma_{\rm sb}}{100}$. The contact value is $\varepsilon_{\rm sb} = 0$ (dashed line—pure hard spheres), $+1.5k_BT$ (dotted line), and $-1.5k_BT$ (full line). Inset: The same for $q = 10$. Dashed line: pure hard spheres; solid line: $\varepsilon_{\rm sb} = 1.5k_BT$.

In summary, we have studied the interplay between the arrested states at low density and the phase separations for mixtures of hard colloids. It is shown that the oscillations with separation between the particles of the effective interaction potential can be responsible for quite specific behaviors. In particular, the repulsive barriers provide a stabilizing mechanism of the physical bonds involved in gelation. As the fluid-fluid phase transition is not observed for some size ratios, gelation is predicted to occur without competition with the fluid condensation. Thus, the behavior of simple asymmetric mixtures can depart from that expected from the "hard core short-range attraction" picture. This observation should stimulate reconsideration at the experimental level of these already known systems (see [36]). They indeed have been much less considered in the literature than colloid-polymer mixtures, perhaps because of the greater convenience of using polymers as the depletant. At the theoretical level, additional simulations should be useful to assess the validity of the methods used to study gelation and, in particular, the quantitative predictions made here from the one-component mode coupling theory. If confirmed, it should have practical applications, besides the additional insight it provides on the mechanisms of arrest in soft condensed matter systems.

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