INVITED ARTICLE

Fluid–fluid demixing curves for colloid–polymer mixtures in a random colloidal matrix

Mario Alberto Annunziataa and Andrea Pelissettob*

aCNR, Istituto dei Sistemi Complessi (Area della Ricerca di Roma Tor Vergata), Via del Fosso del Cavaliere 100, I-00133 Roma, Italy and INFN, Sezione di Pisa, L.go Pontecorvo 3, I-56127 Pisa, Italy; bDipartimento di Fisica, Università degli Studi di Roma “La Sapienza” and INFN – Sezione di Roma I, Piazzale A. Moro 2, I-00185 Roma, Italy

(Received 28 June 2011; final version received 5 September 2011)

We study fluid–fluid phase separation in a colloid–polymer mixture adsorbed in a colloidal porous matrix close to the $q/C_18$ point. For this purpose we consider the Asakura–Oosawa model in the presence of a quenched matrix of colloidal hard spheres. We study the dependence of the demixing curve on the parameters that characterize the quenched matrix, fixing the polymer-to-colloid size ratio to 0.8. We find that, to a large extent, demixing curves depend only on a single parameter $f$, which represents the volume fraction which is unavailable to the colloids. We perform Monte Carlo simulations for volume fractions $f$ equal to 40% and 70%, finding that the binodal curves in the polymer and colloid packing-fraction plane have a small dependence on disorder. The critical point instead changes significantly: for instance, the colloid packing fraction at criticality increases with increasing $f$.

Finally, we observe for some values of the parameters capillary condensation of the colloids: a bulk colloid-poor phase is in chemical equilibrium with a colloid-rich phase in the matrix.

Keywords: polymer solutions; colloids; Asakura–Oosawa model; demixing; theta point

1. Introduction

The study of the fluid phases in mixtures of colloids and non-adsorbing neutral polymers has become increasingly important in recent years; see Refs. [1–6] for recent reviews, Refs. [7–19] for experiments, and Refs. [20–45] for theoretical investigations. These systems show a very interesting phenomenology, which only depends to a large extent on the nature of the solvent and on the ratio $q \equiv R_p/R_c$, where $R_p$ is the radius of gyration of the polymer and $R_c$ is the radius of the colloid. Experiments and numerical simulations indicate that polymer–colloid mixtures have a solid colloidal phase for large enough colloidal concentrations and a corresponding fluid–solid coexistence. Much less obvious is the presence of a fluid–fluid coexistence of a colloid-rich, polymer-poor phase (colloid liquid) with a colloid-poor, polymer-rich phase (colloid gas). Extensive theoretical and experimental work indicates that such a transition occurs only if the size of the polymers is sufficiently large, i.e. for $q > q^*$, where $[1,31,43] \approx 0.3–0.4$.

At least qualitatively, many aspects of the behavior of colloid–polymer suspensions can be understood by using the Asakura–Oosawa (AO) model [46,47], which gives a coarse-grained description of the mixture. The polymers are treated as an ideal gas of point particles of radius $R_p$ (which is usually identified with the radius of gyration) which interact with the colloids by means of a simple hard-core potential. This model is extremely crude since it ignores the polymeric structure and polymer–polymer repulsion, which is relevant in the good-solvent regime. Nonetheless, it correctly predicts polymer–colloid demixing as a result of the entropy-driven effective attraction (depletion interaction) between colloidal pairs due to the presence of the polymers [20–22,25,27–30,36,37]. It is not, however, quantitatively predictive for polymers in the good-solvent regime. For instance, at a given colloid packing fraction, the AO model predicts the binodal curve to be at a polymer volume fraction which is significantly lower than that observed experimentally. In order to reproduce the experimental results one can use realistic atomistic models for the polymers, but this is a very difficult task from a numerical point of view. In the colloid regime $q \lesssim 1$, it is much easier, and still provides good results, to use coarse-grained models in which polymers are modeled as point particles (as in the AO model) interacting with repulsive soft pair potentials [29,31,38,45], which have either a phenomenological origin or are derived by means of exact coarse-graining procedures. Nonetheless, at least for $q \lesssim 1$ (colloidal regime), the AO model is expected to provide...
quantitatively correct results for colloid–polymer solutions close to the $\theta$ point. Indeed, in this regime polymers show an approximate ideal behavior and can be described quite reasonably as non-interacting random walks, as does the AO model.\(^1\)

In this paper we wish to study the demixing of colloid–polymer mixtures in porous materials, which are characterized by a highly interconnected porous structure. They have important technological applications, for instance in catalysis and gas separation and purification.\(^2\) Examples are the Vycor glasses, in which pore sizes range from 1 nm to 100 nm, and high-porosity systems like silica gels (xerogels and aerogels), which are produced by means of silica sol-gel processes. AO colloid–polymer mixtures in a porous matrix have been studied in Refs. [52–56] by means of density-functional theory, integral equations, and Monte Carlo (MC) simulations. The nature of the critical transition has been fully clarified [53–56]: if obstacles are random and there is a preferred affinity of the quenched obstacles to one of the phases, the transition is in the same universality class as that occurring in the random-field Ising model, in agreement with a general argument by de Gennes [57]. If these conditions are not satisfied, standard Ising or randomly dilute Ising behavior is observed instead, see Refs. [58,59]. On the other hand, little is known on how demixing is influenced by the amount of disorder and by its nature (for a polymer matrix some results for the critical-point behavior as a function of the amount of disorder are reported in Ref. [53]). In this paper porosity is introduced by considering a quenched matrix of hard spheres of radius $R_{\text{dis}}$. We will compute the binodal curves in terms of the polymer and colloid packing fractions for different ratios $R_{\text{dis}}/R_c$ and for different disorder concentrations with the purpose of determining how these parameters affect the location of the demixing transition and of the critical (second-order) transition point. We will not instead perform a detailed study of the $q$ dependence and we shall set $q=0.8$ as in Ref. [55]. This work complements the results of Ref. [52], which instead studied the $q$ dependence for a single value of $R_{\text{dis}}/R_c$, $R_{\text{dis}}/R_c = 1$, and of the disorder concentration.

The paper is organized as follows. In Section 2 we discuss the model and the relevant variables. In Section 3 we present our numerical results. Our conclusions are presented in Section 4. In the Appendix we present some details of the MC calculation.

2. The model

In the AO model polymers and colloids are modeled as spheres of radii $R_p$ and $R_c$, respectively. We assume hard-sphere interactions between colloid and colloid–polymer pairs; the pair potentials are given by

\[
 u_{c,p}(r) = \begin{cases} 
 \infty & \text{for } r < 2R_c, \\
 0 & \text{for } r \geq 2R_c,
\end{cases}
\]

\[
 u_{p,p}(r) = \begin{cases} 
 \infty & \text{for } r < R_c + R_p, \\
 0 & \text{for } r \geq R_c + R_p,
\end{cases}
\]

\[
 u_{\text{pp}}(r) = 0,
\]

where $r$ is the center-to-center distance. We consider a cubic box of size $L$ and we characterize the thermodynamic phases in terms of the packing fractions

\[
 \eta_p = \frac{4\pi R_p^3 N_p}{3L^3}, \quad \eta_c = \frac{4\pi R_c^3 N_c}{3L^3},
\]

where $N_p$ and $N_c$ indicate the number of polymers and of colloids in the box, respectively.

The phase behavior of the AO model has been extensively studied. It strongly depends on the polymer-to-colloid size ratio $q \equiv R_p/R_c$. For small values of $q$ the demixing transition is unstable and only the fluid–solid transition occurs. Fluid–fluid demixing occurs [1,31,43] for $q \geq 0.3–0.4$. In this work we have not investigated the $q$ dependence of the binodal curve, since our main objective is the analysis of the role of quenched disorder. We have thus fixed $q=0.8$, as in Ref. [55], at the boundary between the colloid and the protein regimes.

Disorder has been introduced by considering a colloidal quenched matrix which has a hard-sphere interaction both with the colloids and the polymers. In practice, we choose a disorder concentration $c_{\text{dis}}$ and randomly distribute $N_{\text{dis}} = c_{\text{dis}} L^3$ non-overlapping spheres of radius $R_{\text{dis}}$ in the box. The position of these spheres is assumed to be fixed (quenched). Colloids and polymers can only move outside the quenched matrix, which means that the spheres belonging to the matrix and the freely moving particles interact with pair potentials

\[
 u_{c,\text{dis}}(r) = \begin{cases} 
 \infty & \text{for } r < R_c + R_{\text{dis}}, \\
 0 & \text{for } r \geq R_c + R_{\text{dis}},
\end{cases}
\]

\[
 u_{p,\text{dis}}(r) = \begin{cases} 
 \infty & \text{for } r < R_p + R_{\text{dis}}, \\
 0 & \text{for } r \geq R_p + R_{\text{dis}}.
\end{cases}
\]

Note that the matrices considered here are different from those discussed in Refs. [53,54]. The main difference is that here the matrix consists of hard spheres that cannot intersect each other (we call it a colloidal matrix). On the other hand, in Refs. [53,54] the matrix spheres are soft and can freely overlap, as if they were an ideal gas (hence the name polymer matrix). Second, in those works, for a given choice of $c_{\text{dis}}$, the number $N_{\text{dis}}$ is not fixed, but is obtained from
a Poissonian distribution with mean value \( c_{\text{dis}} L^3 \). This second difference should not be important in the infinite-volume limit, since it entails density fluctuations of order \( 1/L^{3/2} \), which vanish as \( L \to \infty \).

In the simple model we consider, disorder is characterized by two parameters, the reduced concentration \( \hat{c} \equiv c_{\text{dis}} R_c^3 \) and the ratio \( R_{\text{dis}}/R_c \). However, \( \hat{c} \) does not directly characterize the free space available to the colloids and to the polymers. We shall use instead the effective matrix filled-space ratio \( f \), which is defined as follows. Consider the region \( \mathcal{R} \) in which the (centers of the) colloids are allowed:

\[
\mathcal{R} = \{ \mathbf{r} : |\mathbf{r} - \mathbf{r}_i| \geq R_c + R_{\text{dis}}, \text{ for all } 1 \leq i \leq N_{\text{dis}} \},
\]

where \( \mathbf{r}_i \) is the position of the \( i \)-th hard sphere belonging to the matrix. If \( V_\mathcal{R} \) is the volume of the region \( \mathcal{R} \), we define

\[
f = 1 - \frac{[V_\mathcal{R}]}{L^3},
\]

where \([V_\mathcal{R}]\) is the average of \( V_\mathcal{R} \) over the different matrix realizations. Note that, for large values of \( L \), \([V_\mathcal{R}]\) is essentially independent of the matrix realization, a property known as self-averaging. The parameter \( f \) represents the volume fraction that is unavailable to the colloids due to the presence of the random matrix and can easily be determined by computing the probability of inserting a colloid in the otherwise empty matrix. In a completely analogous way we can define \( f_{\text{pol}} \), which characterizes the volume fraction unavailable to polymers. Of course, \( f > f_{\text{pol}} \) in the colloid regime in which \( q < 1 \), while \( f < f_{\text{pol}} \) in the opposite, protein regime.

It is interesting to understand qualitatively how the disorder distribution changes with \( R_{\text{dis}} \) at fixed \( f \). In Figure 1 we show the matrix for \( f = 0.5 \) and two values of \( R_{\text{dis}} \), \( R_{\text{dis}}/R_c = 0.1 \) and \( R_{\text{dis}}/R_c = 3 \). To make the figure clearer, we consider a two-dimensional system, that is a matrix of non-overlapping disks on a square of area \( L^2 \). It is evident that the topology of the matrix is quite different. For large \( R_{\text{dis}}/R_c \) the free volume available to the colloids consists of large empty regions connected by narrow channels. This is the case of a porous material with big interconnected pores. On the other hand, for \( R_{\text{dis}}/R_c \) small, pores are significantly smaller and the topology of the network is more complex.

In order to have demixing, the parameter \( f \) cannot be arbitrarily close to 1, but should satisfy \( f < f^* \), where \( f^* \) is related to the percolation threshold of the region \( \mathcal{R} \) in which colloids can move. For \( f > f^* \) the space \( \mathcal{R} \) divides into disconnected finite regions and thus no phase transition is possible. The exact value of \( f^* \) is unknown. However, the arguments of Ref. [60] suggest

\[
f^* \approx 0.85.
\]

For the same reasons – polymers should be able to move in the whole space – the polymer parameter \( f_{\text{pol}} \) must satisfy \( f_{\text{pol}} < f^* \) in order to observe coexistence.

In this paper we shall perform simulations for two values of \( f \), \( f = 0.40 \) and \( f = 0.70 \), the latter being quite close to the threshold \( f^* \), and for \( q = 0.8 \), so that \( f_{\text{pol}} < f \). In Table 1 we report the reduced concentration \( \hat{c} \) and the disorder packing fraction \( \eta_{\text{dis}} = 4\pi R_{\text{dis}}^3 c_{\text{dis}}/3 \) for several values of \( R_{\text{dis}}/R_c \). First, we observe that \( \hat{c} \) converges to a finite positive constant.
Table 1. Estimates of the reduced concentration \( \hat{c} \equiv c_d R_c^3 \) and of the disorder packing fraction \( \eta_{dis} \equiv 4\pi R^3_{dis}/3 \) for two values of \( f \) and several values of \( R_{dis}/R_c \).

| \( f = 0.40 \) | \( f = 0.70 \) |
|----------------|----------------|
| 0.005 | 0.120 | 6.3 \cdot 10^{-8} | 0.283 | 1.5 \cdot 10^{-7} |
| 0.01 | 0.118 | 4.9 \cdot 10^{-7} | 0.279 | 1.2 \cdot 10^{-6} |
| 0.02 | 0.115 | 3.9 \cdot 10^{-6} | 0.271 | 9.1 \cdot 10^{-6} |
| 0.05 | 0.105 | 5.5 \cdot 10^{-5} | 0.248 | 1.3 \cdot 10^{-4} |
| 0.1 | 0.0915 | 3.8 \cdot 10^{-4} | 0.215 | 9.0 \cdot 10^{-4} |
| 0.2 | 0.0700 | 2.3 \cdot 10^{-3} | 0.164 | 5.5 \cdot 10^{-3} |
| 0.4 | 0.0431 | 0.0116 | 0.0972 | 0.026 |
| 0.6 | 0.0280 | 0.0254 | 0.0269 | 0.055 |
| 1.0 | 0.0136 | 0.057 | 0.0278 | 0.116 |

as \( R_{dis}/R_c \rightarrow 0 \). This result is quite easy to understand. If \( R_{dis}/R_c \ll 1 \), the pair potentials (3) become essentially independent of \( R_{dis} \). Hence, the density becomes essentially independent of \( R_{dis} \) for \( R_{dis} \) small. In the opposite limit \( R_{dis}/R_c \gg 1 \), the potentials become essentially independent of \( R_c \). Hence, in this limit \( f \) converges to the disorder packing fraction \( \eta_{dis} \equiv 4\pi R^3_{dis}/3 \). For instance, for \( \eta_{dis} = 0.30 \), we obtain \( f = 0.51 \), \( 0.40 \), \( 0.32 \) for \( R_{dis}/R_c = 5, 10, 50 \). Since a hard-liquid phase exists only up to \( \eta \approx 0.49 \), for large \( R_{dis}/R_c \) [61], the matrix may belong to different hard-phase phases, while still satisfying the condition \( f < f^* \).

3. Results

3.1. Monte Carlo simulation

In this work we investigate the effect of disorder on the fluid–fluid and binary interactions for \( q = 0.8 \). We perform simulations in the absence of the porous matrix – our results are consistent with those of Refs. [37,38] – and for two values of \( f \), \( f = 0.4 \) and \( f = 0.7 \) [note that \( \hat{c}(f = 0.7) \approx 2\hat{c}(f = 0.4) \), in cubic boxes \( L^3 \) with \( L/R_c = 16 \) and \( 20 \). In order to obtain quenched averages we consider 200–400 matrix realizations for each \( f \) and \( R_{dis} \).

For each value of \( f \) we consider a few values of \( R_{dis}/R_c \). For \( f = 0.4 \) we present results for \( R_{dis}/R_c = 0.2, 0.6, 1.0 \) \( (f_{pol} = 0.26, 0.29, \text{ and } 0.31, \text{ respectively}) \), while for \( f = 0.7 \), we use \( R_{dis}/R_c = 0.2 \) and \( 1.0 \) \( (f_{pol} = 0.50 \text{ and } 0.57, \text{ respectively}) \). It should be noted that we are limited by computer power in further decreasing or increasing the ratio \( R_{dis}/R_c \). Indeed, if we further decrease the ratio, the disorder density increases, see Table 1, and so does the number of matrix particles and the computational work.

On the other hand, if we increase \( R_{dis}/R_c \) beyond 1, we should consider quite large systems in order to avoid large size effects, which is unfeasible with our present computer power.

In order to determine the coexistence curves we perform a grand-canonical simulation. The grand partition sum for each disorder realization is

\[
\Xi(V, z_p, z_c) = \sum_{N_p, N_c} z_p^{N_p} z_c^{N_c} Q(V, N_p, N_c),
\]

where \( Q(V, N_p, N_c) \) is the configurational partition function of a system of \( N_p \) polymers and \( N_c \) colloids in a volume \( V \), and \( z_p \) and \( z_c \) are the corresponding fugacities. In Equation (7) we normalize \( Q(V, N_p, N_c) \) so that \( Q(V, 1, 0) = Q(V, 0, 1) = V \), hence \( z_p \) and \( z_c \) are dimensional parameters. We quote our results in terms of the dimensionless combinations \( z_p R_c^3 \) and

\[
\eta_p = \frac{4\pi}{3} z_p R_c^3.
\]

The quantity \( \eta_p \) represents the polymer reservoir packing fraction.

In the presence of a first-order transition, standard local algorithms are unable to sample correctly both phases in the simulation. We therefore combine the grand-canonical algorithm with the umbrella sampling and the simulated-tempering method [62,63], as discussed in the Appendix. Insertions and deletions of colloids and polymers are performed by using the cluster moves introduced by Vink and Horbach [36,64].

3.2. Quenched coexistence curve

The main purpose of this work is the determination of the disorder-averaged coexistence curve. In order to define it precisely, let us define the disorder-averaged colloid and polymer numbers

\[
N_{c,av}(V, z_p, z_c) = z_c \frac{\partial}{\partial z_c} \left[ \frac{\Xi(V, z_p, z_c)}{\Xi(V, z_p, z_c)} \right],
\]

\[
N_{p,av}(V, z_p, z_c) = z_p \frac{\partial}{\partial z_p} \left[ \frac{\Xi(V, z_p, z_c)}{\Xi(V, z_p, z_c)} \right],
\]

where \([ \cdot ]\) indicates the average over the matrix realizations. In the presence of first-order transitions, there is a line \( z_c = z_c^*(z_p) \) in the \((z_p, z_c)\) plane where these two functions become discontinuous in the infinite-volume limit. In other words, for \( z_p > z_p, crit \) we have

\[
\begin{align*}
\lim_{\epsilon \to 0^+} \lim_{V \to \infty} N_{c,av}(V, z_p, z_c^*(z_p) + \epsilon) &= c_{c,liq}, \\
\lim_{\epsilon \to 0^+} \lim_{V \to \infty} N_{p,av}(V, z_p, z_c^*(z_p) + \epsilon) &= c_{p,liq},
\end{align*}
\]
The pair \( c_p, c_c \) gives the polymer and colloid concentrations in the colloid–liquid phase at coexistence, while \( c_p, c_c \) correspond to the colloid–gas polymer-rich phase.

In the MC simulations the position of the demixing curve can be determined by studying the disorder averaged histograms of \( N_c \) and \( N_p \), which are defined as

\[
h_{c, \text{ave}}(N_c, z_p, z_c) = \frac{1}{\Omega} \sum \delta(N_c, \{x,y\})_{\text{GC}, z_p, z_c},
\]

\[
h_{p, \text{ave}}(N_p, z_p, z_c) = \frac{1}{\Omega} \sum \delta(N_p, \{x,y\})_{\text{GC}, z_p, z_c},
\]

where \( \delta(x,y) \) is the Kronecker delta \([\delta(x,y) = 1, \delta(x,y) = 0 \text{ for } x \neq y] \) and \([\{x,y\}]_{\text{GC}, z_p, z_c} \) is the grand-canonical ensemble average. In the two-phase region the histograms show a double-peak structure. In order to obtain \( z_c^* \) at fixed \( z_p \) in a finite volume, several different methods can be used. We followed two different recipes, the equal-area and the equal-height methods. In the first case, we define \( z_c^* \) as the value of the colloid fugacity at which the area below the two peaks is equal. For instance, if we consider the colloid-number distribution, we first compute the position \( N_{\text{min}} \) of the minimum between the two peaks and then require \( z_c^* \) to be the value of the colloid fugacity at which

\[
\sum_{N_c < N_{\text{min}}} h_{c, \text{ave}}(N_c, z_p, z_c^*) = \sum_{N_c > N_{\text{min}}} h_{c, \text{ave}}(N_c, z_p, z_c^*).
\]

Equivalently, one can use the polymer distribution \( h_{p, \text{ave}}(N_c, z_p, z_c) \). In the second method we identify \( z_c^* \) as the value of the fugacity at which the two peaks have the same height. Once \( z_c^* \) has been obtained, the colloid and polymer number at the transition are defined as the positions of the maxima of the histograms.

Since we have two different histograms to analyze, we obtain two different estimates of the colloid fugacity at coexistence: an estimate \( z_c^*(c) \) is obtained from the analysis of the colloid-number histograms, while \( z_c^*(p) \) is obtained from the analysis of the polymer-number histograms. For \( R_{\text{dis}}/R_c = 0.2, 0.6 \) the two estimates are quite close and provide consistent estimates of the colloid and polymer packing fractions at coexistence, although the equal-area method is more thermodynamically consistent. Indeed, the differences \(|z_c^*(c) - z_c^*(p)|\) computed with the equal-area method are always smaller than those computed with the second prescription. For \( R_{\text{dis}}/R_c = 1.0 \), we have been unable to apply the area method. The difficulties can be understood by looking at Figure 2, where we report the colloid histograms for \( f = 0.7 \) and for the largest value of \( z_p \) we consider, \( f = 1.82 (z_p R_c^1 = 0.85) \). While the colloid–liquid peak is quite narrow, the colloid–gas peak is very broad and therefore condition (13) is satisfied only when the colloid–gas peak is barely visible. However, in this case the definition of \( N_{\text{min}} \) is ambiguous and thus \( z_c^* \) is determined with large uncertainty. In some cases, it is even impossible to satisfy the equal-area condition. Thus, for \( R_{\text{dis}}/R_c = 1.0 \) we only use the equal-height method. Note that the two methods should give identical results in the infinite-volume limit. Hence, the difficulties we observe indicate that for this value of the parameters finite-size effects are important. The analyses reported in the following sections confirm these findings. It is interesting to note that, at variance with what happens in the bulk, in the presence of randomness the order parameter distribution shows two well-separated non-overlapping peaks even at the critical point (see Refs. 53, 54 for a discussion in the present context). Thus, it is also possible that the difficulties we observe for some values of the parameters are related to the fact that they belong to the one-phase region, even if the finite-size colloid and polymer histograms are bimodal.

To give an idea of the performance of the two methods, we report the results for \( f = 0.4, R_{\text{dis}}/R_c = 0.6, f_p = 1.24 (z_p R_c^1 = 0.58) \), and \( L/R_c = 16 \), see Figure 3. The equal-area method gives

\[
z_c^* R_c^1 \approx 130.2 \quad \eta_{c, \text{gas}} \approx 0.041 \quad \eta_{c, \text{liq}} \approx 0.294.
\]
from the analysis of the colloid distribution. The analysis of the polymer distribution gives the same estimate of $z_c^*$ (we have data for several values of $z_c$ with step $\Delta z_c = 0.1$). If we apply instead the equal-height method we obtain $z_c^*(c)R_c^3 \approx 129.3$ and $z_c^*(p)R_c^3 \approx 127.5$ from the two distributions. The colloid packing fractions at coexistence are therefore

$$
z_c^*(c)R_c^3 = 129.3 \quad \eta_{c,\text{gas}} \approx 0.039 \quad \eta_{c,\text{liq}} \approx 0.294, \\
z_c^*(p)R_c^3 = 127.5 \quad \eta_{c,\text{gas}} \approx 0.038 \quad \eta_{c,\text{liq}} \approx 0.292. \quad (15)
$$

The results are very close to each other and consistent with those reported in Equation (14). Similar conclusions are obtained for the polymer packing fractions at coexistence. For $f=0.7$, $R_{\text{dis}}/R_c = 1.0$, $\eta_p^r \approx 1.82$ ($z_pR_c^3 = 0.85$), and $L/R_c = 16$, the case reported in Figure 2, we obtain $z_c^*(c)R_c^3 \approx 454$ and $z_c^*(p)R_c^3 \approx 440$ from the two distributions (equal-height method). At coexistence we find then

$$
z_c^*(c)R_c^3 = 454 \quad \eta_{c,\text{gas}} \approx 0.096 \quad \eta_{c,\text{liq}} \approx 0.257, \\
z_c^*(p)R_c^3 = 440 \quad \eta_{c,\text{gas}} \approx 0.100 \quad \eta_{c,\text{liq}} \approx 0.258. \quad (16)
$$

Even though the estimates of the coexistence colloid fugacity differ somewhat, the two estimates of the colloid packing fractions at coexistence are quite close.

### 3.3. Sample-to-sample fluctuations

It is interesting to understand how the results obtained from the sample average compare with those that would be obtained by determining the coexisting phases for each disorder realization. In Figure 4 we report the distributions of the colloid and polymer packing fractions at coexistence computed from each disorder configuration. The distributions of the packing fractions corresponding to the colloid–liquid phase are very narrow and are centered at the value obtained from the analysis of the average distributions. On the other hand, the distributions for the colloid–gas phase are broad, especially for $R_{\text{dis}}/R_c = 0.6$ and 1. Since the broadness of the distribution is a finite-size effect – we expect the width of the distributions to scale as $1/\sqrt{L}$ as $L \to \infty$ – this is an indication that we should expect some finite-size dependence on our determination of the colloid–gas branch of the coexistence curves. The results reported in the next section confirm these expectations.

Finally, we also report the distributions for the case $f=0.7$, $R_{\text{dis}}/R_c = 1$, $\eta_p^r \approx 1.82$ ($z_pR_c^3 = 0.85$) (the average colloid-number histograms are reported in Figure 2), for which we have been unable to determine the coexistence fugacity using the equal-area method. The distribution of the colloid and polymer packing fractions at coexistence are reported in Figure 5 and clearly explain the origin of the difficulties. The position of the colloid–gas branch varies significantly from sample to sample. We are thus far from the infinite-volume limit, since in this limit sample fluctuations are expected to disappear except close to the critical point. These results again provide evidence that size effects are large for these values of the parameters.

### 3.4. Finite-size effects

The analyses presented above show that size effects may still be relevant for the data with $L/R_c = 16$. They appear to increase with increasing $f$ and/or $R_{\text{dis}}/R_c$ and should be particularly large for $f=0.7$ and $R_{\text{dis}}/R_c = 1.0$. To investigate size effects we have performed additional simulations with $L/R_c = 20$. 

---

Figure 3. Polymer histogram $h_{p,\text{ave}}$ and colloid histogram $h_{c,\text{ave}}$ for $L = 16R_c$, $f=0.4$, $R_{\text{dis}}/R_c = 0.6$, $\eta_p^r \approx 1.24$ ($z_pR_c^3 = 0.58$), and several fugacities $z_cR_c^3$. The thicker curve corresponds to the coexistence fugacity obtained by using the equal-area prescription ($z_c^*(c)R_c^3 = 130.2$), while the other two curves correspond to the estimates $z_c^*(c)R_c^3 = 129.3$ and $z_c^*(p)R_c^3 = 127.5$ obtained by using the equal-height method.
In Figure 6 we compare the results for the coexistence curve obtained by using these two different box sizes. We report results both in terms of $/C_17c$ and $/C_17p$ and also in terms of $/C_17c$ and $/C_17r$.

On top we show the results for $f = 0.4$. Corrections here appear to be under control: the plots in terms of $\eta_c$ and $\eta_p$ show a small size dependence, while those in the reservoir representation appear to be reliable except close to the critical point, which is not unexpected since size corrections are large in a neighborhood of a second-order phase transition. For $f = 0.7$, the colloid–gas phase boundary varies significantly when $R$ changes, especially for the case $R_{dis}/R_c = 1.0$. This is not unexpected, given the results shown in the previous sections. Indeed, in all cases the polymer and colloid histograms are characterized by
very narrow colloid–liquid peaks whose positions have a tiny dependence on the fugacity $z_r$, so that, even if $z_r^c$ is not precisely determined, the determined values $\eta_c, \eta_{p,\text{liq}}$ and $\eta_{p,\text{ads}}$ are quite reliable. In the colloid–gas phase the distributions are instead very broad, a clear indication that we are far from the infinite-volume limit. As we have already remarked, it is also possible that, for some values of the parameters, the system is in the one-phase region, even if the finite-size data show double peaks.

3.5. Demixing curves in the reservoir representation

The estimates of $z_r^c$ [we report the average of $z_r^c(c)$ and $z_r^c(p)$] as a function of $\eta_p^c$ for $L/R_c = 16$ are reported in Figure 7. In order to compare our results with those of Ref. [52], we also report the estimates of the polymer reservoir packing fraction $\eta_p^c$ at coexistence in terms of the colloid reservoir packing fraction $\eta_c^c$. Note that, on a logarithmic scale, the values $z_r^c R_3^3$ for each $f$ and $R_{\text{dis}}/R_c$ lie quite precisely on a straight line, indicating that the colloid chemical potential at coexistence is well approximated by a linear function in $\eta_p^c$. Moreover, the position of the demixing curve depends essentially only on $f$. The ratio $R_{\text{dis}}/R_c$, hence the topological structure of the matrix, does not significantly change the coexistence curve. We have not performed a careful finite-size scaling analysis close to the critical point (a detailed discussion of the methods appropriate for random-field Ising critical points is reported in Refs. [54,67,68]) and thus we are not able to estimate $\eta_{p,\text{crit}}^c$ and $\eta_{c,\text{crit}}^c$ precisely. We only note that for $L/R_c = 16$ and $L/R_c = 20$ double peaks are observed only for $\eta_p^c \gtrsim 1.00, 1.03$ for all three values of $R_{\text{dis}}/R_c$. We can thus set the lower bounds $\eta_{p,\text{crit}}^c \gtrsim 1.03$ and $\eta_{c,\text{crit}}^c \gtrsim 0.38$. For $f = 0.7$ size effects are significantly larger than for $f = 0.4$, but we can still obtain the bounds $\eta_{p,\text{crit}}^c \gtrsim 1.6, \eta_{c,\text{crit}}^c \gtrsim 0.405$.

We can use our results to understand qualitatively the behavior of a bulk colloid–polymer mixture in chemical equilibrium with the same dispersion adsorbed in a porous matrix. The main question is whether one can observe different phases in the bulk and in the matrix. If we use $\eta_p^c$ as control parameter, we see that for $\eta_p^c < \eta_{p,\text{crit}}^c \approx 0.37$ there is no transition, neither in the bulk nor in the matrix. If $\eta_p^c$ is larger, one may have a transition in the bulk and no transition in
the matrix, given that $\eta_c^{\text{crit}}$ increases with $f$. For instance, for $f = 0.4$ and $0.37 < \eta_c^{\text{crit}} < 0.385$ we only observe phase separation in the bulk. If we increase $\eta_c^{\text{crit}}$ further ($\eta_c^{\text{crit}} \gtrsim 0.385$ for $f = 0.4$) the behavior is more complex, since phase separation occurs both in the bulk and in the matrix. For small $\eta_p^{\text{crit}}$ the mixture is in the colloid–liquid phase both in the bulk and in the matrix. If $\eta_p^{\text{crit}}$ is increased, that is polymers are added, the bulk coexistence curve is reached, see Figure 7. Above the demixing line, one observes two different phases: in the bulk the system is in the colloid–gas phase, while in the matrix a colloid–liquid phase occurs. Thus, the presence of the matrix may induce, for certain values of the parameters, a capillary condensation of the colloids. Finally, for large $\eta_p^{\text{crit}}$ above the matrix coexistence curve, a colloid–gas phase occurs both in the bulk and in the matrix.

3.6. Binodals in the system representation

In Figure 8 we report the results for the binodals (we interpolate the MC data for $L/R_c = 16$) as a function of $\eta_c$ and $\eta_p$. For $f = 0.4$ they are quite close to the bulk binodal curve and show only a tiny dependence on the ratio $R_{\text{dis}}/R_c$. In the figure we also report an estimate of the critical point obtained by determining the intersection of the diameter with the interpolation of the coexistence data. This provides a very rough estimate of the critical parameters, which can only be accurately determined by performing a careful finite-size scaling analysis. In the bulk the analysis of the results with $L/R_c = 16$ gives $\eta_{c,\text{crit}} \approx 0.12$, $\eta_{p,\text{crit}} \approx 0.31$, which should be compared with the precise determination [36,37]

$$\eta_{c,\text{crit}} = 0.1340(2), \quad \eta_{p,\text{crit}} = 0.3562(6).$$ (17)
Apparently our simple extrapolation underestimates \( \eta_{c,\text{crit}} \) by 10% and \( \eta_{p,\text{crit}} \) by 15%, which we can take as indications of the systematic error. If we perform the same analysis for \( f = 0.4 \) we obtain \( \eta_{c,\text{crit}} \approx 0.17 \) for all values of \( R_{\text{dis}}/R_c \): the colloid packing fraction at criticality is essentially independent of the matrix topology and increases with increasing \( f \). As for the polymer packing fraction, the dependence on the size ratio \( R_{\text{dis}}/R_c \) is somewhat larger. The value \( \eta_{p,\text{crit}} \) decreases with increasing \( R_{\text{dis}}/R_c \) and varies between 0.23 and 0.29. If we assume that the results for \( L/R_c = 16 \) underestimate the correct, infinite-volume results by 10% and 15% as they do in the bulk, we would guess \( \eta_{c,\text{crit}} \approx 0.19 \) and \( 0.27 \leq \eta_{p,\text{crit}} \leq 0.34 \).

As we have already stated our results for \( f = 0.7 \) are only reliable in the colloid–liquid phase. In this regime the binodal curve depends somewhat on \( R_{\text{dis}}/R_c \): for \( R_{\text{dis}}/R_c = 0.2 \) it is close to the bulk curve, while for \( R_{\text{dis}}/R_c = 1 \) it is significantly below it. The critical point position is consistent with what was observed for \( f = 0.4 \): \( \eta_{c,\text{crit}} \) shows little dependence on \( R_{\text{dis}}/R_c \), while \( \eta_{p,\text{crit}} \) decreases with increasing \( R_{\text{dis}}/R_c \).

We can compare our results with those obtained in Refs. [52,55]. By using density-functional methods, Ref. [52] studied the model with \( R_{\text{dis}}/R_c = 1 \) at the slightly lower value of \( f, f = 0.37 \) (corresponding to \( \eta_{\text{dis}} = 0.05 \)), and several values of \( q, q = 0.3, 0.6, 1.0 \) (none of them agrees unfortunately with ours). Their results are not consistent with ours. They find that in all cases the binodal curve in the presence of the matrix is below that in the bulk, while here we find the opposite except deep in the colloid–liquid region, i.e. for \( \eta_c \gtrsim 0.20 \). Moreover, they find that \( \eta_{c,\text{crit}} \) decreases with increasing \( f \) in all cases, which is again in contrast with our results. On the other hand we are fully consistent with the results of Ref. [55], which study the model for \( R_{\text{dis}}/R_c = 1, f = 0.37 \) (\( \eta_{\text{dis}} = 0.05 \)), and \( q = 0.8 \). For the critical point they obtain \( \eta_{c,\text{crit}} = 0.192 \) and \( \eta_{p,\text{crit}} = 0.292 \), confirming that \( \eta_{c,\text{crit}} \) increases in the presence of disorder. From a quantitative point of view, their critical-point estimates are fully consistent with ours. In particular, the naive extrapolation we have performed above apparently estimates correctly the critical-point position at the 5% level.

4. Conclusions

In this paper we determine the fluid–fluid demixing curves for the AO model in a colloidal matrix for \( q = 0.8 \) and several values of \( R_{\text{dis}}/R_c \) and \( f \) (equivalently, of the disorder concentration \( c_{\text{dis}} \)). This study should provide quantitative informations on the phase behavior of a polymer–colloid mixture in a porous material close to the \( \theta \) point. Our main results are the following:

- Disorder is specified by two parameters: the disorder packing fraction \( \eta_{\text{dis}} \) and the ratio \( R_{\text{dis}}/R_c \). At least for \( R_{\text{dis}}/R_c \leq 1 \), the parameter range we consider, most of the disorder dependence of the results can be parametrized by using a single parameter, the effective matrix filled-space ratio \( f \), which gives the volume fraction unavailable to the colloids. In the \((\eta_{\text{dis}}, \eta_c)\) plane (or equivalently in terms of the reservoir packing fractions \( \eta_{p} \) and \( \eta_{c} \)) the coexistence curve depends essentially only on \( f \).
- It is possible to observe capillary condensation of the colloids. For certain values of the parameters a colloid–gas bulk phase is in equilibrium with a colloid–liquid phase in the matrix.
- At least for \( f \lessgtr 0.4 \) the binodal curves expressed in terms of the packing fractions (system representation) show a relatively small dependence on disorder. The critical point instead changes significantly. The critical colloid packing fraction \( \eta_{c,\text{crit}} \) is, to a large extent, only a function of \( f \) and it increases as \( f \) increases. The critical polymer packing fraction \( \eta_{p,\text{crit}} \) depends instead both on \( f \) and \( R_{\text{dis}}/R_c \). At fixed \( f \) it decreases as \( R_{\text{dis}}/R_c \) increases.

Acknowledgments

The authors gratefully acknowledge extensive discussions with Ettore Vicari. The MC simulations were performed at the INFN Pisa GRID DATA center and on the INFN cluster CSN4.

Notes

1. This is correct only for infinite-length polymers. For finite-length chains, polymers interact weakly (as an inverse power of \( L \), where \( L \) is the degree of polymerization) and a proper coarse-grained description requires the introduction of an attractive pair potential and of a repulsive three-body potential (needed for thermodynamic stability), see [48–50].
2. For a list of experimental studies of binary mixtures in porous materials, see the references cited in [51].
3. We use the Carnahan–Starling expression to relate the colloid reservoir packing fraction \( \eta_c \) to the fugacity \( z_c \): \( z_c R_c^3 = 3 \eta_c^3/(4\pi) \exp[f(\eta_c^2)] \) with \( f(\eta) = \eta(8 - 9\eta + 3\eta^2)/(1 - \eta)^3 \); see [65,66].
Monte Carlo simulations: some technical details

We have performed simulations in the grand-canonical (GC) ensemble, which physically describes a system adsorbed in a colloid matrix in chemical equilibrium with a reservoir of pure polymers and a reservoir of pure non-interacting colloids. The basic parameters are the colloid and polymer fugacities $z_c$ and $z_p$, and in the bulk partition function is

$$\Xi(V, z_p, z_c) = \sum_{N_p, N_c} z_p^{N_p} z_c^{N_c} Q(V, N_p, N_c),$$

where $Q(V, N_p, N_c)$ is the configurational partition function of a system of $N_p$ polymers and $N_c$ colloids in volume $V$. We drop the irrelevant thermal length so that $Q(V, 1, 0) = Q(V, 0, 1) = V$. In the presence of first-order transition it is quite difficult to sample correctly the GC distribution. To bypass the difficulties we use the umbrella-sampling (sometimes also called multicanonical) method [62]. Instead of generating configurations with the GC weight, we use an umbrella distribution

$$\frac{1}{\pi(N_c)} z_p^{N_p} z_c^{N_c} e^{-\beta U},$$

with a properly chosen $\pi(N_c)$ which is defined below. If $\langle \cdot \rangle_{GC}$ and $\langle \cdot \rangle_z$ are the averages with respect to the GC distribution and to the distribution (19), respectively, we have

$$\langle O(N_c, N_p) \rangle_{GC} = \frac{\langle \pi(N_c) O(N_c, N_p) \rangle_z}{\langle \pi(N_c) \rangle_{GC}}.$$  

This relation allows us to obtain GC averages from simulations using the distribution (19). The function $\pi(N_c)$ must be chosen so that in the simulation the system can move easily between the two phases. Consider the histogram of $N_c$ in the GC distribution, i.e.

$$h(N_c, \theta) = \delta(N_c, N_c, \theta))_{GC},$$

where $\delta(x, y)$ is Kronecker’s delta. Assume that the system is close to phase separation so that $h(N_c)$ has two peaks at $N_{c,\text{min}}$ (colloid–gas phase) and $N_{c,\text{max}}$ (colloid–liquid phase).

The optimal choice is then

$$\pi(N) = a h(N_{c,\text{min}}) \quad N \leq N_{c,\text{min}},$$  

$$\pi(N) = a h(N) \quad N_{c,\text{min}} \leq N \leq N_{c,\text{max}},$$  

$$\pi(N) = a h(N_{c,\text{max}}) \quad N \geq N_{c,\text{max}},$$  

where $a$ is an irrelevant constant. Indeed, if $N_{c,\text{min}} \leq N \leq N_{c,\text{max}}$, the observed histogram in the umbrella distribution is flat, i.e. independent of $N_c$. Hence, the system can move freely between the two phases, allowing a precise determination of any required thermodynamic property.

In order to determine the colloid fugacity $z_c^*$ at coexistence for a given value of the polymer fugacity $z_p$, we consider $N_m$ colloid fugacities $\{z_{c,m}\}$, such that for $z_{c,1}$ ($z_{c,N_m}$) the system is in the colloid–gas (colloid–liquid) phase. Then, we determine the umbrella functions $\pi_m(N_c)$ iteratively. First, we perform a short hysteresis cycle in which we perform $N_{\text{therm}}$ GC iterations at $z_c = z_{c,1}$, then at $z_c = z_{c,2}$, and so on, up to $z_c = z_{c,N_m}$; then we decrease $z_c$ till we reach again $z_{c,1}$. If $h^{(k)\text{+}}_{m}(N_c)$ and $h^{(k)\text{–}}_{m}(N_c)$ are the histograms obtained at $z = z_m$ (the plus to the distribution obtained while increasing $z_c$ and the minus to that obtained while decreasing the fugacity), we set $h^{(k)\text{+}}_{m}(N_c) = h^{(k)\text{+}}_{m}(N_c) + h^{(k)\text{–}}_{m}(N_c)$ and

$$\pi^{(k)}_m(N_c) = h^{(k)\text{+}}_{m}(N_c)/M \quad \text{if } h^{(k)\text{+}}_{m}(N_c) \geq M,$$

$$\pi^{(k)}_m(N_c) = 1 \quad \text{if } h^{(k)\text{+}}_{m}(N_c) \leq M,$$

where $M = \max_N [h^{(1)\text{+}}_{m}(N_c)]/10$. Then, we repeat the same hysteresis cycle several times. At iteration $k$, for each $z_{c,m}$ we perform the simulation using the distribution (19) with $\pi = \pi^{(k)}_m$. Then, we set

$$\pi^{(k)}_m(N_c) = h^{(k)\text{–}}_{m}(N_c)/M \quad \text{if } h^{(k)\text{–}}_{m}(N_c) \geq M,$$

$$\pi^{(k)}_m(N_c) = 1 \quad \text{if } h^{(k)\text{–}}_{m}(N_c) \leq M,$$

where $M = \max_N [h^{(1)\text{–}}_{m}(N_c)]/10$. We stop when we observe that, for at least some values of $m$, $h^{(k)\text{+}}_{m}(N_c)$ and $h^{(k)\text{–}}_{m}(N_c)$ are non-vanishing in an interval of values of $N_c$ that extends between the two phases.

Once we have a reasonable estimate of the functions $\pi_m(N_c)$, we could just perform an extensive simulation at single value of $z_{c,m}$ (an optimal choice would be to take the value for which $\pi_m(N_c)$ is clearly bimodal). Data for different values of $z_c$ could just be obtained by standard reweighting techniques. However, we have found it more convenient to use all the information we have collected and simulate all systems together, using the simulated-tempering method [63]. Note that, in the standard implementation of the method, one should be careful that the fugacities $z_{c,m}$ are such that the colloid-number distributions overlap; otherwise, no fugacity swap is accepted. In our case, since we use umbrella distributions, the overlap condition is always verified, and thus the number $N_m$ of required systems is always small. Typically we take $N_m = 10$. If

$$\Xi_{\pi_m}(V, z_p, z_{c,m}) = \sum_{N_p, N_c} \pi_m(N_c) Q(V, N_p, N_c),$$

we consider the extended partition function

$$\Xi^{ST} = \sum_m f_m \Xi_{\pi_m}(V, z_p, z_{c,m}).$$
The constants $f_m$ are chosen so that all terms in the sum are approximately equal. If we require
\[ f_m \Xi_{nm}(V, z_p, z_{c,m}) = f_{m-1} \Xi_{n,m-1}(V, z_p, z_{c,m-1}), \]  
we obtain
\[ \frac{f_m}{f_{m-1}} = R_m \frac{f_{m-1}}{f_m} = S_m, \]  
with
\[ R_m = \left( \frac{z_{c,m+1}}{z_{c,m}} \right)^{Nc} \frac{\pi_m(N_c)}{\pi_{m-1}(N_c)}, \]
\[ S_m = \left( \frac{z_{c,m}}{z_{c,m-1}} \right)^{Nc} \frac{\pi_{m-1}(N_c)}{\pi_m(N_c)}, \]  
where $\langle \cdot \rangle_{z_m}$ indicates the mean value with respect to the umbrella distribution (19) with $z_c = z_{c,m}$, $\pi = \pi_m$. Combining these expressions we define the ratios as
\[ \frac{f_m}{f_{m-1}} = \sqrt{\frac{R_m}{S_m}}. \]  
The constants $R_m$ and $S_m$ are determined together with the umbrella sampling functions $\pi_m$. Then, we set $f_1 = 1$ and use Equation (31) to determine the constants $f_m$, $m \geq 2$.

In the matrix case, the GC partition function is still given by Equation (18), with the only difference that one should take into account the interactions between the freely moving particles and the matrix. Since the GC partition function depends on the matrix, also the functions $\pi_m$ and the constants $f_m$ are matrix dependent. Thus, we recompute them when we restart the simulation with the different matrix.

In the MC simulations we take $N_m \approx 10$. One MC iteration consists of three fugacity swaps and 1000–5000 GC moves in which colloids and polymers are inserted or removed. For this purpose we use the cluster move discussed in Ref. [64] together with standard moves in which a single polymer is removed or inserted. For each disorder instance, we perform $N_{\text{ini}}$ iterations to determine the umbrella functions and then $N_{\text{iter}}$ iterations to measure several histograms. Typically, $N_{\text{ini}}$ varies between 5000$N_m$ and 20,000$N_m$, while $N_{\text{iter}}$ is of the order of 20,000$N_m$.

In the simulation we determine the colloid and polymer histograms for a large number (typically 100) of colloid fugacities $z_{c,r}$. They are obtained by measuring, for each matrix realization $\alpha$, the reweighted histograms $p_c(\alpha, z_{c,r}, N_c, 0)$ and $p_p(\alpha, z_{c,r}, N_p, 0)$:
\[ p_c(\alpha, z_{c,r}, z_{c,m}, N_c, 0) = \sum_{i} \left( \frac{z_{c,i}}{z_{c,m}} \right)^{N_c} \pi_m(N_c) \delta(N_c, N_c, 0) \delta(z_{c,m}, z_{c,i}), \]
\[ p_p(\alpha, z_{c,r}, z_{c,m}, N_p, 0) = \sum_{i} \left( \frac{z_{c,i}}{z_{c,m}} \right)^{N_c} \pi_m(N_c) \delta(N_p, N_p, 0) \delta(z_{c,m}, z_{c,i}), \]  
where $i$ refers to the MC iteration, and $N_{p,i}$, $N_{c,i}$, $z_{c,i}$ are the number of polymers and colloids and the colloid fugacity at the $i$-th iteration. The colloid histogram is then
\[ h_{c,\text{ave}}(N_c, 0, z_p, z_{c,r}) = \frac{1}{N_{\text{iter}}} \sum_{\alpha} \frac{p_c(\alpha, z_{c,i}, z_{c,m}, N_c, 0)}{\sum_{\alpha} p_c(\alpha, z_{c,i}, z_{c,m}, N_c, 0)}, \]  
where $N_{\text{iter}}$ is the number of matrix realizations. Note that we obtain a different estimate of the distributions at $z_{c,r}$ for each of the $z_{c,m}$.

As a final comment, note that our estimates (34) are biased, since they are disorder averages of a ratio of thermal averages. This means that, if we take the limit $N_{\alpha} \to \infty$ at fixed $N_{\text{iter}}$, we obtain estimates that differ from the correct result by a term (the bias) of order $1/N_{\text{iter}}$. One could perform a bias correction, as discussed in Ref. [69]. However, given the small number of disorder instances, we have found that in the present case the bias correction is not relevant.