Influence of Polymer-Excluded Volume on the Phase-Behavior of Colloid-Polymer Mixtures

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We determine the depletion-induced phase-behavior of hard-sphere colloids and interacting polymers by large-scale Monte Carlo simulations using very accurate coarse-graining techniques. A comparison with standard Asakura-Oosawa model theories and simulations shows that including excluded-volume interactions between polymers leads to qualitative differences in the phase diagrams. These effects become increasingly important for larger relative polymer size. Our simulation results agree quantitatively with recent experiments.

Adding a sufficient amount of nonadsorbing polymer chains to a stable colloidal dispersion can cause a depletion-induced separation of the dispersion into colloid-rich and colloid-poor phases, a striking effect which has been extensively investigated experimentally [1–8] and which has important industrial [9] and biological [10] implications. The entropy-driven depletion attraction between colloidal particles can be tuned by varying the polymer-to-colloid size ratio $q = R_g/R_c$ (where R_g is the polymer radius of gyration and R_c the radius of the spherical colloids) and the polymer concentration, thus providing a unique opportunity of generating rich phase behavior. A theoretical description of colloid-polymer mixtures is a challenging statistical mechanical problem because of the large length scale differences between the size of the colloids and the polymer segments. The simplest and most widely made assumption is to consider ideal (noninteracting) polymers obeying Gaussian or random walk statistics [11]. A further simplification is provided by the Asakura-Oosawa (AO) model [12] whereby polymer coils are treated as mutually penetrable spheres, which are excluded from a sphere of radius $(R_c + R_g)$ around each colloid. Gast *et al.* [13] and Lekkerkerker *et al.* [14] used this model to calculate the phase diagrams of colloid-polymer systems. Computer simulations of hard-sphere (HS) colloids and ideal lattice polymers [15] yielded results in good agreement with predictions based on the simpler AO model. Thus the phase behavior of mixtures of HS colloids and ideal polymers is well understood, at least for size ratios $q \lesssim 1$. However, polymers rarely behave as ideal, except perhaps near the θ point [11]. The more general problem involving *interacting* polymer chains is much more difficult and over half a century of theoretical work has shown that excluded-volume interactions between monomers lead to important qualitative and quantitative differences in the properties of polymer solutions [11]. This Letter presents the first large-scale systematic simulations of the phase behavior of mixtures of colloids and interacting polymers for three size ratios q and compares the calculated phase diagrams to recent experimental data [3–7].

Some earlier attempts to account for polymer interactions in colloid-polymer mixtures were based on a perturbation theory around θ-point conditions [16] or on integral equations [17]. In the present work, the self-avoiding walk (SAW) model is adopted for the interacting polymers, which is known to be a very good representation of polymers in good solvent [11]. A full scale simulation of N_c colloidal hard-sphere particles and N_p polymer chains, each made up of $L \gg 1$ monomers or Kuhn segments, would be a daunting task. However, large-scale simulations become feasible within a coarse-grained description of the polymers, whereby the latter are represented as single particles interacting via an effective pair potential between their centers of mass (CM). Such effective pair potentials can be calculated by tracing out of the individual monomer degrees of freedom along the "polymer as soft colloids" approach we have recently put forward [18–21]. This approach was shown to reproduce, within statistical simulation uncertainties, the correct equation of state of interacting polymer solutions [19,21], as well as the correct one-body free energy of inserting a single colloid into a polymer solution, and the related polymer surface tension [22]. Compared to very time-consuming monomer-level simulations, the coarse-graining method moreover yields accurate depletion potentials between two plates [19] or between two colloidal spheres [23] for polymer volume fractions up to $\phi_p \equiv \frac{4}{3}\pi R_g^3 N_p/V \approx 2$. The success with the two-colloid problem suggests that the coarse-graining procedure may be fruitfully extended to the full many-body problem of the phase behavior of polymer-colloid mixtures as long as ϕ_p is not much greater than 1 (the crossover to the semidilute regime).

First, as described in our previous publications, the effective potentials for the polymer-polymer interaction were obtained from simulations of a bulk system of self-avoiding walks at various concentrations. All simulations were for polymer chains of length $L = 500$ segments, with $R_g = 16.83$ lattice units at zero concentration. This length is sufficient to show proper scaling behavior in the semidilute regime [19]. The concentration-dependent

effective interactions $v_{pp}(r; \phi_p)$ were obtained by inversion of the CM radial distribution function $g(r)$ using the hypernetted chain (HNC) integral equation [19] and were accurately parametrized by sums of Gaussians [21]. The concentration-dependent potentials $v_{cp}(r; \phi_p)$ for the colloid-polymer interaction at each q and ϕ_p were obtained from simulations of a single hard sphere in a solution of SAW polymers. The CM concentration profile was inverted by using a two-component version of the HNC equation, and the resulting $v_{cp}(r; \phi_p)$ was fitted to an exponential form [21].

With these effective interactions, each polymer is reduced to a single effective particle, opening the way to large-scale simulations of a binary mixture of polymers and colloids. It is important to note that, in a system with a finite density of colloids, the polymer concentration parameter ϕ_p in the effective potentials $v_{pp}(r; \phi_p)$ and $v_{cp}(r; \phi_p)$ must be chosen to be that in a reservoir of a pure polymer system in *osmotic equilibrium* with the two-component system of interest. In other words, as discussed in detail by other authors [14,24,25], the effective interactions should be taken at the chemical potential μ_p of the polymers in an osmotic reservoir.

The Gibbs-ensemble Monte Carlo (GEMC) technique [26,27] is naturally suited for studying fluid-fluid phase separation. The chemical potential μ_p was fixed by a standard grand canonical prescription [28] and the number of colloidal particles was fixed at $N_c = 108$, $N_c = 150$, and $N_c = 200$ for polymer-colloid size ratios of $q = 0.34$, $q = 0.67$, and $q = 1.05$, respectively. The GEMC simulations yielded histograms for the polymer and colloid densities in both boxes. At chemical potentials above a critical value, the two boxes show different colloid densities, corresponding to phase separation.

Besides fluid-fluid phase separation, colloid crystallization can also occur in colloid-polymer mixtures. At zero polymer concentration, fluid-solid coexistence occurs at colloid volume fractions of $\phi_c = 0.494$ and $\phi_c = 0.545$, as expected for a pure HS system. The effect of the added polymer is initially to widen the coexistence region. At very high polymer concentration, a dense colloidal crystal can be in equilibrium with a very dilute colloidal "gas" (see, e.g., Ref. [29]). Experiments and previous approximate theoretical work show that if $q \lesssim 0.3$ the fluid-fluid critical point becomes metastable with respect to the crystallization phase-line. For this reason, it is important to also calculate the fluid-solid phase-lines, which was done using Kofke's Gibbs-Duhem integration technique [26,30]. Starting with zero polymer activity at HS fluid-solid coexistence, we performed a series of $N\mu_pPT$ ensemble simulations, integrating the Clausius-Clapeyron equation $dP/d\mu_p = \Delta N_p/\Delta V$ along the coexistence line, where ΔN_p and ΔV are the differences in the number of polymers and in the volume between the two phases, respectively.

To compare with ideal polymer theories, full GEMC simulations were also performed for the AO penetrable sphere model of polymers [12], with the same numbers of colloids and size ratios as for the interacting polymer systems. These simulations should provide an accurate representation of a true ideal polymer system [15]. For comparison, we also calculated the phase diagrams within the free-volume theory of Lekkerkerker *et al.* [14].

The complete phase diagrams for the ideal and interacting polymer models at all three size ratios are plotted in Fig. 1, in the polymer reservoir concentration-colloid volume fraction representation. Although the polymer chemical potential is the natural control variable in the
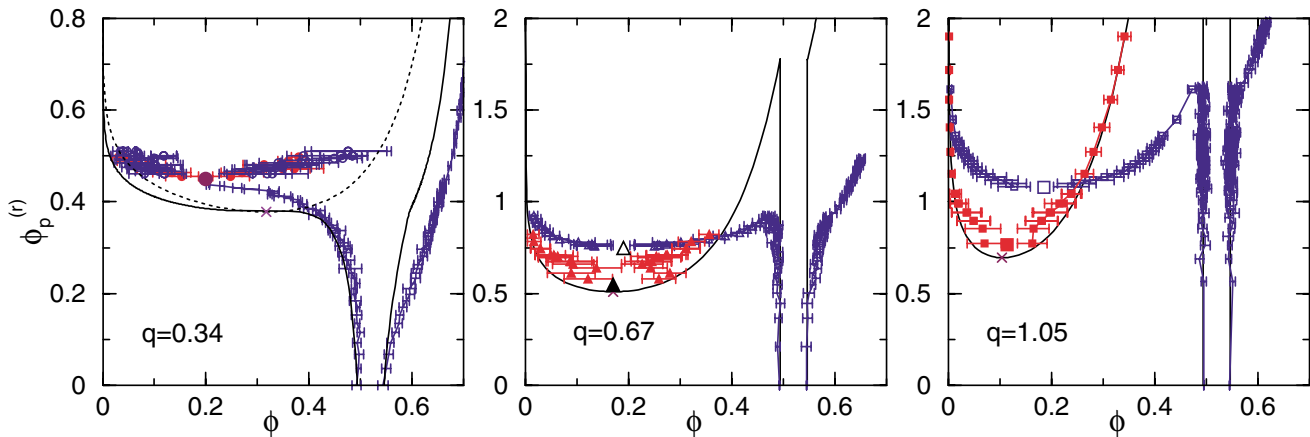
FIG. 1 (color online).   Phase diagrams in the polymer reservoir concentration–colloid volume fraction representation. The open symbols denote the fluid-fluid and the dashed lines with error bars the fluid-solid coexistence curves for interacting polymers. The solid symbols denote the fluid-fluid phase-lines for the two-component AO model. The critical points are indicated by a larger open and closed symbol for the interacting polymers and AO model, respectively. The thin solid curves represent free-volume perturbation theory phase diagrams, with a cross denoting the location of the critical point. The dashed line in the left panel is the free-volume theoretical metastable fluid-fluid binodal.

simulations, the reservoir polymer concentration $\phi_p^{(r)}$, directly obtainable from μ_p through the SAW equation of state [19,21], is a more suitable variable because this brings the interacting and noninteracting polymer phase-lines much closer to each other than a direct comparison of the chemical potentials would.

For $q = 0.34$ the fluid-fluid binodal has just become metastable. This result is consistent with experiments [3] and close to the prediction of the AO model and other noninteracting polymer theories [14,15]. The direct AO model simulations show fairly good agreement with the interacting polymer simulations and are in good qualitative agreement with the free-volume perturbation theory, although the latter overestimates the critical colloid volume fraction $\phi_c^{(cp)}$. Although we did not explicitly calculate the triple point for the two-component AO system, it is expected to be fairly well located by the simpler free-volume theory shown in the figure [14,15]. For $q = 0.67$ and $q = 1.05$, larger differences are seen between the interacting polymers and the noninteracting AO model system. The triple point predicted by the latter moves to much higher polymer reservoir concentration than that found for interacting polymers. Whereas the critical point for interacting polymers stays near $\phi_c = 0.2$, the ideal polymer critical point moves to lower colloid densities, an effect that was predicted in the literature [31]. Finally, we point out that since $\phi_p^{(r)} < 2$, i.e., in the regime where we previously found good agreement for the two-body problem, we expect our coarse-graining model to provide a very accurate representation of the fully interacting polymer-colloid system.

Experiments are usually done at fixed polymer concentration, so that the tie-lines are no longer horizontal. This representation is shown in Fig. 2 for $q = 0.67$. Triple points turn into triangular areas in which three phases coexist. These have been measured experimentally using a mixture of latex and polystyrene [3,6]. We compare the experimental triple point results for $q = 0.57$ to the theoretical $q = 0.67$ diagram. Although the systems are not entirely equivalent, a much better agreement is found with the interacting polymer simulations than with the AO model estimates. The simulations also agree quantitatively with the fluid-fluid binodal which was accurately measured for $q = 0.677$ in recent experiments on silica particles in toluene [7]. Similar quantitative agreement (not shown) was also found between the $q = 0.34$ simulations and $q = 0.377$ experimental binodals [7].

It is also instructive to compare the fluid-fluid binodals for different size ratios, as done in Fig. 3. For a small size ratio, the AO and the interacting polymer estimates are close, as also seen in Fig. 1. This is not surprising, since we have shown previously that a cancellation of errors in the AO model leads to fairly good effective pair potentials for small q and ϕ_p [23]. But the simulations for $q > 0.34$ exhibit qualitatively different behavior: within the AO model, $\phi_c^{(cp)}$ decreases with q, whereas the critical
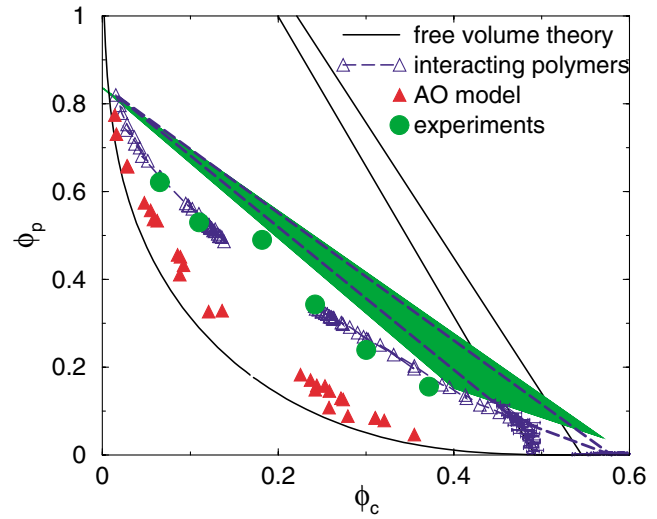
FIG. 2 (color online).   Phase diagram in the polymer volume fraction-colloid volume fraction representation for $q = 0.67$. Symbols as in Fig. 1. The large triangular areas denote the estimates for the triple point: the shaded area corresponds to the experimental data [3]. The simulated binodal agrees quantitatively with the experimental data of Ref. [7].

polymer concentration $\phi_p^{(cp)}$ does not change much. Including polymer interactions has the opposite effect: $\phi_p^{(cp)}$ increases and the colloid density hardly changes. Recent integral equation calculations [7,17] of the spinodal phase-lines also show an increase in the polymer concentration with increasing q.

The behavior of the critical point is summarized in Fig. 4, where the predicted trend for the critical colloid density is shown to agree very well with another set of experiments [4,5]. We have recently performed direct simulations for much larger size ratios ($q > 5$) and found
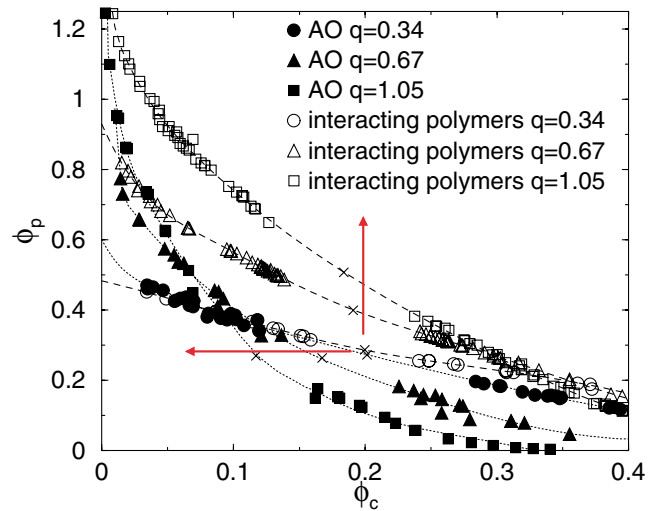
FIG. 3 (color online).   Fluid-fluid binodals in the polymer volume fraction-colloid volume fraction plane. Symbols as in Fig. 1. The crosses indicate the estimated position of the critical point. Note the qualitative differences in the effect of increasing q on the critical points as indicated by the arrows.
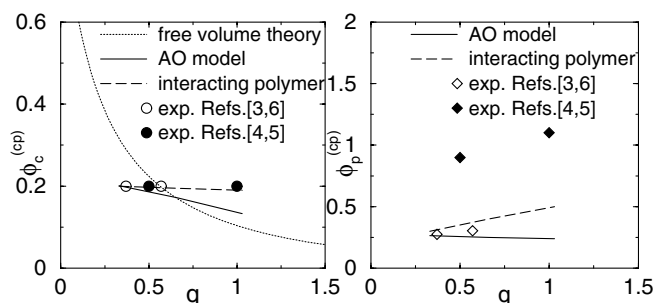
FIG. 4.   The behavior of the critical concentrations as a function of size ratio q. Left: The interacting polymer predictions for $\phi_c^{(cp)}$ agree with experimentally determined critical concentrations. The free-volume theory overestimates $\phi_c^{(cp)}$ for a small size ratio but underestimates it for a large size ratio. Right: The interacting polymer results for $\phi_p^{(cp)}$ are in reasonable agreement with the experiments of Refs. [3,6] but compare less favorably to those of Refs. [4,5].

that the colloid critical point is near the same density as found here [32]. This suggests that even in the so-called "protein limit," $q \to \infty$, $\phi_c^{(cp)}$ is finite. The situation for $\phi_p^{(cp)}$ is less clear. The present simulations seem to agree fairly well with the experimental estimates from Refs. [3,6], although we should stress that the critical point was not determined accurately. Two other experimental results based on mixtures of silica and poly(dimethylsiloxane) are also included [4,5]. These studies determined the critical point accurately, and the colloid density agrees well with our simulations. However, the polymer concentrations are twice as large, which might be due to the highly polydisperse polymers used by these authors.

In summary, this Letter presents the first large-scale computer simulations of the full equilibrium phase-diagram of a binary mixture of colloids and interacting polymers. These simulations would not have been possible without using the accurate polymers as soft colloids coarse-graining approach. Even though the phase separation happens mainly in the dilute regime of the polymer solution, we find important qualitative differences with ideal polymer behavior. In particular, the absolute polymer concentration ϕ_p at the critical point increases with increasing q for interacting polymers, while it decreases with increasing q for noninteracting polymers. Similarly, the critical colloid packing fraction $\phi_c^{(cp)}$ remains nearly constant for interacting polymers, while it decreases with increasing q for noninteracting polymers. We also showed that by including excluded-volume interactions we find quantitative agreement with experiments. In conclusion then, just as excluded-volume interactions are known to strongly influence the behavior of polymer solutions, we find that these interactions have important qualitative effects on the behavior of polymer-colloid mixtures.

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