Colloid–Polymer Mixtures Confined Between Asymmetric Walls: Simulation Evidence for an Interface Localization Transition

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Phase separation of colloid–polymer mixtures, described by the Asakura–Oosawa (AO) model, confined in a thin slit pore is studied by grand–canonical Monte Carlo simulation. While one wall is a hard wall for both particles, at the other wall there acts an additional repulsive potential on the colloids only. Varying the strength of this potential, a crossover from capillary condensation to an interface localization transition is found. The latter occurs under conditions where in the bulk almost complete phase separation has occurred.

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I. INTRODUCTION AND MOTIVATION

The current paradigm to create nanoscopic devices has enhanced the interest in the changes of phase behavior and structure when fluids are confined to linear dimensions that are no longer very large compared to the particle sizes. E.g., for a fluid (or fluid mixture) in a nanoscopic slit pore an interesting interplay of finite size effects, wetting or drying, and capillary condensation or evaporation–like behavior can be expected. A particularly interesting theoretical prediction concerns systems that can undergo phase separation (a fluid separating into vapor and liquid, or a binary mixture with a miscibility gap) confined between “competing walls”. By competing walls we mean that one wall favors one of the coexisting phases and the other wall favors the other one (the generic model is a thin ferromagnetic Ising film with oppositely oriented surface fields at both surfaces). When one brings the system in a state where phase separation occurs in the bulk, the thin film also exhibits...
phase separation, with an interface parallel to the walls in the center of the film \[3, 4, 5, 6, 7, 9, 10, 11, 12, 15, 16, 19\]. However, sufficiently far off from bulk criticality then a transition occurs where the interface gets localized at the wall(s). This transition can be of first order or of second order \[3, 4, 5, 6, 7\] and in the latter case it was argued to belong to the universality class of the two-dimensional (2d) Ising model. However, while interfaces parallel to the walls of thin films could be observed experimentally in thin films of polymer mixtures \[19\], no experimental observation of this novel type of transition has as yet been reported. Indeed, the theoretical models have always invoked perfect symmetry between the two coexisting phases in the bulk (spin reversal symmetry of the Ising magnet \[3, 4, 5, 6, 7\], or strictly symmetric polymer blends \[9, 10, 11, 12, 15\], which are hard to realize in nature).

In the present work we show that this interface localization should also be observable in colloid–polymer mixtures, which are known to be model systems for the experimental study of phase separation \[20\] and interfacial fluctuations \[21, 22\]. The large size of the colloid particles (of the order of 1 \(\mu\)m) should allow to prepare slit pores which are of the order of 10 – 100 particle diameters wide, with strongly repulsive walls which are essentially perfectly flat on this mesoscopic scale, modeling thus a “hard wall” boundary. However, coating a wall with a layer of long endgrafted flexible polymers of the same chemical type as used in the colloid–polymer mixture, one could create an additional repulsive interaction to the colloids to cancel (partially or fully) the depletion attraction \[14, 23\] of the colloids to the hard walls. Varying the grafting density in the resulting “polymer brush” \[24\] and/or the molecular weight of the grafted chains the range and strength of this short range repulsion between colloids and the wall could be fine-tuned, within some limits \[25\].

In the following we shall present model calculations of a simple model for colloid–polymer mixtures, the Asakura–Oosawa (AO) model \[26\], confined between two inequivalent walls: a hard wall on one side, and a hard wall plus short range repulsion acting only on the colloids on the other side. Varying the strength of this repulsion we demonstrate a crossover from capillary condensation–like behavior to interface localization transitions.

### II. MODEL AND SIMULATION TECHNIQUE

The colloids are modeled as hard spheres with diameter \(\sigma_c\), the polymers are (soft) spheres with diameter \(\sigma_p\). The polymers may not overlap with colloids, but there is no interaction
between the polymers. Recall that flexible polymers in solution form random coils with a rather large gyration radius which may interpenetrate at very low energy cost. We use a size ratio \( q = \sigma_p/\sigma_c = 0.8 \), since the phase diagram of this model in the bulk has been carefully studied previously \[27, 28\]. We choose \( \sigma_c = 1.0 \) as our unit of length. When there are \( N_p \) polymers and \( N_c \) colloids in the considered volume \( V \), the polymer and colloid packing fractions are defined as \( \eta_p = \pi \sigma_p^3 N_p / (6V) \) and \( \eta_c = \pi \sigma_c^3 N_c / (6V) \), respectively. The volume is given by \( V = L \times L \times D \). Here, \( D \) is the width of the slit pore in \( z \)-direction. Periodic boundary conditions are used in \( x \)- and \( y \)-directions parallel to the walls. The \( L \times L \) wall at \( z = 0 \) simply is a hard wall, while the wall at \( z = D \) is described by an additional repulsive potential. It has the following form (we absorb a factor \( k_B T \) here, \( k_B \) = Boltzmann’s constant, \( T \) = temperature):

\[
u_{cw}(z) = \begin{cases} \infty & \text{for } z \leq 0 \\
\varepsilon & \text{for } 0 < z \leq \sigma_c/2 \\
0 & \text{otherwise.} \end{cases}
\]  

(1)

The strength \( \varepsilon \) of this wall–colloid repulsion is varied between 0 and 2.5, while for polymers both walls are purely repulsive. Slit widths \( D = 5 \) and \( D = 10 \) were studied, while \( L \) was varied from \( L = 10 \) to \( L = 30 \), in the framework of a finite size scaling \[29\] analysis.

The simulation is carried out in the grand–canonical ensemble, with the chemical potentials \( \mu_p, \mu_c \) of polymers and colloids (or fugacities \( z_p, z_c \)) as independent variables. Following common practice, we use the so–called “polymer reservoir packing fraction” \( \eta_{pr}^p \equiv \pi z_p \sigma_p^3 / 6 \) rather than \( z_p \) as the temperature–like variable. As in the study of bulk critical behavior \[27, 28\] and “capillary condensation” \[17, 18\] of the colloids on hard walls we use a grand–canonical cluster move \[26\] together with a very efficient reweighting scheme, successive umbrella sampling \[30\], to obtain the distribution function \( P_L(\eta_c | \eta_{pr}^p, z_c) \). This distribution function is defined as the probability to observe the system with colloid packing fraction \( \eta_c \) at “inverse temperature” \( \eta_{pr}^p \) and colloid fugacity \( \eta_c \). For states far away from phase coexistence, \( P_L \) is a single–peaked function, while near phase coexistence a double–peak structure develops \[17, 18, 27, 28, 29, 30\]. The precise location of the value of \( z_c \) at which two–phase coexistence occurs is given by the equal weight rule \[31\]. The positions of the two peaks of \( P_L \) then yield (preliminary) estimates for the two branches of the coexistence curve, the “liquid” branch \( \eta_{lc}^p \) and the “vapor” branch \( \eta_{uc}^p \). However, near criticality these estimates are affected by finite size effects \[27, 28, 29\]. To deal with the latter, we study reduced moments
FIG. 1: Colloid concentration profiles $\eta_c(z)$ and polymer concentration profiles $\eta_p(z)$ as function of $z$ for a thin film with asymmetric walls (hard wall at $z = 0$, while for the other wall at $z = D = 10$ the potential of Eq. (1) acts, with $\varepsilon = 2.5$). Profiles were obtained at $\eta_c = 0.18$, $\eta_p = 0.70$ (a), $\eta_c = 0.18$, $\eta_p = 0.95$ (b), $\eta_c = 0.05$, $\eta_p = 1.20$ (c), and $\eta_c = 0.33$, $\eta_p = 1.20$ (d). For profiles (c) and (d), the choices $\eta_c = 0.05, 0.33$ roughly correspond to the two branches of the coexistence curve, see Fig. 2.

$P_L$ at phase coexistence, defining an analogue of the order parameter of the Ising model,

$$m = \eta_c - \langle \eta_c \rangle, \quad \langle \eta_c \rangle = \int_0^\infty \eta_c P_L(\eta_c | \eta_p^c, z_c) d\eta_c,$$

and higher order moments, $\langle m^p \rangle = \int m^p P_L(\eta_c | \eta_p^c, z_c) d\eta_c$. Following the behavior of ratios such as $U_4 = \langle m^2 \rangle^2 / \langle m^4 \rangle$ along the path in the $(z_c, \eta_p^c)$ phase along which phase coexistence occurs for several choices of $L$ one can estimate the critical point ("cumulant intersection method" [29]).
FIG. 2: Coexistence curves for $D = 5$, $L = 30$ (a) and $D = 10$, $L = 20$ (b), showing four choices of $\varepsilon$ in each case. The data points with open symbols show the vapor–like ($\eta^v_c$) and liquid–like ($\eta^l_c$) branches of the coexistence curve, as extracted from the peaks of $P_L$. The broken curves show the coexistence diameter $\delta = (\eta^v_c + \eta^l_c)/2$, on which the critical points are marked with full symbols. The critical values $\eta^r_p$,crit of $\eta^r_p$ are highlighted by dotted horizontal lines.

III. SIMULATION RESULTS

Figure 1 shows typical concentration profiles for a slit of width $D = 10$ at $\eta_c = 0.18$ and $\varepsilon = 2.5$ and three choices of the polymer reservoir packing fraction: $\eta^r_p = 0.7$ (in the one phase region of the bulk), $\eta^r_p = 0.95$ (in the two phase region of the bulk) and at $\eta^r_p = 1.20$ (as we shall see, this is in the two phase region of the thin film: therefore two profiles are shown here, corresponding to the two coexisting phases). For $\eta^r_p = 0.7$ one can see that there is an enhancement of the colloid concentration on the hard wall, as expected from the depletion attraction already noted in previous studies [13, 14, 17, 18]. On the repulsive wall, the colloid concentration is somewhat depressed (and the polymer concentration slightly enhanced), but in the center of the film both concentrations are roughly constant, as expected for bulk–like behavior.

For $\eta^r_p = 0.95$, on the other hand, the profiles are very different: phase separation in a colloid–rich and a colloid pure phase has occurred, separated by an interface in the center of the slit. The interfacial profile resembles that of an interface between bulk coexisting phases (broadened by capillary waves [32]). For $\eta^r_p = 1.2$, finally, the interface is localized either at
FIG. 3: Fourth–order cumulant $U_4$ (a) and susceptibility (b) $k_B T \chi = L^2 D (\langle m^2 \rangle - \langle |m| \rangle^2)$ plotted vs. $\eta^r_p$, for a slit of thickness $D = 5$ and $\varepsilon = 1.0$, for several values of $L$ as indicated in the figure. Insert in a) shows the slope $Y_1$ of the cumulants, evaluated at $\eta^r_{p,\text{crit}} = 0.937 \pm 0.003$, on log–log scales to extract the exponent $\nu$ (note $Y_1 \propto L^{1/\nu}$), yielding $1/\nu \approx 1.056$. The inset in b) shows the extrapolation of the peak positions, from which $\eta^r_{p,\text{crit}} = 0.935 \pm 0.005$ results, consistent with (a).

FIG. 4: Phase boundary $\mu_{\text{coex}} (D, \varepsilon)$ plotted vs. $\eta^r_p$ for several choices of $\varepsilon$. For comparison, also the symmetric slit, $\varepsilon = 0$ [17] and the bulk phase boundary $\mu_{\text{coex}}^{\text{bulk}}$ [27] are included. Full symbols mark the locations of the critical points. Inset shows $\Delta \mu = \mu_{\text{coex}} - \mu_{\text{coex}} (D, \varepsilon)$ versus $\eta^r_p$. 
FIG. 5: Dependence of the critical value $\eta^r_{p,\text{crit}}$ on $\epsilon$, for $D = 5$ (circles) and $D = 10$ (squares).

the right wall or at the left wall (Fig. 1c,d): phase separation has occurred in the thin film (Fig. 2).

Since Fig. 2 refers to finite $L$, the data for the coexistence curves do not merge at the critical points, but rather extend somewhat into the one–phase region ("finite size tails"). However, repeating the simulation for several choices of $L$ and performing a finite size scaling analysis, as done for this model both in the bulk [27, 28] and in thin films with symmetric walls [17, 18], the critical point can be determined rather reliably. Figure 3 gives an example for $\epsilon = 1.0$. Due to crossover effects the cumulant intersections do not occur precisely in a point, but rather are spread out over some region, but nevertheless, the critical point $\eta^r_{p,\text{crit}}$ can be inferred with reasonable accuracy. The effective exponents $\nu_{\text{eff}} \approx 0.947$ (extracted from $Y_1$, Fig. 2(a)) and $(\beta/\nu)_{\text{eff}} \approx 0.155$ (extracted from $\Delta = (\eta_c^r - \eta_c^v)/2$ at $\eta^r_{p,\text{crit}}$ {not shown}) deviate somewhat from the 2$d$ Ising values ($\nu = 1$, $\beta/\nu = 0.125$), similarly as in thin Ising films with competing walls [6].

When $\epsilon$ increases, $\eta^r_{p,\text{crit}}$ is shifted to considerably larger values and at the same time the chemical potential $\mu_{\text{coex}}(D, \epsilon)$ moves towards the bulk curve, $\mu_{\text{coex}}^{\text{bulk}}$ (Fig. 4), and is almost reached for $\epsilon = 2.5$. The limiting value $\eta^r_{p,\text{crit}}(D \to \infty)$ for which $\mu_{\text{coex}}(D \to \infty, \epsilon) = \mu_{\text{coex}}^{\text{bulk}}$ would yield an estimate for the wetting transition $\eta^r_{p,w}$ [4, 5, 6, 7, 12] of this model. Very roughly, we estimate $\eta^r_{p,w} \approx 1.20 \pm 0.05$.

Comparing to the case of symmetric hard walls ($\epsilon = 0$), a non–monotonic variation of
$\eta_{p,\text{crit}}^r$ on $\varepsilon$ is found (Figs. 4–5). A similar behavior has been seen for asymmetric polymer mixtures studied by self-consistent field theory \[10\]. Our finding implies that this non-monotonic variation is a rather general phenomenon, and it holds beyond mean field theory.

IV. CONCLUSIONS

In a colloid–polymer mixture confined by hard walls, depletion attraction leads to the formation of colloid–rich layers near the walls. By adding a suitable short range interaction at one of the walls, polymers can be effectively attracted to this wall whereas the depletion attraction of colloids is reduced at it. In this case of a colloid–polymer mixture confined between asymmetric walls, our simulations demonstrate that an interface localization transition can occur. Our results also imply that semi-infinite colloid–polymer mixtures, confined by a hard wall, should exhibit a wetting transition at sufficiently large polymer fugacity. We suggest that interface localization transitions could be realized experimentally by suitable coating of one wall of a slit pore with a polymer brush.

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