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Surface transition in athermal polymer solutions

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According to a recently developed density functional theory, athermal polymer solutions, in which the solvent particles are smaller than the monomers, may undergo a bulk fluid-fluid phase separation, driven by excluded volume effects. In recent work, we showed that an inert surface immersed in the dilute polymer phase can, in principle, be wetted by the condensed phase. However, we show here that the "prewetting transition" we assumed in our earlier studies is in fact a different type of surface transition. Rather than completely wet the surface at coexistence, the condensed phase layer which forms in the presence of the dilute bulk remains globally stable (and is finite in width) even as the bulk coexistence conditions are approached. Hence, the adsorbed phase inhibits complete wetting of the surface by the dilute phase. The surface transition is first order for the systems we study here and, for longer polymers, the surface phase coexistence line meets the bulk coexistence curve nontangentially to give rise to a lower transition point. For short polymers, we find that the surface transition can occur for a supercritical bulk. We develop a simple one-component thermal model, which displays analogous behavior at an adsorbing surface and provides us with some insight into the qualitative mechanisms responsible.

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I. INTRODUCTION

Depletion attractions arising from excluded volume effects have been the focus of numerous studies of colloidal phenomena in recent years. Theoretical [1–12] and experimental [8,13–16] studies suggest that an excluded volume driven demixing transition may occur in binary athermal mixtures, in which there is a sufficient size disparity between species, or where the repulsive interactions are nonadditive. In additive binary hard sphere mixtures, it appears that demixing will only occur at volume fractions high enough to render at least one of the phases solid.

Colloid dispersions with added polymers or rod-like particles offer a different scenario [7,11,12,17–19] as, in this case, the depletion attraction is caused by configurational restrictions imposed on the polymers or rods by the surfaces of the large particles. This is a fundamentally different mechanism to that acting in asymmetric hard sphere mixtures.

In this work, we consider a model wherein the polymer solute consists of hard sphere monomers, which are larger in size than the hard sphere solvent in which they are dissolved. Thus the depletion of solvent particles leads to an attraction between monomers. The thermodynamic consequences of this attraction are accentuated by their mutual bonding, leading to a higher propensity for the mixture to undergo a demixing transition, compared with simple hard sphere mixtures.

Recently, we developed a density functional theory [20] (DFT), which predicted this very behavior. The functional utilizes the generalized Flory-dimer (GFD) equation of state [21]. The GFD equation of state is based on a scaled particle approach, and for a simple binary hard sphere mixture it reduces to the Boublik-Mansoori-Carnahan-Starling-Leland equation of state [22,23]. Our theory predicts that when the larger spheres are linked to form polymers, as in the model described above, demixing occurs in the bulk, even for relatively modest size disparities and volume fractions. However, if the monomer bonds are removed, to give a mixture of spheres there is no demixing.

Solvent depletion will also cause polymer molecules to be effectively attracted to hard or repulsive surfaces, especially when the total volume fraction is high. Acting against this is the role the surface plays in restricting polymer configurations, causing an entropic penalty for molecules close to the surface. At high pressures, excluded volume effects will dominate, and lead to the preferential adsorption of polymers. In recent work [24], we studied surface transitions occurring at a simple hard, inert surface, immersed in our polymer solution model, with a size disparity ratio (solvent-radius/monomer-radius) of 0.5. By calculating surface tensions for bulk fluid phases against the surface, we were able to establish conditions for complete wetting. We also found what we believed to be a prewetting transition. However, further investigations (inspired by recent discussions [25]) now indicate that this surface phase does not fully wet the surface as the bulk coexistence line is approached. Instead, the thin prewetting layer remains finite in width, indicating a *frustrated wetting* scenario.

The discussion above suggests that one can understand the behavior of our two-component model in terms of effective interactions between monomers. Some previous work has sought to formalize this view. Effective interactions are obtained by integrating over solvent degrees of freedom,

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while holding the polymer configurations fixed [12,19]. By this process, one obtains a hierarchy of many-body potentials, between monomers and also between monomers and the surface. However, these interactions become dependent on a thermodynamic quantity, e.g., solvent chemical potential, or total pressure. Note, that the system remains independent of temperature even after this pre-averaging process.

Mutually attractive fluid particles will have fewer neighbor interactions close to a surface. However, wetting by the gaseous phase may occur in the presence of a (one-body) surface attraction. This can be a first-order transition if the surface field is sufficiently strong. Beyond the critical conditions of the bulk, a wetting transition is not expected due to the absence of a stable bulk liquid phase. Indeed, the critical end points of the first-order prewetting lines are expected to be below the bulk critical point, because of the reduction in fluid-fluid attractions at the surface. If, on the other hand, the attractive fluid-fluid interactions were *enhanced* by the presence of the surfaces, it is possible that first-order prewetting lines would extend into the supercritical region [26]. Surface transitions of this type have been well studied for ferromagnetic models. However, the application of these results to fluids is not always straightforward [27,28]. In particular, physical mechanisms that give rise to enhanced interactions between fluid molecules at surfaces are not commonplace. On the other hand, in previous studies we observed that, for short polymers, the surface transition in our model did project into the supercritical region of the bulk solution. Thus, we conjecture that the surface does enhance the effective polymer-polymer depletion attraction in our model system, and that it is primarily this effect which drives the surface transition that we observed in our earlier work. A similar enhancement of depletion attraction by a surface was recently found by Xiao, Gua, and Li [29] using Monte Carlo simulations. In order to further elucidate the consequences of this conjecture, we will investigate a simple one-component thermal analogue, that displays a behavior analogous to that found in the athermal polymer model.

We provide a brief description of the polymer DFT in the next section, which is followed by a presentation of the results obtained. The paper ends with a few summarizing comments and conclusions.

II. THEORY AND MODEL DESCRIPTION

We consider monodisperse polymer molecules, each containing r monomers. We shall restrict ourselves to a "pearl-necklace" model, where neighboring monomers are connected with a rigid bond potential, $V_b(\mathbf{R})$, defined by: $e^{-\beta V_b(\mathbf{R})} \propto \prod \delta(|\mathbf{r}_{i+1}-\mathbf{r}_i|-\sigma_{mm})$. β is the inverse thermal energy, while σ_{mm} is the monomer-monomer hard sphere diameter. A polymer configuration is denoted by $\mathbf{R}=(\mathbf{r}_1,\ldots,\mathbf{r}_r)$, where $\mathbf{r}_i$ is the coordinate of monomer i. We define the multipoint density distribution $N(\mathbf{R})$, such that $N(\mathbf{R})d\mathbf{R}$ is the number of polymer molecules having configurations between $\mathbf{R}$ and $\mathbf{R}+d\mathbf{R}$. An ideal polymer solution is fully described by the following *exact* free energy functional [30]

$$\beta\mathcal{F}_p^{id} = \int N(\mathbf{R})(\ln[N(\mathbf{R})]-1)d\mathbf{R} + \beta\int N(\mathbf{R})V_b(\mathbf{R})d\mathbf{R} + \int n_s(\mathbf{r})(\ln[n_s(\mathbf{r})]-1)d\mathbf{r}, \qquad (1)$$

where $n_s(\mathbf{r})$ is the solvent particle density. In this work we consider athermal solutions, i.e., monomers and solvent particles only interact as hard spheres. Assuming pairwise additivity, we have the following relations $\sigma_{\alpha\beta}=(\sigma_{\alpha\alpha}+\sigma_{\beta\beta})/2$, where indices's α and β denote either monomer or solvent species, i.e., "m" or "s." Specifically, we will in this work only consider cases where $\sigma_{ss}/\sigma_{mm}=0.5$. Consequently, $\sigma_{ms}/\sigma_{mm}=0.75$. The generalized Flory-dimer (GFD) equation of state was developed by Wichert, Gulati, and Hall [21], and Forsman *et al.* [20,31] derived the corresponding grand potential, $\Omega[N(\mathbf{R}),n_s(\mathbf{r})]$

$$\begin{aligned}\beta\Omega = {} & \int (n_m(\mathbf{r})-n_e(\mathbf{r}))f_c^{ex}(r,\bar{n}_m^m,\bar{n}_s^m)d\mathbf{r} \\ & + \frac{1}{2}\int n_e(\mathbf{r})f_e^{ex}(\bar{n}_m^m,\bar{n}_s^m)d\mathbf{r} + \int n_s(\mathbf{r})a_0^{ex}(\bar{n}_m^s(\mathbf{r}),\bar{n}_s^s(\mathbf{r}))d\mathbf{r} \\ & + \beta\mathcal{F}_p^{id} + \beta\int n_m(\mathbf{r})[V_m^{ext}(\mathbf{r})-\mu_p]d\mathbf{r} + \beta\int n_s(\mathbf{r}) \\ & \times[V_s^{ext}(\mathbf{r})-\mu_s]d\mathbf{r}, \qquad (2)\end{aligned}$$

where V_α^{ext} is an external potential, while μ_p and μ_s are the polymer and solvent chemical potentials, respectively. The weighted densities, $\bar{n}_\alpha^\beta(\mathbf{r})$, are given by [32]

$$\bar{n}_\alpha^\beta(\mathbf{r}) = 3(4\pi\sigma_{\alpha\beta}^3)^{-1}\int n_\alpha(\mathbf{r}')\,\theta(\sigma_{\alpha\beta}-|\mathbf{r}-\mathbf{r}'|)\mathbf{d}\mathbf{r}' \qquad (3)$$

with $\theta(x)$ denoting a step function. The density of end monomers is denoted $n_e(\mathbf{r})$. They exclude more volume than inner ones do [21,30]. The free energies per particle for central and end monomers are denoted f_c^{ex} and f_e^{ex}, respectively, while the corresponding quantity for solvent particles is a_0^{ex}. These have been explicitly reported elsewhere [31].

We shall investigate mondisperse polymer solutions in contact with an inert flat surface, either completely hard or softly repulsive. We define the z direction to be perpendicular to the surface, and symmetry allows us to integrate out the lateral (x,y) dimensions parallel with the surface. The grand potential per unit area can be expressed as $\Omega/S=-\int_0^\infty P_\parallel(z)dz$, where S is the surface area, and $P_\parallel(z)$ is the local component of the pressure tensor acting parallel with the surface. The surface is located at $z=0$. Hence, in the case of a hard wall, monomers are confined to a region $z/\sigma_{mm} \geqslant 0.5$, while for solvent particles, $z/\sigma_{mm} \geqslant 0.25$. The reduced interfacial tension, $\gamma_{\alpha w}=\beta g_{\alpha w}\sigma_{mm}^2$, between the wall (w) and a bulk phase (α), is obtained from: $g_{\alpha w}=\int_0^\infty (P^b-P_\parallel^{(\alpha)}(z))dz$, where P^b is the bulk pressure. In order to simplify the notation, we also introduce a reduced pressure, P^*, defined as $P^*=P/P_c(r=200)$, where $\beta P_c(r=200)\sigma_{mm}^3=13.571$ is the critical pressure of a 200 mer solution.

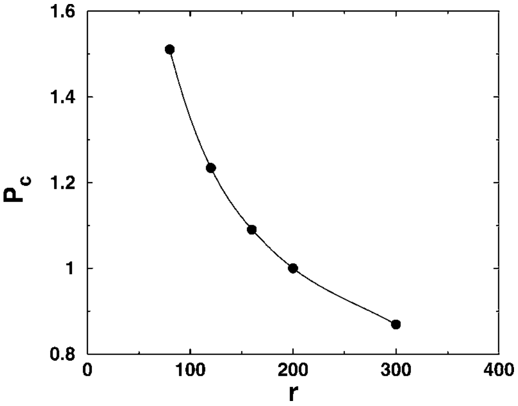

FIG. 1. Bulk critical pressures for monodisperse athermal polymer solutions, with $\sigma_{ss}/\sigma_{mm}=0.5$, as predicted by the generalized Flory-dimer equation of state; r is the number of monomers/chain. The pressures are reduced by the critical pressure for a 200 mer solution, i.e., $P_c^*=P_c/P_c(r=200)$, where $\beta P_c(r=200)\sigma_{mm}^3=13.571$.

Integrals were explicitly performed on a grid in a region $0 \leqslant z \leqslant L$. Bulk conditions were assumed for $z > L$. In order to facilitate a large truncation distance, we usually adopted a variable grid spacing, gradually increasing away from the wall. In order to increase the accuracy of the free energy estimations further, we have adopted the Romberg rule [33]. Several tests have convinced us that a variable grid spacing combined with the Romberg rule leads to very accurate predictions, at a low computational cost. Explicit demonstrations of this accuracy will be provided below.

III. RESULTS

A. Athermal polymer solutions

We first consider bulk demixing, which is germane to our later study on surface phenomena. Bulk demixing was investigated in our previous work [24]. As described earlier, the polymer solvent mixture has a greater tendency to phase separate, compared with simple hard sphere mixtures, due to the cooperativity introduced by intra-molecular bonding between monomers. The phase separation itself is driven by depletion of the smaller solvent particles in regions of high total volume fraction. As the pressure is increased, these excluded volume considerations become more important, which increases the propensity of the system to phase separate. Figure 1 shows how the bulk critical pressure, predicted by the density functional theory, varies with chain length. The critical pressure decreases rapidly as the chain length increases and there is some indication of saturation at the larger polymer lengths. We expect that the dilute polymer phase approaches zero concentration as the polymer length becomes infinite. Furthermore, the critical point will occur at some value of the solvent chemical potential, which could be denoted the "theta" point in analogy with thermal systems. In this study, we shall restrict ourselves to finite polymer lengths. The longest polymer we considered was $r=300$. In the following discussion, the bulk *dilute* and *concentrated* phases will be denoted as (d) and (c), respectively.

1. 300 mer solution at a hard wall

In our previous work [24], we used the density functional theory to investigate the effect of introducing a hard surface into the dilute polymer solution, with the intention of studying wetting phenomena at the surface. At high degrees of under saturation, the dilute polymer solution in contact with the surface remains stable, establishing a small excess adsorption of polymer. We denote this as the *thin* phase. If the system were to behave analogously to simple thermal fluids, one would expect that, in our model, wetting would occur on the dilute branch of the coexistence line below some wetting pressure, P_w, provided the depletion attraction of polymers to the surface was large enough. As the pressure decreases from P_w to the bulk critical pressure, the surface tension between dilute and concentrated phases should decrease, thus favoring wetting. That is, in our model, the pressure behaves analogously to an "inverse temperature" and wetting should occur when

$$\gamma_{thin-w} \geqslant \gamma_{c-w} + \gamma_{d-c} \tag{4}$$

We have denoted the [concentrated phase/wall], [dilute (thin) phase/wall] and [dilute/concentrated] interfacial tensions as γ_{c-w}, γ_{thin-w} and γ_{d-c}, respectively. As was reported in our previous work, we were able to establish conditions for which Eq. (4) was satisfied. This was done by using the DFT to solve for surface free energies for the three interfacial scenarios to obtain, γ_{c-w}, γ_{thin-w} and γ_{d-c}. Additionally, we found (metastable) *thick* phase solutions along the dilute bulk coexistence line, for a range of pressures. The thick phase contains a macroscopically thick concentrated polymer layer of width l, which would become infinite as the coexistence curve is approached under complete wetting conditions. For large thicknesses the total interfacial energy, $\gamma_{thick-w}$, is a numerically flat function of l and will be essentially equal to the sum, $\gamma_{c-w}+\gamma_{d-c}$. In our calculations, we chose for l a value beyond which we could not numerically discern changes in $\gamma_{thick-w}$. This was typically in the range $l=40\sigma_{mm}$ to $80\sigma_{mm}$.

Interestingly, when the bulk conditions are moved off the coexistence curve into the undersaturated regime, the thick phase becomes unstable. The width collapses dramatically so that only a single narrow layer of the concentrated phase remains adjacent to the surface, even for minute degrees of undersaturation. We denote this narrow layered phase as the *limited* phase. Upon increasing the degree of undersaturation, the system eventually undergoes a first-order transition from this limited phase to the thin phase. This behavior is typical of a prewetting scenario, suggesting that the limited phase is a prewetting phase that should grow in width as the bulk coexistence curve is approached. This was conjectured in our previous report [24]. However, we have now found that, if the dilute branch of the bulk coexistence curve is approached, starting with a stable limited phase in the undersaturated bulk, one observes a hysteresis and the limited phase remains stable up to and at coexistence. This curious behavior suggests that the thin-limited transition is not a normal prewetting transition and that we are observing a *frustrated wetting* situation [39] The apparent stability of the limited phase means that we are able to determine its free

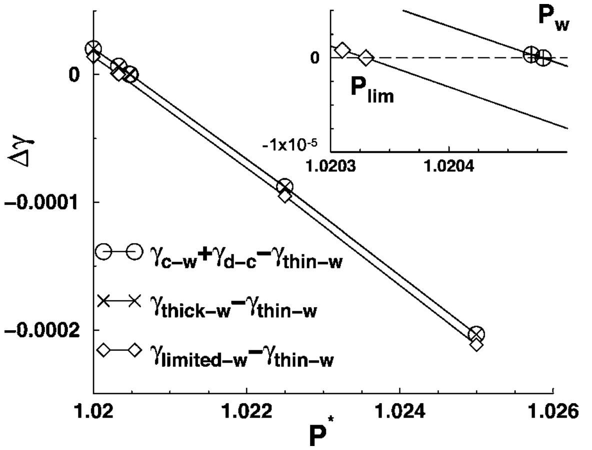

FIG. 2. Interfacial tension differences of a 300 mer solution, where "w" denotes a hard wall. It should be pointed out that the dilute-concentrated interfacial tension, γ_{d-c}, is much smaller in magnitude than all other interfacial tensions. Note also that the agreement between $\gamma_{c-w}+\gamma_{d-c}-\gamma_{thin-w}$ and $\gamma_{thick-w}-\gamma_{thin-w}$ confirms that the calculations are accurate.

energy, γ_{lim-w}, on the dilute coexistence branch. This can be compared with the surface free energies described above, in order to establish the absolute stabilities of the possible surface phases. In Fig. 2 we show how the various surface free energies vary with pressure along the dilute branch of the bulk coexistence line. The wetting pressure, P_w, occurs where either of the quantities, $\gamma_{c-w}+\gamma_{d-c}-\gamma_{thin-w}$ or $\gamma_{thick-w}-\gamma_{thin-w}$ is zero. It is clear from Fig. 2 that both quantities predict numerically identical wetting pressures, confirming the accuracy of our calculations. Curiously, the surface free energy of the wetting phase decreases with increasing bulk pressure. This implies the existence of a *lower* wetting pressure, which is the opposite to what we expected in this system. A study of the individual surface components shows that, while γ_{d-c} increases with pressure, as expected, the quantity $\gamma_{c-w}-\gamma_{thin-w}$ decreases more rapidly with increasing pressure. The fluid-surface terms dominate the free energy of the wetting layer, which is the opposite to what occurs in typical thermal systems. In thermal systems, a lower wetting temperature comes about due to the dominant temperature dependence of the fluid-fluid surface tension. This arises from the higher-order density dependence of the fluid-fluid interfacial term compared with the fluid-surface terms.

While our prediction for the wetting pressure is anomalous, our calculations show that, even though Eq. (4) is satisfied, complete wetting is thermodynamically not preferred in any case. Indeed, Fig. 2 shows that the surface free energy of the limited phase is marginally lower than that of the thick (wetting) phase, which means that the system will preferentially partially wet the surface with the limited phase at pressures above some value, P_{lim}, which is slightly lower than P_w. Thus, complete wetting is frustrated by the existence of the limited phase. The difference between P_{lim} and P_w was not discerned in our previous work. We traced the thin-limited coexistence line, which is presented in Fig. 3. As demonstrated by Hauge and Schick [34], ordinary prewetting lines are expected to approach the bulk coexistence tangentially. A crucial criterium in their derivation is that the thickness of the wetting phase diverges on the approach to bulk coexistence conditions. In our case, the surface transition line meets the bulk coexistence curve at P_{lim} nonasymptotically. This is not surprising, given that the width of the limited phase remains strictly finite. An example of the corresponding monomer density profiles is given in Fig. 4. The limited phase appears to be related to layered phases, which appear in highly structured fluids. We were not able to discern other layered phases in these calculations. However, in our previous study, we showed that the DFT predicts the existence of several multilayered phases for shorter polymers. It is, therefore, of interest to determine whether the limited phase exists in the presence of a soft repulsive wall.

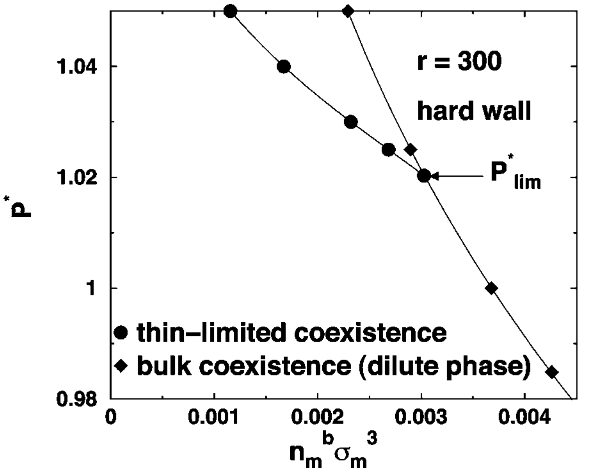

FIG. 3. Coexistence line for the thin-limited phase transition at a hard surface, immersed in a 300 mer solution.

2. 300 mer solution at a soft repulsive wall

We performed density functional calculations of the same model solution, in the presence of a surface which interacts

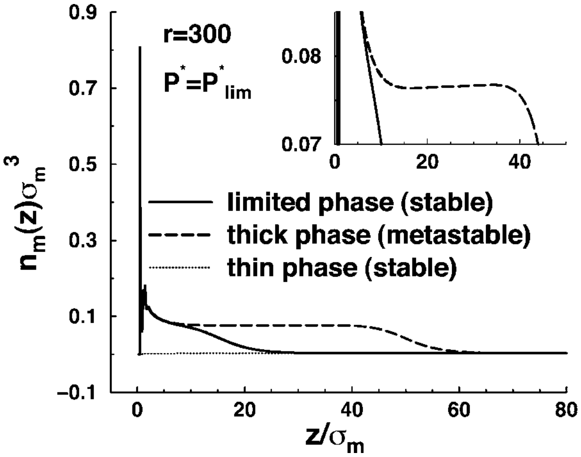

FIG. 4. Monomer density profiles for the thin, thick, and limited phase, respectively, at bulk coexistence conditions. The thin and limited phases also coexist, which means that this is the lowest pressure, P_{lim}, where such a coexistence is possible. The thick phase is slightly less stable, i.e., P_{lim} is lower than the wetting pressure, P_w.

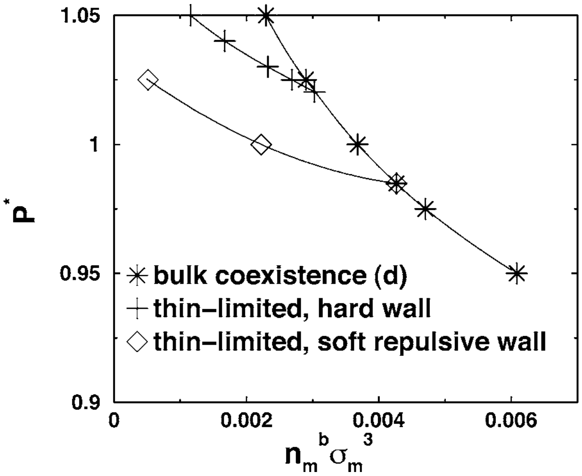

FIG. 5. The thin-limited coexistence lines of a 300 mer solution, in the presence of a hard and soft repulsive wall, respectively.

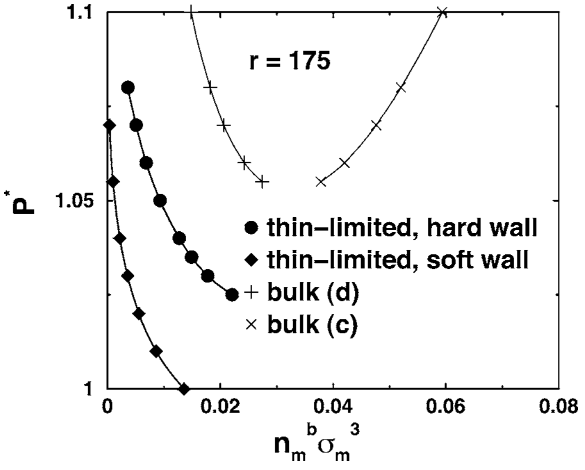

FIG. 6. The thin-limited coexistence lines of a 175 mer solution, in the presence of a hard and soft repulsive wall, respectively.

with all solution species via the repulsive part of the Lennard-Jones interaction. This surface potential is truncated and shifted to zero at $z=5\sigma_{mm}$. Specifically, a solution particle of type α will experience an external potential $V_\alpha^{ex}(z)$, where

$$\beta V_\alpha^{ex}(z)=\begin{bmatrix} 0, & z>5\sigma_{mm} \\ \dfrac{4\pi}{45}\left(\dfrac{\sigma_{m\alpha}}{\sigma_{mm}}\right)^3\left[\left(\dfrac{\sigma_{m\alpha}}{z}\right)^9-\left(\dfrac{\sigma_{m\alpha}}{5\sigma_{mm}}\right)^9\right] & z\leqslant 5\sigma_{mm} \end{bmatrix} \tag{5}$$

An advantage of using a soft (rather than hard) repulsive wall, is that the density profiles are less rapidly varying, which admits the use of a coarser grid in the calculations. The results are summarized in Fig. 5, which shows the limited phase coexistence line in the presence of the softer repulsion. It is apparent that the softer potential enhances the formation of the limited phase, as evidenced by its existence at even lower bulk pressures, compared with the hard wall. Detailed structural analysis reveals that the monomers are better able to approach the surface further, relative to the solvent, when the wall is soft. Consequently, better mixing between the two components promotes the formation of the limited phase.

3. 175 mer solution at hard and soft walls

We repeated our calculations with hard and soft repulsive walls, but with shorter polymers in an otherwise identical solvent ($q=0.5$). The effect of reducing the polymer length to $r=175$ has a marked qualitative effect on the behavior of the limited phase. As was already noted in Ref. [24] the thin-limited coexistence line no longer meets the bulk coexistence curve, but in fact proceeds below the corresponding bulk critical point. This behavior is more pronounced with the soft repulsive surface. This is illustrated in Fig. 6. The thin-limited coexistence line terminates at a critical point. In Fig. 7 we illustrate how the adsorption of the two surface phases merges at some surface critical pressure, which in this case is slightly below unity on our reduced scale. We conjecture that the line of thin-limited critical points that result from polymers of increasing length, would meet the bulk coexistence curve at a surface/bulk multi-critical point (allowing for interpolation between integral values for r). Relating this to simpler magnetic systems [26] is difficult due to the mixing of scaling fields inherent to intrinsically asymmetric fluid models [27], as well as the added complication of the additional scaling field mixing that can easily be seen in the effective interaction approach.

IV. DISCUSSION

What physical mechanism drives the formation of the limited phase? As mentioned earlier, it appears to have a structural origin, but is, nevertheless, quite different from ordinary layered phases [35]. The latter have been rather thoroughly studied for simple one-component thermal systems against very attractive surfaces. They are characterized by strongly oscillatory density profiles with a spatial fre-

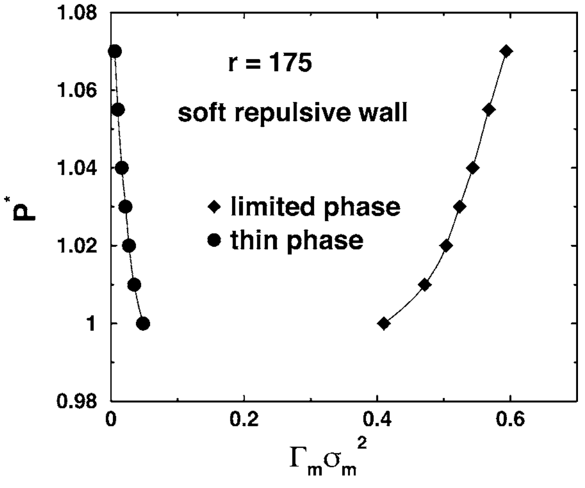

FIG. 7. The net monomer adsorption, Γ_m, of coexisting thin and limited phases at a soft repulsive surface. Γ_m is defined as $\Gamma_m=\int_0^\infty(n_m(z)-n_m^b)dz$, where n^b is the bulk monomer density.

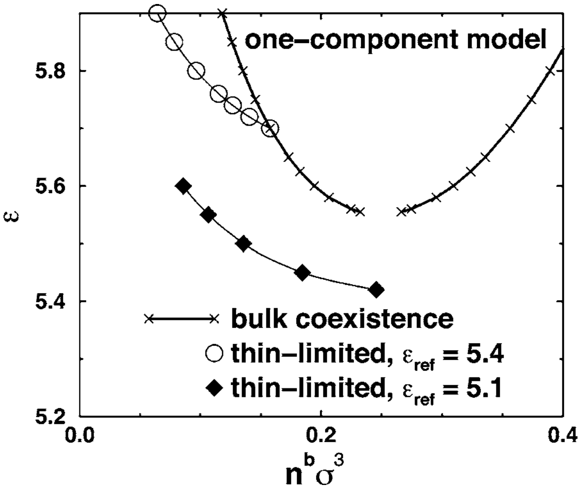

FIG. 8. Thin-limited equilibrium conditions in a simple one-component analogue, designed to qualitatively mimic the behavior of an athermal polymer solution, in which there is an entropy driven fluid-fluid transition. The effective attraction to an inert surface is here generated by an external potential, $V_{ex}=V_{L-J}^{tr+sh}(\epsilon-\epsilon_{ref})n_c\sigma^3$, where n_c is a coarse grained (weighted) density and V_{L-J}^{tr+sh} is a standard truncated and shifted Lennard-Jones surface potential. The truncation distance is $z_c/\sigma=1.5$. The strength of the surface potential is regulated by the parameter ϵ_{ref}. In the binary reference system, this corresponds to shifting the position of the bulk critical pressure, i.e., the location of the bulk coexistence envelope. Note that the amplitude factor of V_{L-J}^{tr+sh} has been chosen such that the thin-limited coexistence curve terminates at $\epsilon=5.7(\equiv\epsilon_{lim})$, when $\epsilon_{ref}=5.4$.

quency reflecting the molecular size of the constituent fluid. As the coexistence curve is approached under wetting conditions, one would expect to observe a progression of transitions between surface phases of increasing numbers of layers, unless they are rendered nondiscrete above the roughening transition. On the other hand, the limited phase observed in our system appears to intrude between the thin and thick phase, so as to frustrate complete wetting, by its subsequent lowering of the surface tension. As the bulk coexistence curve is approached, the limited phase persists. For longer polymers the thin-limited coexistence line is terminated when it meets the dilute branch of the bulk coexistence curve, while for shorter polymers the coexistence line can proceed below the bulk critical point, terminating at a surface critical point.

The fact that, for short polymers, the limited phase exists when the bulk is supercritical, suggests that its formation is largely driven by the enhancement of fluid-fluid interactions. In particular, the presence of the surface increases the effective depletion attraction between polymer molecules. This can be understood if one considers the fact that the surface locally enhances the concentration of solvent particles, due to hard sphere packing. In the DFT, local thermodynamics are described with a free energy function (and weighted particle densities). That free energy function predicts bulk demixing at high solvent densities. The greater density of solvent particles adjacent to the surface can in some cases be sufficient to drive a local phase separation, even if the bulk is supercritical. In terms of the *effective* potential model, the surface provides an effective one-body depletion attraction, but also enhances the effective two-body interaction between polymer monomers, because of the larger local solvent density. Unlike many effective potential models, our approach does take account of variations in solvent densities, and implicitly includes all orders of effective interactions, via the highly nonlinear form of the free energy functional. The behavior of the surface free energies depicted in Fig. 2 is indicative of the nonlinear dependence on fluid density of the surface-fluid components of the surface tension.

For a typical thermal fluid interacting with an attractive surface, there is generally a lower wetting temperature, with wetting continuing up to the bulk critical temperature. In this case, the surface-fluid surface tension is lowered by the direct surface interaction, which is roughly linear in the fluid surface density. This competes with a second-order fluid-fluid term (due to the loss of nearest neighbors for fluid particles at the surface). The wetting behavior of the fluid is thus determined by the fluid-fluid interfacial term, which is nonlinear and more strongly dependent on temperature. In our model, it appears that, if wetting is to occur, then it will happen *above* a certain (wetting) pressure, which is anomalous, given that the bulk has a lower bulk critical pressure. As described above, the mechanisms that lower the local free energy at the surface are highly nonlinear and respond more strongly to changes in the bulk pressure than the fluid-fluid interfacial tension, γ_{d-c}. The result being that the surface phase transition becomes more favored at higher pressures.

These mechanisms must compete with surface depletion, due to the restriction on polymer configurations at the surface. This provides an effective repulsive force with a range of the order of the radius of gyration for dilute polymer solutions. Hence, the thick phase is disfavored by the fact that adding polymers to the vicinity of, but actually at, the surface will decrease their configurational entropy, without much gain in excluded volume (since the surface is already saturated). This general mechanism, where a strong short-ranged attraction, coupled with a weak but long-ranged repulsion, leads to a "thick" phase of finite width (the limited phase, in our nomenclature), has been suggested and observed also in simple thermal systems [36–38].

As we observed, for longer polymers ($r=300$), polymer depletion was sufficient to cause the thin-limited coexistence line to intercept the bulk coexistence curve (at P_{lim}). We conjecture that, as the polymer molecules are made shorter, the intersection with the bulk coexistence curve approaches the bulk critical point, and then branches off into the supercritical region along a line of surface critical points (as indicated in the case $r=175$). The thin-limited coexistence line obtained for 200 mers in our previous work [24], suggests that this bulk critical point intersection will occur for chains with a length just slightly below 200.

We expect that the limited phase remains at least metastable, even at bulk coexistence, because it is the solvent layer immediately adjacent to the surface which drives the transition. However, the reason why the limited phase is marginally more stable than a thick wetting phase at bulk coexistence seems more elusive. It appears to be related to

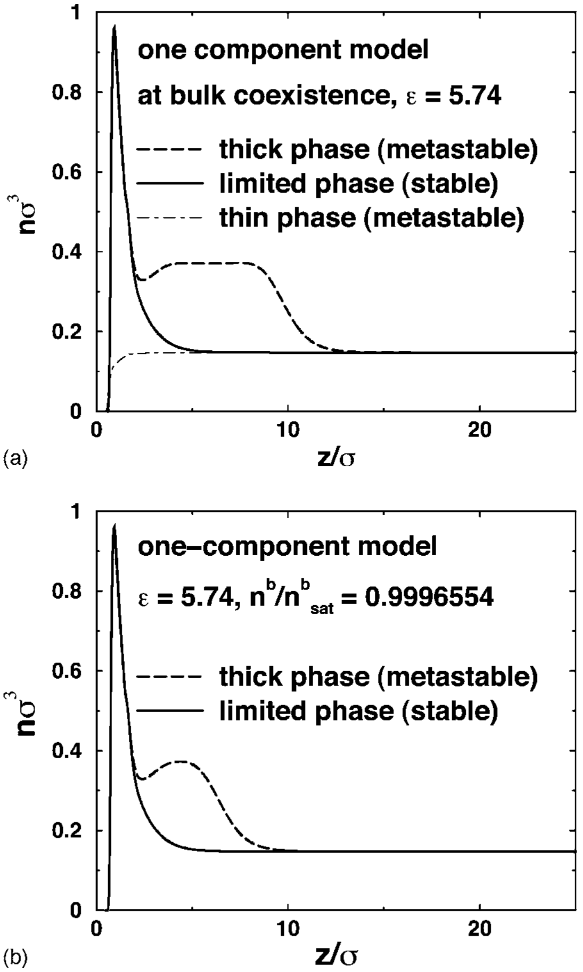

FIG. 9. Density profiles of thin, limited and thick phases, at $\epsilon = 5.74$. (a) At bulk coexistence conditions. Since $\epsilon > \epsilon_{lim}$, the limited phase is the most stable one. The inset is a blow-up of the first density maximum, for the limite and thick phase. (b) A very slightly undersaturated bulk fluid. The thin phase is not shown in this case.

structural changes in the fluid density profiles. In particular, inspection of the limited phase monomer profile and the thick phase profile close to the surface reveals a slightly greater monomer density at the surface for the limited phase. The effect is only minor, but it is sufficient to marginally lower the free energy of the limited phase relative to the thick phase. We expect that it is due to polymer molecules having a greater tendency to lie flatter on the surface in the limited phase compared with the thick phase.

In order to investigate the plausibility of the arguments outlined above, we constructed a simple effective one-component thermal model containing some aspects of the mechanisms we have invoked.

A. Simple one-component thermal analogue

The model is described by the following free energy functional:

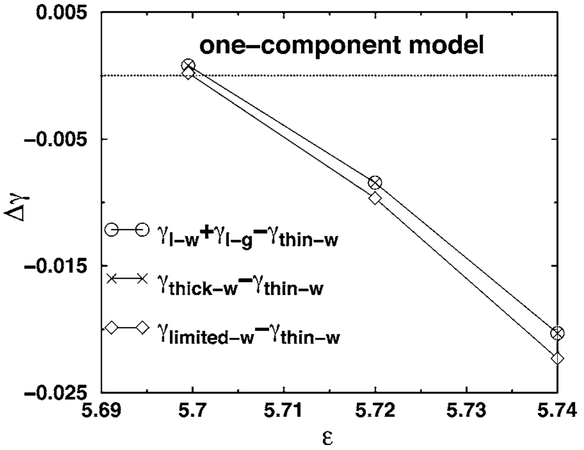

FIG. 10. Interfacial tension differences for the one-component thermal model.

$$\beta F[n(\mathbf{r})] = \int n(\mathbf{r})(\ln[n(\mathbf{r})] - 1)d\mathbf{r} + \int n(\mathbf{r})a_{CS}[n_c(\mathbf{r})\sigma^3]d\mathbf{r} - \epsilon \int n(\mathbf{r})n_c(\mathbf{r})\sigma^3 d\mathbf{r}, \tag{6}$$

where n is the fluid density, σ is the hard core diameter and n_c is the coarse-grained density, defined analogously to Eq. (3). The a_{CS} is the hard core contribution to the free energy per particle and is derived from the Carnahan-Starling equation of state

$$a_{CS}(x) = \frac{2}{1 - \frac{\pi x}{6}} + \frac{1}{\left(1 - \frac{\pi x}{6}\right)^2} - 3. \tag{7}$$

Fluid cohesion is provided by a step function pair potential with a range equal to σ and strength parameter, ϵ. This system will display a bulk liquid-gas phase separation for appropriate choices of ϵ.

In order to incorporate the effect of surface enhancement of fluid-fluid interactions, we will introduce a nonstandard surface interaction potential into the model

$$V_{ex}(\epsilon,z) = V_{L-J}^{tr+sh}(z)n_c(z)\sigma^3(\epsilon - \epsilon_{ref}), \tag{8}$$

where the truncated and shifted Lennard-Jones potential is given by

$$V_{L-J}^{tr+sh}(z) = \begin{bmatrix} 0, & z > 1.5\sigma; \\ V_{L-J}(z) - V_{L-J}(1.5\sigma), & z \leqslant 1.5\sigma; \end{bmatrix} \tag{9}$$

V_{L-J} given by its usual form

$$\beta V_{L-J} = 2\pi\left[\frac{2}{45}\left(\frac{\sigma}{z}\right)^9 - \frac{1}{3}\left(\frac{\sigma}{z}\right)^3\right]\epsilon_s\rho_s\sigma^3. \tag{10}$$

The "amplitude factor" $\epsilon_s\rho_s\sigma^3 = 2.8356$. The form of V_{ex} causes fluid particles close to the surface to experience an enhanced fluid-fluid attraction. However, this interaction can become repulsive as ϵ is decreased. The actual value at which this happens is set by the choice of ϵ_{ref}.

1. Fully optimized profiles

The one-component fluid model in the presence of V_{ex} predicts a limited surface phase, analogous to that observed in the athermal polymer solution model. The corresponding thin-limited transition lines, for two different choices of ϵ_{ref}, are shown in Fig. 8. As in the polymer solution, the limited phase remains finite in width at bulk coexistence. At the larger value of ϵ_{ref}, the thin-limited coexistence line intercepts the bulk coexistence curve nontangentially. For the lower value of ϵ_{ref}, the coexistence line becomes supercritical, ending at a critical point. This is analogous to the behavior of the polymer solutions, for different length of polymer.

In contrast to the case for polymer solutions, we were able to obtain a thick phase solution at undersaturated conditions, although the degree of undersaturation is extremely small. In Fig. 9, we see how the thick profile almost immediately collapses as the density is lowered from the bulk coexistence value. We also observe how the immediate drop to gas phase values outside the first "layer" allows a higher peak height for the limited phase, as compared with the thick phase.

We have also measured relevant interfacial tensions along the bulk coexistence curve. These are analogous to the ones we reported for polymer solutions, although we have used the notation "(l)" and "(g)" for the liquid and gas phases, respectively. The results are presented in Fig. 10. Here we observe that the limited phase is more stable than the thick (wetting) phase, with a difference that increases with ϵ.

2. Step function profile ansatz

We also used a simple step-function approximation for the surface phase in order to investigate how the free energy varies with the width of the adjacent liquid phase. That is,

$$n(z,d) = \left[\begin{array}{ll} n_g, & z \leq d; \\ n_l, & z > d; \end{array}\right. \tag{11}$$

where n_l and n_g are the coexisting liquid and gas bulk densities. The free energy was then obtained as a function of the thickness d. This approximation suppresses the structure of the fluid density profile. Inspection of the surface free energy as a function of the width d indicates a limited (step-function) phase, which does not grow in width as the bulk coexistence curve is approached. Coexisting thin and limited phases, at various choices of ϵ, are given in Fig. 11(a). The thin phase corresponds to the case $d=0$. At bulk coexistence, the free energy becomes a flat function of d, and the limited phase is no longer absolutely stable. Instead, a macroscopic thick layer phase of undetermined width can form. As this does not happen until the system is right at coexistence, the thin-limited coexistence line does not *approach* the bulk coexistence curve tangentially, Fig. 12. Note that the wetting behavior is more usual, i.e., at bulk coexistence conditions, the thick phase (of indeterminate width) is more stable than the thin one as long as $\epsilon > \epsilon_w$ (inverse wetting temperature). This behavior is a consequence of the short-ranged fluid-fluid and fluid-surface interactions, coupled with the step-function ansatz. This confirms (at least in the one-component model), that fluid structure is responsible for the stability of the limited phase compared with the complete wetting case, when the density profiles are allowed to fully relax.

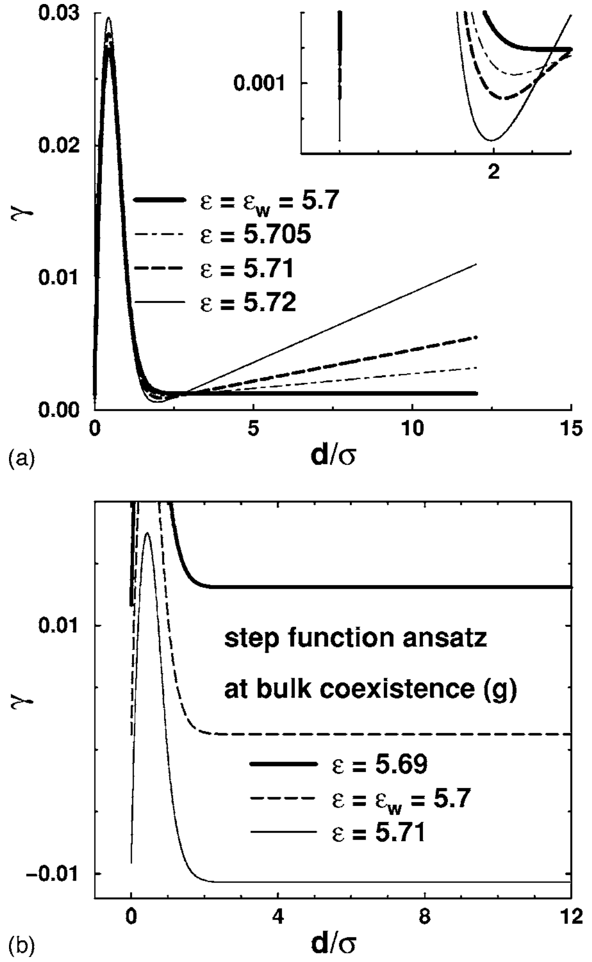

FIG. 11. The interfacial tension as a function of the liquid-gas truncation distance, d, with a step function ansatz of the one-component thermal model. (a) Coexisting thin and limited phases, i.e., the minimum tension at $d \approx 2$ (limited phase) is in each case identical to $\gamma(d=0)$ (thin phase). The inset is a blow-up demonstrating that the width of the limited phase varies very slowly as the bulk coexistence curve (at $\epsilon=5.7$) is approached. (b) $\gamma(d)$ along the bulk coexistence curve, where the width of the thick phase is unbounded, i.e., the interfacial tension profile is flat. Notice that the plateau value is below $\gamma(d=0)$ when $\epsilon > \epsilon_w$, indicating complete wetting. An opposite relation exists when $\epsilon < \epsilon_w$.

V. CONCLUSION

Using density functional theory, we have investigated an athermal polymer solution, where the solvent diameter is half the size of the monomers. The bulk displays a fluid-fluid phase separation, driven by depletion attraction between polymers. This attraction is enhanced by cooperativity effects due to the intra-molecular bonding between monomers. If a hard surface is immersed in the dilute phase, a surface phase transition may occur whereby a layer of concentrated polymer forms adjacent to the surface—the limited phase. For long polymers, this phase forms above a certain limiting

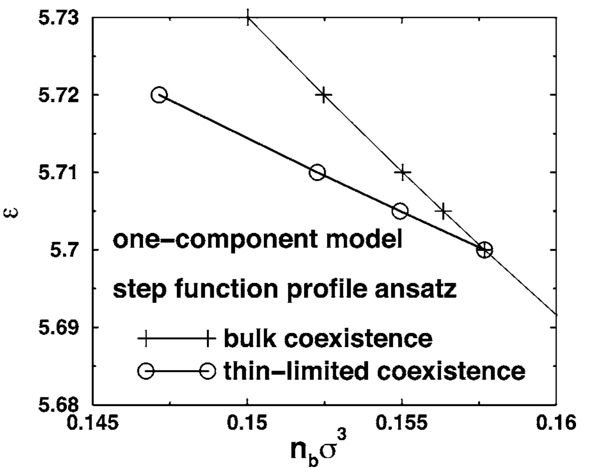

FIG. 12. The thin-limited coexistence curve, obtained with a step-function ansatz of the one-component thermal model.

pressure, P_{lim}, the pressure at which the thin-limited coexistence line intersects with the bulk coexistence curve. For shorter polymers the thin-limited coexistence curve can become supercritical, ending at its own critical point. This behavior is atypical of normal wetting and, indeed, complete wetting is not observed in our system. Instead, the limited phase remains slightly more stable than the complete wetting phase, even under conditions of bulk coexistence in the bulk.

The major driving force for the limited phase transition is the indirect enhancement of effective fluid-fluid attractions close to the surface, rather than the direct fluid-surface interaction. This is a nonlinear effect, which may explain the dominant role played by the surface-fluid surface energy in determining the pressure dependence of the surface phase.

We have constructed a useful, one-component thermal model, with the mechanisms necessary to mimic the phase behavior seen in the polymer solutions. In this way, we have illustrated the plausibility of the arguments we have invoked to describe the polymer solution.

We emphasize that these transitions not only are interesting in their own right. The presence of thick and limited phases also have a *dramatic* influence on surface forces and colloid stability [20]. Furthermore, enhancement of depletion attraction at surfaces will be present in simple asymmetric hard sphere mixtures and should thus have an influence on the surface behavior of those systems.

We will carry out more investigations on similar systems in the future. In particular, we will investigate the role played by the asymmetry parameter, q. It is our conjecture, that reducing q may lead to more normal wetting behavior. We will also explore the use of simulations in order to verify our density functional results, though recent simulation studies by Xiao, Guo, and Li [29] do support our findings. More indirectly, some comparisons exist between simulations and density functional theory predictions, for fluid density profiles of the polymer solution model considered here (but with $r=16$) [31]. Though that system was not phase separating, good agreement between simulation and our theory places the results presented in this paper on a firm foundation.

Finally, it would be interesting to investigate how depletion and compressibility effects will influence the bulk phase and wetting properties in thermal model systems, where attractive interactions are included.

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