

Determination of the interaction force between two adsorptive surfaces delimiting a critical binary polymer blend

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We consider a mixture of two incompatible polymers A and B , confined between two parallel surfaces of the same chemical nature, separated by a distance L . It is assumed that both surfaces strongly adsorb one of the species (A) at high temperature. It is also assumed that a demixing transition occurs at a critical temperature T_c below the adsorption temperature T_a . The strong adsorption implies that the composition of species A on surfaces is quenched even when the temperature is lowered. The presence of strong density fluctuations near the critical point induces an interaction between the surfaces. We reexamine this attractive force and determine its dependence with the thickness L , when the latter is smaller than the thermal correlation length. We find that, in the vicinity of the critical point, this force decreases with distance as L^{-4} . We show that the corresponding amplitude is a universal number, independent of the value of the composition on surfaces, and we give its *exact* expression. Finally, we note that the present system may be considered as a typical model enabling one to understand qualitatively and quantitatively the flocculation of colloids embedded in critical binary polymer blends.

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I. INTRODUCTION

The physics of phase separation of binary polymer blends in contact with an adsorbing surface is a very rich problem. For example, under certain special conditions, the mixture can exhibit a wetting transition at some characteristic temperature T_w below the critical temperature T_c . From a thermodynamic point of view, wetting is a genuine phase transition, which is characterized by the appearance of a film of the preferred phase in contact with the wall. Wetting in polymer blends is the subject of a great deal of attention both from theoretical [1–3] and experimental points of view [4].

Very recently [5], we considered another problem concerning a binary mixture of two incompatible polymers in the presence of an adsorbing surface. In fact, this problem differs from wetting by the nature of surface preparation. We have assumed that the surface irreversibly adsorbs one or both polymers at high temperatures. Consequently, chains cannot desorb once they are linked to the surface. We have also supposed that the surface is completely saturated, and that phase separation takes place at a critical temperature T_c below the adsorption temperature T_a . The strong adsorption implies that the density fluctuations at the surface are quenched even when temperature is lowered. We studied quantitatively the effects of these frozen fluctuations on the bulk critical properties of the mixture. In particular, we determined the shape of the composition profile [5] for any value of the surface composition and temperature near the critical point. In this work, the physical system we consider is rather a mixture of two polymers A and B of different

chemical nature confined between two parallel plane surfaces, separated by a distance L . In this problem, two effects are simultaneously present, namely (i) the interactions between the mixture and the surfaces, and (ii) the finite-size effects due to the finite value of the thickness L [6]. The presence of the surfaces induces changes in the effective interactions that rule the phase separation and in the chemical potential. This implies that the phase equilibrium between A and B near surfaces is different from that in the bulk [7–9]. Finite-size effects are related to the fact that the system is finite in one direction, say, the z direction ($0 \leq z \leq L$). A quantitative study of these effects may be achieved comparing the thickness L and the bulk thermal correlation length [10], $\xi_t \sim aN^{1/2}(1 - T_c/T)^{-1/2}$. Here, N is the degree of polymerization, a the monomer size, and T_c the critical demixing temperature. When L is larger than ξ_t ($L > \xi_t$), finite-size effects are less important and they contribute only by exponentially small corrections. Thus when L becomes very large, these effects may be neglected, and only the surface effects have to be taken into account. However, when L becomes smaller than ξ_t ($L < \xi_t$), finite size effects cannot be neglected, and they induce a drastic change of the behavior near the critical point. In particular, this constrains the system to undergo a two-dimensional phase transition or phase separation in the directions parallel to the surfaces.

Now consider a binary mixture of two incompatible polymers A and B confined between two parallel surfaces localized respectively at $z=0$ and $z=L$. These surfaces are then parallel to the (x,y) plane. We denote by $\phi \equiv \phi_A$ the monomer fraction (or composition) of polymer A , and because of the incompressibility condition, the composition of polymer B is $\phi_B = 1 - \phi$. We assume that the surfaces are prepared chemically in such a way that they strongly adsorb one or both polymers at high temperature. Thus the system is con-

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strained to have quenched compositions on surfaces. We denote by ϕ_0 and ϕ_L the respective surface compositions. There are essentially three distinct physical situations, depending on the preference of surfaces to adsorb A or B polymers: (i) both surfaces adsorb A (or B) species, (ii) one surface adsorbs A and the other B , or (iii) both surfaces equally adsorb A and B . In a previous work [11], we determined the composition profile of one species (say, A), as a function of the distance z from the surface located at $z=0$ for all values of the parameters of the problem, which are the absolute temperature T , the size L , and the quenched surface compositions ϕ_0 and ϕ_L . Also, we have evaluated numerically, in all cases, the expression of the interaction forces between the two plates originating from the strong density fluctuations that are present near the critical point.

In this work, we reexamine the problem of the computation of this interaction force as a function of the distance L between the two plates. We restrict ourselves to the case where the species A is dominant on both surfaces, and in addition, we assume that $\phi_0 = \phi_L$. This condition means that the two plates have the same chemical nature. More precisely, we show that the expected force Π , which is attractive [11], decreases with the distance $L < \xi_t$ as $\Pi \sim L^{-4}$. Also, we show that the associated amplitude is universal and we give its *exact* value. Our motivation for evaluating this interaction force is the following. The present system may be regarded as a typical example of a *three*-phase system, made up of a colloidal dispersion in a binary mixture of two incompatible polymers A and B . Colloids are particles of mesoscopic size, which are the subject of numerous studies because of their abundant industrial applications. We can imagine that one polymer, say A , strongly adsorbs on colloids at high temperatures. When the temperature is lowered, the mixture phase separates in two phases alternatively rich in A and B species. Colloids clothed by species A located in the B -rich side experience an attractive force, as we have already shown in the case of lamellar colloids [11]. This attraction force is responsible for flocculation. This problem was discussed in a short note by Fisher and de Gennes [7], but for liquid mixtures made of small molecules. Very recently, in a series of experiments [12,13], the behavior of silica beads with diameters of about $0.1 \mu\text{m}$, immersed in a binary liquid mixture of lutidine (A) and water (B) was investigated. Near the critical point, it was found that the silica colloids exhibit a sharply defined reversible aggregation, termed flocculation. Those colloids prepared using the Stöber method are known to adsorb on lutidine preferentially [12]. The flocculation occurs in the water-rich side of the phase diagram. In the same context, Netz has introduced a theoretical model of Landau-Ginzburg type [14] for studying the flocculation phenomenon observed experimentally [12,13]. Theoretical results seem to be in good agreement with the experiment.

This paper is organized as follows. In Sec. II, we present the model of interest and compute the interaction force within the framework of such a model. Our conclusions are given in Sec. III.

II. MODEL AND RESULTS

We first define the model that allows us to evaluate the interaction force. We start by recalling the definition of the

order parameter or composition fluctuation ψ . This is usually defined as the distance between two points on the coexistence curve of an infinite system [10,15]. Explicitly, we have

$$\phi = \frac{1 + \psi}{2}. \quad (1)$$

In this definition appears the critical composition $\phi_c = 1/2$ [10].

In a previous work [11], we showed that the free energy (per unit area) governing the physics of the system is a functional ΔF of the order parameter ψ , which is given by

$$\frac{\Delta F}{k_B T} = a^{-3} \int_0^L dz \left\{ \frac{1}{4} [\chi_c - \chi] \psi^2 + \frac{1}{12N} \psi^4 + \frac{a^2}{9} \left(\frac{d\psi}{dz} \right)^2 \right\}. \quad (2)$$

This free energy is of Landau-Ginzburg type, and is obtained by expanding the usual Flory-Huggins free energy [10,15] in the vicinity of the critical composition $\phi_c = 1/2$ or equivalently around $\psi = 0$. In the above expression, $\chi \sim T^{-1}$ stands for the Flory interaction parameter, $\chi_c = 2/N \sim T_c^{-1}$ for its critical value, where N is the polymerization index assumed to be the same for both polymers A and B , and a is the Kuhn statistical segment. In the right-hand side of relation (2), the last term accounts for the interfacial free energy between A -rich and A -poor phases. As shown in Ref. [11], the presence of surfaces manifests itself through the boundary conditions

$$\psi(z=0) = \psi(z=L) = \psi_0, \quad (3)$$

with $\phi_0 = (1 + \psi_0)/2$. We recall that the surface composition ψ_0 is a known quantity [5], which depends on the necessary free energy to adsorb one monomer on the surface.

Let us comment briefly about the situation where the adsorption of chains is reversible [16]. This means that the latter can desorb once they are attached to surfaces. This implies that the order parameter fluctuates at surfaces, and that the true free energy should include, in addition to the bulk contribution (2), a surface free energy $F_s[\psi_0, \psi_L]$ that is a functional of both surface compositions ψ_0 and ψ_L [17,18]. This surface free energy may have the form usually encountered in critical phenomena in the presence of surfaces [19,20], that is,

$$F_s[\psi_0, \psi_L] = \sum_{a=0,L} (\mu_a \psi_a + g_a \psi_a^2/2). \quad (4)$$

Here, μ_a and g_a are, respectively, the chemical potential change at the surface and the surface coupling constant. We denote by $\delta\psi_0$ and $\delta\psi_L$ the thermal fluctuations of order parameter ψ at surfaces. Under the change $\psi_a \rightarrow \psi_a + \delta\psi_a$ ($a=0,L$), the variation of the surface energy reads

$$\delta F_s = \left(\frac{\delta F_s}{\delta \psi_0} - \frac{2a^{-1}}{9} \partial_z \psi_0 \right) \delta \psi_0 + \left(\frac{\delta F_s}{\delta \psi_L} + \frac{2a^{-1}}{9} \partial_z \psi_L \right) \delta \psi_L. \quad (5)$$

The notation $\delta/\delta\psi_a$ is the functional derivative. Here $\partial_z \psi_a$ ($a=0,L$), which naturally emerges when integrating by parts the squared gradient term in formula (2), stands for the nor-

mal derivative of the composition ψ at the surfaces. In our case, because the surface compositions are quenched for all temperatures ($\delta\psi_0=0$, $\delta\psi_L=0$), the surface free energy is a constant ($\delta F_s=0$), and therefore does not contribute to the critical properties of the mixture. Hence the system is constrained to have fixed compositions on both surfaces at any temperature.

In the annealed case, when the surface compositions are not quenched, the order parameter must satisfy the following boundary conditions:

$$\frac{2a^{-1}}{9} \partial_z \psi_0 = \delta F_s / \delta \psi_0, \quad (6a)$$

$$\frac{2a^{-1}}{9} \partial_z \psi_L = -\delta F_s / \delta \psi_L. \quad (6b)$$

This will be considered elsewhere.

Now it will be convenient to introduce the following simplified notations:

$$t \equiv \frac{\chi_c - \chi}{\chi_c} = \frac{T - T_c}{T}, \quad (7a)$$

$$u \equiv 1/3N, \quad (7b)$$

$$\kappa \equiv a^2/9, \quad (7c)$$

where Eq. (7a) is the reduced temperature shift and Eq. (7b) the coupling constant.

The standard minimization of the free energy ΔF , with respect to the order parameter ψ , yields a nonlinear second-order differential equation. We give merely its first integral:

$$\kappa \left(\frac{d\psi}{dz} \right)^2 = G(\psi) - G(\psi_m), \quad (8)$$

where $G(\psi)$ is the dimensionless bulk free-energy density, which is

$$G(\psi) = \frac{t}{2N} \psi^2 + \frac{u}{4} \psi^4. \quad (9)$$

In relation (8), $\psi_m = \psi(L/2)$ is the unique minimum of the profile ψ [11], which is reached in the middle of the film ($z=L/2$). Such a minimum is found to be given by the quadrature formula

$$L = 2 \int_{\psi_m}^{\psi_0} d\psi \sqrt{\frac{\kappa}{G(\psi) - G(\psi_m)}}. \quad (10)$$

We note that the right-hand side of relation (10) is an elliptic integral [21]. This relation expresses the dependence of the minimum ψ_m upon the absolute temperature T , the thickness of the film L , and the surface value ψ_0 of the order parameter. In addition, this relation tells us that the minimum of the profile may be written in the following scaling form:

$$\psi_m = |t|^{\beta_t} g(L/\xi_t, \psi_0 |t|^{-\Delta_t}), \quad (11)$$

where $g(x,y)$ is a two-factor scaling function. In the above relation, $\beta_t=1/2$ is the critical exponent characterizing the

behavior of the order parameter $\psi_b \sim |t|^{\beta_t}$ of an infinite system, and $\Delta_t=1/2$ a crossover exponent. The latter expresses a natural comparison between bulk and surface compositions; respectively, ψ_b and ψ_0 . $\xi_t \sim a\sqrt{N}|t|^{-\nu_t}$ ($\nu_t=1/2$) is the bulk thermal correlation length.

Our aim is the determination of the interaction force between the two plates originating from the fluctuations in composition, which are strong near the critical point. This force (per unit area) Π , which is attractive for $L < \xi_t$ [11], is defined as the first derivative of the free energy; i.e., $\Pi = -\partial\Delta F/\partial L$. We have shown previously that [11]

$$\Pi = -\frac{k_B T}{a^3} G(\psi_m), \quad (12)$$

where $G(\psi)$ is defined above, in Eq. (9). The above relation clearly shows that the interaction force (per unit area) between the two plates depends only on the minimal value ψ_m of the profile and not on its shape.

Relations (10) and (12) are two parametric equations giving the variation of the force Π as a function of the thickness L by eliminating the parameter ψ_m . This problem was solved numerically in Ref. [11].

We wish to determine the scaling law giving the dependence of the interaction force Π with L . Combining relations (9), (11), and (12), we find, in the critical region, the following scaling law:

$$\Pi = -\frac{k_B T}{Na^3} |t|^{2-\alpha_t} h(L/\xi_t, \psi_0 |t|^{-\Delta_t}), \quad (13)$$

where $h(x,y)$ is a two-factor scaling function, whose expression is known. The extra critical exponent has a value $\alpha_t=0$. We note that the scaling function $h(x,y)$ has the correct limit when the reduced variable $y = \psi_0 |t|^{-\Delta_t}$ becomes large ($y \gg 1$). This can be realized when the surface composition ψ_0 reaches its saturation value, which is 1, at a fixed temperature, or when ψ_0 is fixed but $t \rightarrow 0$. In this limit, we have a universal scaling law, independent of the surface composition ψ_0 , which is

$$\Pi = -\frac{k_B T}{Na^3} |t|^{2-\alpha_t} \tilde{h}(L/\xi_t). \quad (14)$$

Here $\tilde{h}(x)$ is a universal scaling function, independent of the surface value of the composition. In the limit $L \ll \xi_t$, the force must be independent of temperature. This constrains the scaling function $\tilde{h}(x)$ to follow a power law in the variable x ; i.e., $\tilde{h}(x) \sim x^m$. We easily find that the exponent m has a value $m = -4$. Finally, we get the following scaling law for the interaction force:

$$\Pi \equiv -\frac{Nk_B T}{a^3} A \left(\frac{a}{L} \right)^4 \quad (L \ll \xi_t). \quad (15)$$

The latter result may be understood by noting that because mean field applies here, the exponent α_t in relation (14) vanishes. This implies that $\Pi \sim t^2 \sim \xi_t^{-4}$ for an infinite system. For a finite one, the L^{-4} dependence follows directly if one assumes the scaling relation (14). As expected, the calculated

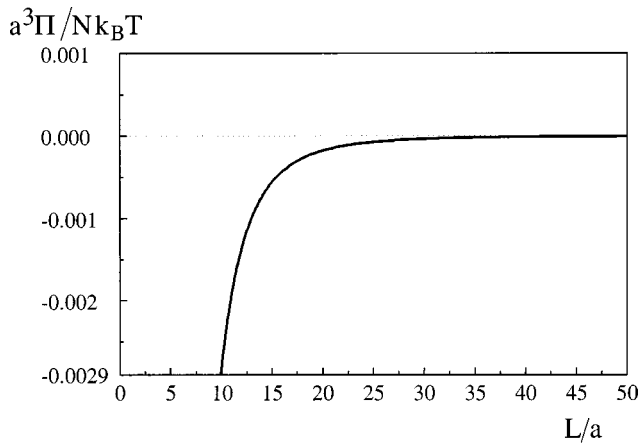


FIG. 1. Variation of the (reduced) force $a^3\Pi/Nk_B T$ with the thickness L of the film, expressed in monomer-size a units.

force is proportional to the polymerization index per chain N . We find that the universal amplitude A is given by

$$A = \frac{64}{27} I^4, \quad (16)$$

where I is the elliptic integral [21]

$$I = \int_1^{+\infty} \frac{du}{\sqrt{u^4 - 1}} \cong 1.854\,074\,68. \quad (16a)$$

Then the final value of the amplitude is

$$A \cong 28.010\,773\,52, \quad (17)$$

which is a pure number. The variation of the interaction force (per unit area) experienced by the two plates with the thickness L of the film is shown in Fig. 1.

III. CONCLUSIONS

We calculated the attractive force between two parallel plates clothed by a thin irreversible adsorption layer of a polymer A , and delimiting a polymer mixture $A+B$. This force, which results from the existence of strong fluctuations in the composition, is naturally a function of the separation L between the two plates. To evaluate such a force, we used a Landau-Ginzburg model, which is a direct consequence of the classical Flory-Huggins theory. The presence of the surface manifests itself through a condition that the composition on surfaces is quenched, at any temperature. In the critical region of the phase diagram, we have shown that the expected force Π decreases with the separation L between the surfaces according to a power law, $\Pi \sim L^{-4}$, and that the associated amplitude is a universal number, independent of the surface value of the composition. We have found the exact value of this amplitude: $A \cong 28.010\,773\,52$.

In the reversible adsorption case, the profile is sensitive to the boundary conditions on surfaces [equations (6)]. Consequently, the corresponding force should be affected by these boundary conditions. Such considerations are in progress [16].

We emphasize that in a recent work [22], Tran *et al.* considered a similar problem. More precisely, within the framework of the Alexander-de Gennes model, they have shown that the interaction force per unit area (or disjoining pressure) between two polymer brushes in a binary solvent mixture obeys the same decay with distance L ; that is, $\Pi \sim L^{-4}$. Finally, as we pointed out in the Introduction, the present system may be regarded as a typical example of a three-phase system, made up of a colloidal dispersion in a binary mixture of two incompatible polymers A and B .

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