



# Finite size effects on the phase diagram of a binary mixture confined between competing walls

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## Abstract

A symmetrical binary mixture AB that exhibits a critical temperature  $T_{cb}$  of phase separation into an A- and a B-rich phase in the bulk is considered in a geometry confined between two parallel plates a distance  $D$  apart. It is assumed that one wall preferentially attracts A while the other wall preferentially attracts B with the same strength (“competing walls”). In the limit  $D \rightarrow \infty$ , one then may have a wetting transition of first-order at a temperature  $T_w$ , from which prewetting lines extend into the one phase region both of the A- and the B-rich phase. It is discussed how this phase diagram gets distorted due to the finiteness of  $D$ : the phase transition at  $T_{cb}$  immediately disappears for  $D < \infty$  due to finite size rounding, and the phase diagram instead exhibit two two-phase coexistence regions in a temperature range  $T_{trip} < T < T_{c1} = T_{c2}$ . In the limit  $D \rightarrow \infty$   $T_{c1}, T_{c2}$  become the prewetting critical points and  $T_{trip} \rightarrow T_w$ . For small enough  $D$  it may occur that at a tricritical value  $D_t$  the temperatures  $T_{c1} = T_{c2}$  and  $T_{trip}$  merge, and then for  $D < D_t$  there is a single unmixing critical point as in the bulk but with  $T_c(D)$  near  $T_w$ . As an example, for the experimentally relevant case of a polymer mixture a phase diagram with two unmixing critical points is calculated explicitly from self-consistent field methods. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Although the finite size effects on phase transitions in thin films have been studied since a long time [1–14], only during the last decade it was discovered [15–23] that in ferromagnetic Ising films with surface fields of different sign but of the same strength  $\pm H_1$  (“competing walls”) novel types of phase transitions occur: namely, a phase transition occurs for zero bulk field  $H$  from a state with an interface freely fluctuating in the center of the thin film to a state where the interface is bound either to the lower

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or to the upper wall confining the film, which then acquires a nonzero (positive or negative) magnetization. This interface localization–delocalization transition at  $T_c(D)$  may be either second [16–22] or first-order [17,22,23], and for film thicknesses  $D \rightarrow \infty$  the transition temperature  $T_c(D)$  does not converge towards the bulk critical temperature  $T_{cb}$  as usual [1–8,12–14], but rather towards the wetting transition temperature  $T_w(H_1)$  [16–23].

Now it is well known that, in general, wetting transitions [24] can be second or first-order [25]. Thus it is plausible that also the interface localization–delocalization transition can be either second or first-order. However, recently it was shown [22] that also in cases where the wetting transition is first-order, the transition  $T_c(D)$  may be second order for small enough thickness ( $D < D_t$ ) and become first-order only for  $D > D_t$ . Thus the transition at  $T_c(D_t)$  is the finite-thickness analog of a wetting tricritical point [17–22].

All this work [15–23] has only considered the case  $H = 0$ , however. It is well known of course, that for  $D \rightarrow \infty$ , in the case of a first-order wetting transition at  $T_w(H_1 < 0)$  there exists at  $T = T_{pre}(H, H_1)$  a prewetting transition [24,25], where the distance of the interface bound to the wall discontinuously jumps from a smaller value to a larger value. While the analog of this prewetting transition in thin films has been studied occasionally for the case of “capillary condensation” (where on both walls fields act that have the same sign) [11,14], it is only in the present work that the effect of prewetting phenomena on the interface localization–delocalization transition is considered (for a much more detailed account of our calculations, see Müller et al. [26]). The physical systems that we have in mind are not magnets, of course, but rather binary (A,B) mixtures: as is well known, in an Ising model context the “magnetization” simply translates into the relative concentration  $\phi$  if one component (A, say), and the field  $H$  translates into the chemical potential difference  $\Delta\mu$  between the species (for simplicity we deal here with perfectly symmetric mixtures for which the bulk critical concentration is  $\phi_{cb} = 0.5$ ).

However, one important aspect of binary mixtures is that physically it is a density of an extensive thermodynamic variable (namely  $\phi$ ) that is the fixed independent thermodynamic variable, rather than the intensive variable  $\Delta\mu$ . As we shall see below, this fact has important consequences for the phase diagram of confined mixtures: the typical situation is that one encounters two successive lateral phase separation transitions!

In Section 2 we elaborate these ideas by a qualitative discussion of the phase diagrams {both in the space of intensive variables ( $\Delta\mu, T$ ) and in the space ( $\phi, T$ )} and of the corresponding physical state of the confined mixture. Section 3 exemplifies these considerations by presenting a specific calculation for a symmetric polymer mixture, treated within a self-consistent field framework [26]. There are numerous experimental studies of confined polymer mixtures [27,28] and these systems might be convenient for testing our predictions. Finally Section 4 summarizes our conclusions.

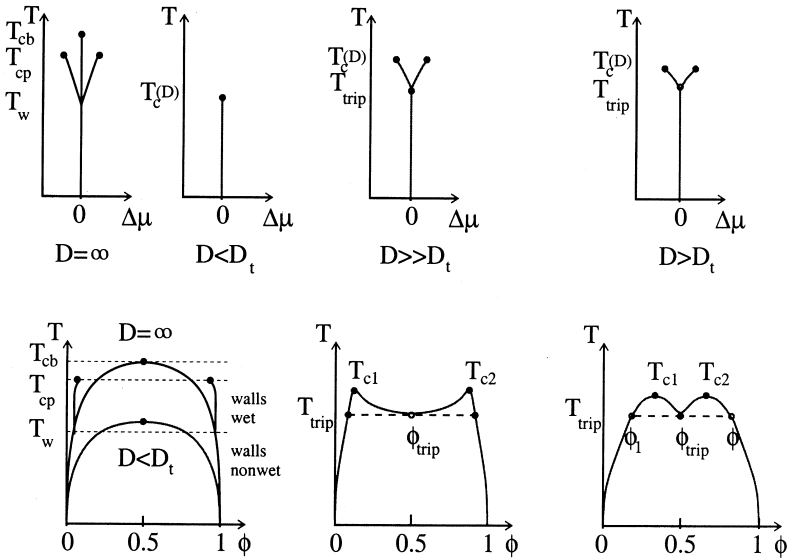


Fig. 1. Qualitative phase diagrams of a bulk system (thickness  $D = \infty$ ) confined by two walls at which competing “fields” act, as well as corresponding phase diagrams of thin films of various thicknesses  $D$ :  $D < D_t$  (left part),  $D \ll D_t$  (middle part) and  $D > D_t$  (right part). Upper part of the panel presents the phase diagrams in the space of two intensive variables, lower part chooses as abscissa instead the concentration  $\phi$ , a density of an extensive variable. Characteristic temperatures shown are the bulk critical ( $T_{cb}$ ), wetting ( $T_w$ ) and prewetting critical ( $T_{cp}$ ) temperatures, while in the thin film critical temperatures  $T_c(D)$  occur at  $\Delta\mu = 0$  and  $\phi = \phi_{cb} = \frac{1}{2}$  only for  $D < D_t$ , while for  $D > D_t$  one has for  $\Delta\mu = 0$  and  $\phi_{trip} = \frac{1}{2}$  rather a triple point of three phase coexistence. However, two critical points  $T_{c1} = T_{c2} = T_c(D)$  still occur, but at concentrations  $\phi_{1c}, \phi_{2c}$  that move towards the concentrations of the prewetting critical points as  $D \rightarrow \infty$ . For further explanations cf. text.

## 2. Qualitative phase diagrams of confined binary mixtures

We assume here a binary mixture confined by “competing” walls in the sense that one wall attracts species A with the same strength as the opposite wall attracts species B, and consider the case of first-order wetting. Then the phase diagram is qualitatively as shown in the left part of Fig. 1: In the space  $(T, \Delta\mu)$ , bulk ( $D \rightarrow \infty$ ) phase separation occurs for  $\Delta\mu = 0$ , and the walls are incompletely wet for  $T < T_w$  but wet for  $T_w < T < T_{cb}$ . From the point  $T = T_w$ ,  $\Delta\mu = 0$  there extend two (first-order) prewetting lines, which end at the prewetting critical points  $T_{cp}$ . These prewetting transitions correspond to singularities of the surface free energies associated with the lower and upper wall confining the mixture (Fig. 2). Due to the special symmetries chosen for our model, both the wetting transitions for the lower and upper wall coincide, and the prewetting critical temperatures are also the same. There is a mirror symmetry of the phase diagrams around the line  $\Delta\mu = 0$  (upper part) or  $\phi = 0.5$  (lower part), respectively.

For finite thickness  $D$  it may happen, as demonstrated by Monte Carlo simulations for Ising models with enhanced exchange interactions near the walls [22], that a tricritical

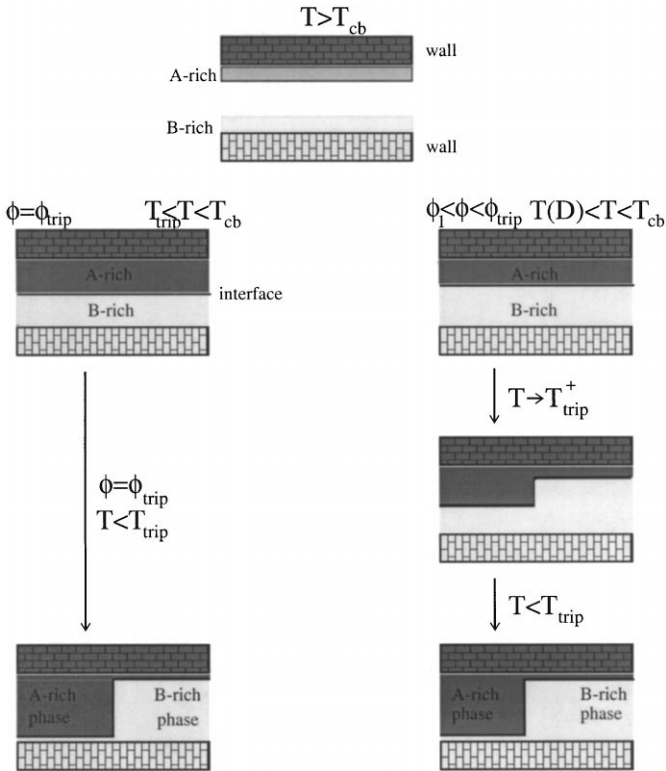


Fig. 2. Qualitative explanation of the different phases that occur in a binary mixture confined between competing walls. Already at  $T > T_{cb}$  there are A- and B-rich enrichment layers at the respective walls, having a finite thickness  $\xi_b$  (the bulk correlation length of concentration fluctuations), so for  $D \gg 2\xi_b$  the system is still disordered in the center, while in the region of temperatures where  $D$  and  $\xi_b$  are comparable a rounded transition to a layered structure with one A–B interface at  $T \lesssim T_{cb}$  occurs. For  $\phi = \phi_{trip}$  the position of this interface is just in the middle of the thin film, while for  $\phi_1 < \phi < \phi_{trip}$  the location of the interface reflects the asymmetry of composition. For  $\phi = \phi_{trip}$  one encounters a single transition at  $T = T_{trip}$ , where the localization of the interface at the walls requires lateral phase separation between A- and B-rich phases of equal amounts. For  $\phi_1 < \phi < \phi_{trip}$  one encounters two lateral phase separations: the first one is a coexistence between the phase with delocalized interface (in the center of the film as  $T \rightarrow T_{trip}^+$ ) with a phase where the interface is localized at the upper wall (the B-rich phase). In a second transition at  $T < T_{trip}$  the phase with delocalized interface disappears in favor of the phase with the interface bound to the lower wall (the A-rich phase). Note that the amount of this phase must be less, to comply with the lever rule.

point at  $D = D_t$ ,  $T_c(D_t)$ ,  $\Delta\mu = 0$  (and  $\phi = 0.5$ ) occurs. For  $D < D_t$  then there exists a single critical point at  $T = T_c(D)$ ,  $\Delta\mu = 0$  (and  $\phi = 1/2$ ), there is no remnant of the prewetting phenomena left, and the phase diagram both in the  $(T, \Delta\mu)$  plane as well as in the  $(T, \phi)$  plane looks qualitatively exactly like in the bulk three-dimensional case. Of course, we do expect a flatter shape near the critical point due to the occurrence of the two-dimensional Ising exponents  $\{\phi_{coex} - 1/2 \propto (1 - T/T_c(D))^{1/8}$  rather than  $\phi_{coex} - 1/2 \propto (1 - T/T_{cb})^\beta$  with  $\beta \approx 0.325$  in the bulk [1–8,13]}. But the situation differs very much for  $D > D_t$  (middle and right part of Fig. 1). In the semi-grand-canonical ensemble

( $\Delta\mu$  fixed), one experiences a single first-order transition for  $-\Delta\mu_c(D) < \Delta\mu < \Delta\mu_c(D)$  where  $\pm\Delta\mu_c(D)$  is the chemical potential reached for  $T = T_c(D)$  along the remnants of the prewetting lines. In the canonical ensemble ( $\phi$  fixed), we encounter a single first-order phase transition only if  $\phi = \phi_{\text{trip}} = \frac{1}{2}$ , which corresponds to  $\Delta\mu = 0$ , while for  $\phi_1 < \phi_{\text{trip}}$  or for  $\phi_{\text{trip}} < \phi_2 = 1 - \phi_1$  one encounters two successive first-order transitions when one lowers the temperature. Only if one chooses  $\phi = \phi_{c1}$ , (the critical concentration corresponding to the critical point  $T_{c1}$ ) or  $\phi = \phi_{c2} = 1 - \phi_{c1}$  (corresponding to  $T_{c2}$ ) one still encounters a (two-dimensional) critical behavior of phase separation,  $\phi_{\text{coex}} - \phi_{c1} \propto (1 - T/T_{c1})^{1/8}$ , and similarly  $\phi_{\text{coex}} - \phi_{c2} \propto (1 - T/T_{c2})^{1/8}$ . While  $\phi_1$  as well as  $\phi_2$  merge at  $\phi_{\text{trip}} = \frac{1}{2}$  as  $D \rightarrow D_t$ ,  $\phi_1$  and  $\phi_2$  move outwards towards the prewetting critical concentration when  $D \rightarrow \infty$ . In this limit, the width of the two-phase coexistence regions for  $T > T_{\text{trip}}$  must shrink and ultimately vanish, since the difference in concentration on both sides of the pseudo-prewetting first-order lines with respect to the average concentration  $\phi$  of the film is an effect of order  $1/D$ , and therefore for  $D \rightarrow \infty$  the prewetting transitions are lines in the  $(T, \phi)$  phase diagram and not split up in two-phase coexistence regions.

From this description it already is clear that the approach to the phase diagram of the bulk ( $D = \infty$ ) as  $D \rightarrow \infty$  is very nonuniform: for any finite  $D$  the bulk transition is still rounded, and (for  $\phi_1 < \phi_{\text{trip}}$  or  $\phi_{\text{trip}} > \phi_1$ ) the first transition is a lateral phase separation corresponding to the prewetting transition and the second transition is another lateral phase separation at  $T_{\text{trip}}$  (Fig. 2). For  $D \rightarrow \infty$  the phase diagram, hence, contains prewetting lines (as in the left part of Fig. 1) and a horizontal line at  $T_w$  (to which the triple line in the middle part of Fig. 1 has converged). Of course, the pictures explaining the various phases in Fig. 2 are highly schematic, and in reality one expects the interface to turn around rather smoothly and avoid the  $90^\circ$  kinks. Such smooth interfaces (which also have an intrinsic width which need not be negligibly small in comparison with  $D$ ) have in fact been observed in two-phase coexistence states associated with capillary condensation [14].

### 3. A quantitative example: a confined polymer mixture

Thin polymeric films confined between walls may have interesting applications and can also be studied conveniently by a variety of experimental tools [27,28]. In fact, the “soft mode” – phase [18] with a single fluctuating interface in the middle of the film (as shown in the upper part of Fig. 2) has been experimentally observed [29,30], and we consider it likely that by fine-tuning of experimental control parameters it should also be possible to observe some of the transitions predicted in Figs. 1 and 2. In fact, for polymers one need not have special interactions to get a first-order wetting transition as in the Ising model [22], rather one finds always first-order wetting behavior except close to the critical point of the bulk [14].

As in our previous work [14,23] we consider a situation where the wetting transition temperature  $T_w$  lies in the strong segregation regime, for which the self-consistent field

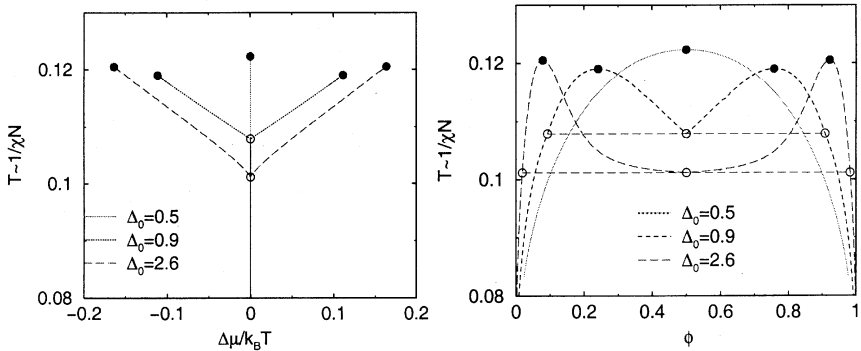


Fig. 3. Phase diagram of a symmetric polymer mixture in a thin film with antisymmetric boundary fields calculated in the framework of the self-consistent field theory for Gaussian chain molecules. Three film thicknesses  $D = 0.5R_e, 0.9R_e$  and  $2.6R_e$  are shown ( $R_e$ : end-to-end distance of the molecules). The ratio of  $D/R_e$  is denoted as  $\Delta_0$  in the figure. The smallest film thickness corresponds to the situation  $D < D_t$  while films of thickness  $D = 0.9R_e$  and  $2.6R_e$  exhibit two critical points. Panel (a) displays the phase diagrams in the  $(T \sim 1/\chi N, \Delta\mu/k_B T)$  plane, while (b) shows the results as a function of temperature  $1/\chi N$  and composition  $\phi$ . Note that the critical temperature of the bulk is at  $1/\chi N = 0.5$ .

theory is accurate. The technical aspects of this approach are explained in detail elsewhere [14,26,31]. Fig. 3 shows that for a typical choice of parameters indeed a phase diagram of the type of Fig. 1, right part, is reproduced. Note that the self-consistent field theory near the critical points  $T_{c1}(D), T_{c2}(D)$  implies mean-field like behavior,  $\phi_{\text{coex}} - \phi_{c1} \propto (1 - T/T_{c1}(D))^{1/2}$ , rather than yielding the expected two-dimensional Ising exponent [10]. But for large molecular weight this Ising like critical region is expected to be rather narrow [27,28], and thus we consider Fig. 3 as a useful hint for the phase diagram to be searched for in the experiments.

#### 4. Conclusions

In this paper we have considered the problem of phase-separating binary mixtures confined between “competing walls” and have shown that the phase diagram has either critical points and first-order regions coexisting at a triple line or a single critical point resulting from the merging of these two critical points at the tricritical thickness  $D_t$ . In previous work treating the case  $D > D_t$ , only the case  $\Delta\mu = 0$  in the semi-grandcanonical ensemble was studied [22,23], which in the  $(T, \phi)$  plane means that one cools the system at  $\phi = \phi_{\text{trip}} = 0.5$  and then a single first-order transition (Fig. 2, left part) occurs: thus the existence of the two critical points was not previously discussed.

Of course, in reality one will have to abandon the special symmetry assumptions used in Figs. 1–3, allowing for asymmetric mixtures, differences in strength of the wall forces, etc. and thus the space of parameters to be considered gets much enlarged. However, as long as one works in the subspace where the wetting transition

temperatures  $T_w$  of both walls are the same, the phase diagrams still should have the topology of Fig. 1, only the mirror symmetry around  $\Delta\mu = \Delta\mu_{\text{coex}}(T)$  or  $\phi = \phi_{\text{cb}}$  is lost, and thus in general  $\phi_{\text{trip}}$  will differ from  $\phi_{\text{cb}}$ . Also  $T_{c1}$  and  $T_{c2}$  will differ. Of course, in the most general case one must allow also for  $T_{w1} \neq T_{w2}$ , different wetting transition temperatures of both walls. One can also consider first-order wetting at one wall and second order wetting at the other. A description of the phase diagrams for these more complicated cases is a challenging task for future work.

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