

First-order versus second-order interface localization transition of thin Ising films with competing walls

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From extensive Monte Carlo simulations of a lattice gas model we present evidence that the order of the gas-liquid transition of a fluid confined between “competing” walls can change from second to first order when the thickness D of the thin film is varied. This situation typically arises when the wetting transition of the corresponding semi-infinite system is first order, and thus permits the study of a tricritical interface-localization-delocalization transition via control of the film thickness. [S1063-651X(98)07609-0]

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Thin fluid films which are adsorbed on substrates or confined in slitlike capillaries pose challenging fundamental problems due to a subtle interplay between finite size and surface phenomena. The recognition of this situation has resulted in great activity which has attempted to elucidate various features of these phenomena [1–17]. Of particular interest is the case where the two surfaces of the fluid film favor different phases: e.g., in the case of a fluid near a gas-liquid coexistence in the bulk, one wall favors high-density liquid and the other wall prefers low-density gas. Similarly, for a binary mixture (A, B) undergoing phase separation in the bulk, one surface favors an A -rich phase, the other favors a B -rich phase. In the latter case, a situation equivalent to such “competing walls” is also often realized when the mixture is on a substrate and the other surface is “free” (i.e., against air [16]).

The generic model for the study of this problem is actually the Ising (or lattice gas) model, where the local order parameter of the corresponding phase transition is a pseudospin variable $s_i = \pm 1$ at lattice site i , and the competing surfaces at lattice planes $n = 1$ and $n = D$ (we henceforth take the lattice spacing as our unit of length) are described by surface fields of opposite sign, $H_1 = -H_D$. Assuming nearest neighbor pairwise interactions J in the bulk and J_s in the surface planes, we find that the Hamiltonian for this model is

$$\mathcal{H} = -J \sum_{\langle i,j \rangle}^{(b)} s_i s_j - J_s \sum_{\langle i,j \rangle}^{(s)} s_i s_j - H_1 \sum_{\langle i \in n=1 \rangle} s_i - H_D \sum_{\langle i \in n=D \rangle} s_i, \quad (1)$$

where the sum $\sum_{\langle i,j \rangle}^{(b)}$ runs once over all pairs of neighboring spins where at least one site is *not* in a surface plane, while the sum $\sum_{\langle i,j \rangle}^{(s)}$ is restricted to pairs with both sites in one of the two surfaces. The total magnetization M of the film serves as the order parameter for the transition; above the transition the interface is in the middle so the mean value of M is zero, but below the transition the interface is near to one of the walls so the magnetization becomes strongly nonzero.

For temperatures below the critical temperature T_{cb} in the bulk, but sufficiently above the wetting transition T_w of the corresponding semi-infinite system ($D \rightarrow \infty$), this geometry

stabilizes a coexistence between two phases of opposite sign of the order parameter, with a freely fluctuating interface in the middle of the film, the mean order parameter of the film being zero. However, there exists a phase transition at $T_c(D)$ [7–10,12–14] such that for $T < T_c(D)$, the interface becomes localized at one of the walls, and then the average order parameter of the film is nonzero. Since $T_c(D \rightarrow \infty) \rightarrow T_w$ rather than T_{cb} , unlike the more familiar situation of noncompeting walls where “capillary condensation” [6,11] occurs, this unconventional phase transition has evoked great interest [7–10,12–14]. Most work, however, addresses the issue of critical wetting for the corresponding semi-infinite geometry [18,19], and then the transition in a thin film is also second order [8,10,12–14]. Even with short-range forces, one can obtain pronounced first-order wetting transitions in semi-infinite geometry by choosing a suitable enhancement of the pairwise interaction near the wall [18] such as in Eq. (1). A mean field theory [9] which treated the corresponding thin film case suggested that first-order interface localization transitions would be found as the thickness varied.

It is well known, however, that in real fluids the long range of the van der Waals forces exerted by walls on the fluid molecules has the consequence that the wetting transition is almost always first order [5] in a semi-infinite geometry. Thus it is likely that under many circumstances the interface-localization-delocalization transition in thin films is first order as well.

In the present paper we describe an examination of such a first-order transition in a thin film by Monte Carlo simulations, thus going beyond mean field theory [9]. In the framework of our simplified model, Eq. (1), this can be done by choosing a sufficient enhancement of the exchange interaction J_s in the surface planes relative to the bulk [18]. For the semi-infinite geometry, it was estimated that first-order wetting transitions occur for the model of Eq. (1) if $J_s/J > 1.25$ for an inverse temperature of $J/k_B T = 0.25$ [18].

We now present the first results for Eq. (1) in the case where $J_s > J$, confining ourselves to the region $J_s \geq 1.3$, where the wetting transition at the surface of a semi-infinite system would be very strongly first order at $J/k_B T = 0.25$. We show that in a thin film the tricritical point, i.e., the ratio

J_{st}/J where the transition changes from second order to first order, is enhanced. This also implies that at a fixed ratio of J_s/J we may have a second-order transition for thin films and a first-order transition for thick films; i.e., one can change the order of the interface-localization-delocalization transition by changing the thickness of the film and encounter a tricritical point at fixed J_s/J at some critical thickness D_t .

We carry out single-spin-flip Monte Carlo simulations on systems with an $L \times L \times D$ geometry with periodic boundary conditions in the directions parallel to the two $L \times L$ surfaces. L varies from $L=16$ to 96, primarily for very thin films ($D=4,6,8$) since for thick films, slow interfacial fluctuations make it impossible to attain the desired statistical accuracy. In our previous work on second-order interface localization transitions [13,14] these small thicknesses were found to be sufficient to verify the nontrivial fluctuation phenomena predicted by recent theories [20]. For each set of parameters (L, D, J_s) six independent simulations were performed, each ranging from 2×10^6 Monte Carlo steps (MCS) for the smaller systems to 3×10^6 MCS for $L=64$ and 4×10^6 MCS for $L=96$. The results were then analyzed by histogram reweighting [21] to produce the smooth curves shown. Error bars are determined by the variation between the six independent runs [22]. The appropriate choice of coupling constants $K=J/k_B T$ at which these runs were made was determined from preliminary shorter runs where K was systematically varied.

Figures 1 and 2 show typical ‘‘raw data’’ for the average order parameter $\langle |M| \rangle$ and the logarithmic derivative of $\langle |M| \rangle$ of these thin films. For $J_s/J=1.3$ and $D=6$ [Fig. 1(a)] the variation of the order parameter near $K_c=J/k_B T_c$ is very smooth and strongly rounded by finite size: The data have exactly the same features as corresponding data for $J_s/J=1$ [13,14] and all related evidence [23] (e.g., profiles of order parameter, energy, etc., across the film) support the conclusion that the transition for this thickness is still second order (although it is first order for $D \rightarrow \infty$ [18]). For $J_s/J=1.5$, however, the steep variation of $\langle |M| \rangle$ with K [Fig. 1(b)] indicates that this is already a rounded first-order transition. This interpretation is supported by the positions of the maxima of the specific heat C , and logarithmic derivative of $\langle |M| \rangle$,

$$\frac{\partial \ln(\langle |M| \rangle)}{\partial K} = \frac{1}{\langle |M| \rangle} \frac{\partial \langle |M| \rangle}{\partial K},$$

both of which have characteristic divergencies at the transition and which are plotted in the insets of Figs. 1(a) and 1(b). By varying J_s/J we have, thus, passed through a tricritical point.

Another and more interesting way to cross the tricritical point is to vary the thickness D while holding the surface coupling constant. (This approach is more relevant because it corresponds more closely to the situation that can be realized in an experiment.) The data for the logarithmic derivative of $|M|$, shown in Fig. 2(a) (for $D=4$) and Fig. 2(b) (for $D=8$) have maxima which grow systematically and rapidly with increasing L . The positions of the peaks are compatible with an extrapolation $[K_{\max}(L)-K_c] \propto L^{-2}$ as expected from finite-size scaling for first-order transitions [24,25] while in

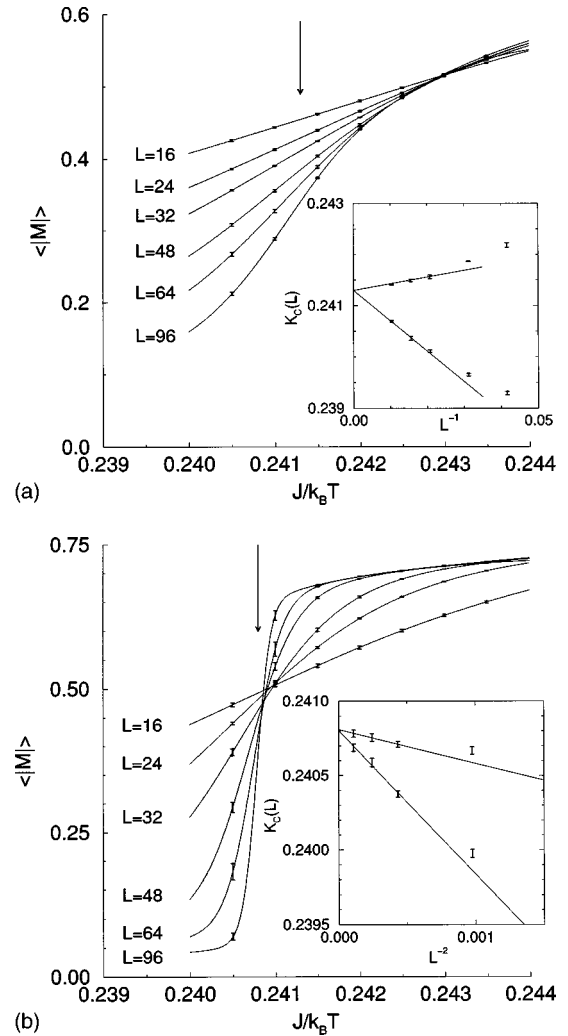


FIG. 1. Order parameter $\langle |M| \rangle$ plotted vs $J/k_B T$ for $D=6$, $J_s/J=1.3$ (a) and $J_s/J=1.5$ (b), respectively, for linear dimensions $L=16, 24, 32, 48, 64$, and 96. Arrows show the location of $T_c(D)$ obtained from extrapolations of peak positions, shown in the insets, for specific heat (lower data set) and logarithmic derivative (upper data set) vs L^{-2} (first-order case) or L^{-1} (second-order case), respectively.

the second-order case we have $[K_{\max}(L)-K_c] \propto L^{-1}$ as found previously [13,14]. Note that at a second-order transition the extrapolation should vary as $L^{-1/\nu}$, where $\nu=1$ for the (two-dimensional Ising-like delocalization) transition.

There are several other quite convincing pieces of evidence for the change in the order of the transition. Lee and Kosterlitz [26] have introduced a method to determine the order of a phase transition by studying the scaling behavior of the free energy barrier. For $J_s/J=1.45$ the energy distribution for $D=4$ shows only a single peak for all lattice sizes, thus clearly demonstrating that the transition is second order. For $D=6$, however, the distribution is double peaked and the resulting free energy barrier first grows with increasing L before beginning to decrease (see Fig. 3). With a thicker film, $D=8$ the free energy barrier rapidly increases with L and indicates that the transition is already strongly first order. The correlation time becomes quite long in this case because the time needed for the system to ‘‘tunnel’’ back and forth between the two peaks is of the order of 10^6 MCS. Thus

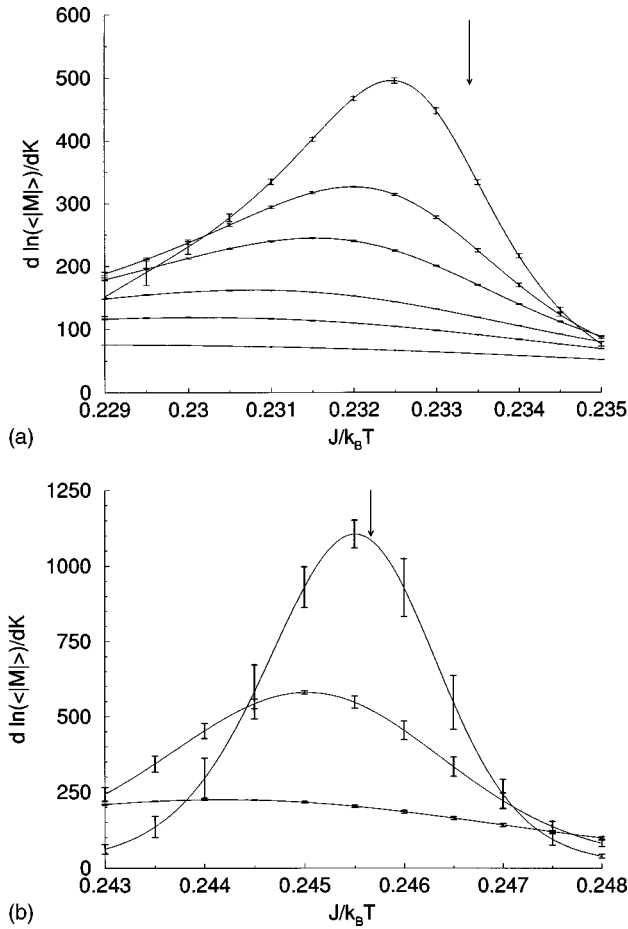


FIG. 2. $[\partial \ln(\langle |M| \rangle) / \partial K]_{\max}$ plotted vs $J/k_B T$ for $J_s/J=1.45$, $D=4$ (a) and $D=8$ (b). Curves shown in (a) are for linear dimensions $L=16, 24, 32, 48, 64$, and 96 . For $D=8$, the transition is so strongly of first order that $L > 32$ could not be equilibrated and these data are omitted in (b). Arrows show the location of $T_c(D)$ obtained from an extrapolation of peak positions.

even runs of 6×10^6 MCS are insufficient to give robust estimates for the free energy barrier, and six such runs were averaged together before the result became reliable. Additional strong evidence for the change of the order of the transition comes from a study of the variation of the maxima

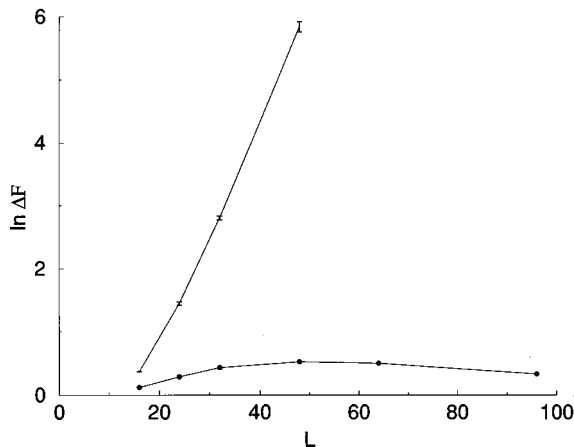


FIG. 3. Free energy barrier height vs L for $J_s/J=1.45$ and $D=8$ (top curve), $D=6$ (bottom curve).

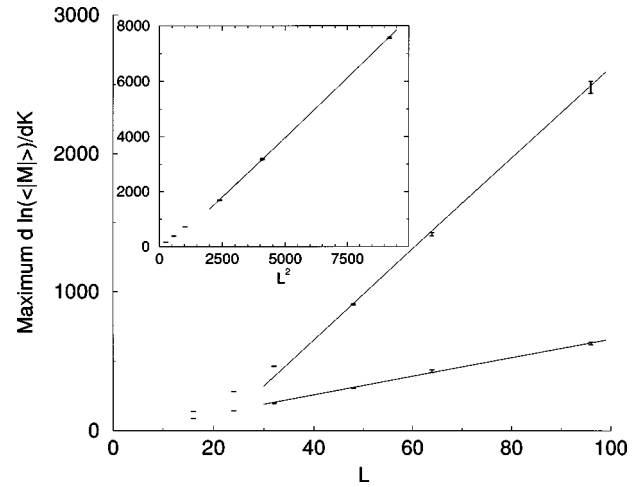


FIG. 4. Plot of the maximum $[\partial \ln(\langle |M| \rangle) / \partial K]_{\max}$ vs L for $D=6$, $J_s/J=1.3$ (lower curve), $J_s/J=1.45$ (upper curve), and $J_s/J=1.5$ (inset). The theoretical behavior of second-order transition in the two-dimensional Ising universality class ($\propto L$) and for a first-order transition in the inset ($\propto L^2$) is indicated by the solid lines.

of the specific heat, susceptibility, as well as the logarithmic derivative of $|M|$ with L . The maximum value of the logarithmic derivative of $|M|$ is plotted versus lattice size L for $D=6$ and different values of J_s/J in Fig. 4. For $J_s/J=1.3$ (lower curve) and $J_s/J=1.45$ (upper curve) the variation for sufficiently large L is linear, implying $1/\nu=1$, but for $J_s/J=1.5$ (inset) it varies quadratically with L as expected for a first-order transition. We plan to give a more detailed discussion of this crossover behavior elsewhere [23].

In conclusion, we have presented evidence that in thin Ising films one can change the order of the transition from second to first order by increasing the thickness, keeping the surface fields and exchange couplings near the wall constant. The occurrence of such a tricritical point can be inferred from the mean field treatment of Swift, Owczarek, and Indekeu [9], but our work provides evidence that this new type of tricritical point persists beyond mean field theory. The critical behavior of this special tricritical point still remains to be investigated [23]. It is also interesting to ask which features of our results will carry over to real systems. For liquid-gas transitions, one expects that the van der Waals forces imply first-order wetting [5], and it is not clear whether second-order interface localization transitions become possible in a thin film geometry. On the other hand, for “symmetrical” binary polymer mixtures it is conceivable that the difference between the van der Waals forces of the two species is very small, and an effectively short-range interaction dominates [16]. Recent experiments on interfaces in confined geometry are consistent with such a picture, but experimental evidence for an interface localization transition is still lacking. Clearly, more experiments on related systems are urgently needed to resolve these issues.

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- [1] *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, New York, 1986).
- [2] *Liquids at Interfaces*, edited by J. Charvolin, J. F. Joanny, and J. Zinn-Justin (North-Holland, Amsterdam, 1990).
- [3] *Physics of Polymer Surfaces and Interfaces*, edited by I. C. Sanchez (Butterworth-Heinemann, Boston, 1992).
- [4] K. Binder, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8, p. 1.
- [5] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), Vol. 11, p. 1.
- [6] H. Nakanishi and M. E. Fisher, *J. Chem. Phys.* **78**, 3279 (1983).
- [7] E. V. Albano, K. Binder, D. W. Heermann, and W. Paul, *Surf. Sci.* **223**, 157 (1989).
- [8] A. O. Parry and R. Evans, *Phys. Rev. Lett.* **64**, 439 (1990).
- [9] M. R. Swift, A. L. Owczarek, and J. O. Indekeu, *Europhys. Lett.* **14**, 475 (1991).
- [10] A. O. Parry and R. Evans, *Physica A* **181**, 250 (1992).
- [11] K. Binder and D. P. Landau, *J. Chem. Phys.* **96**, 1444 (1992).
- [12] K. Binder, A. M. Ferrenberg, and D. P. Landau, *Ber. Bunsenges. Phys. Chem.* **98**, 340 (1994).
- [13] K. Binder, D. P. Landau, and A. M. Ferrenberg, *Phys. Rev. Lett.* **74**, 298 (1995); *Phys. Rev. E* **51**, 2823 (1995).
- [14] K. Binder, R. Evans, D. P. Landau, and A. M. Ferrenberg, *Phys. Rev. E* **53**, 5023 (1996).
- [15] Y. Rouault, J. Baschnagel, and K. Binder, *J. Stat. Phys.* **80**, 1009 (1995).
- [16] T. Kerle, J. Klein, and K. Binder, *Phys. Rev. Lett.* **77**, 1318 (1996).
- [17] A. Werner, F. Schmid, K. Binder, and M. Müller, *J. Chem. Phys.* **107**, 8175 (1997).
- [18] K. Binder and D. P. Landau, *Phys. Rev. B* **37**, 1745 (1988); K. Binder, D. P. Landau, and S. Wansleben, *ibid.* **40**, 6971 (1989).
- [19] It has been suggested [M. E. Fisher and A. J. Jin, *Phys. Rev. Lett.* **69**, 792 (1992)] that the wetting transition of the Ising model is never second order but actually weakly first order for $J_s=J$. If this is true, it would only affect the behavior extremely close to $T_c(D)$, a region that is not accessible here.
- [20] C. J. Boulter and A. O. Parry, *Phys. Rev. Lett.* **74**, 3403 (1995); *Physica A* **218**, 109 (1995); A. O. Parry and C. J. Boulter, *ibid.* **218**, 77 (1995).
- [21] A. M. Ferrenberg and R. H. Swendsen, *Phys. Rev. Lett.* **61**, 2635 (1988); **63**, 1195 (1989).
- [22] A. M. Ferrenberg, D. P. Landau, and R. H. Swendsen, *Phys. Rev. E* **51**, 5092 (1995).
- [23] D. P. Landau, A. M. Ferrenberg, and K. Binder (unpublished).
- [24] See K. Binder, *Rep. Prog. Phys.* **60**, 487 (1997), and references therein.
- [25] D. P. Landau, *Finite Size Scaling and Numerical Simulations of Statistical Systems*, edited by V. Privman (World Scientific, Singapore, 1990).
- [26] J. Lee and J. M. Kosterlitz, *Phys. Rev. Lett.* **65**, 137 (1990).