Character of the Phase Transition in Thin Ising Films with Competing Walls

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By extensive Monte Carlo simulations of a lattice gas model we have studied the controversial nature of the gas-liquid transition of a fluid confined between two parallel plates that exert competing surface fields. We find that the transition is shifted to a temperature just below the wetting transition of a semi-infinite fluid but belongs to the two-dimensional Ising universality class. In between this new type of critical point and bulk criticality, a response function $x_{nn}^{\max}$ varying exponentially with D is observed, $2 \ln\chi_{nn}^{\max}/D = \ell^{-1}$, where ℓ is a new length characterizing interfaces.

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Phase transitions in confined geometry, such as liquid-gas condensation in pores or between parallel walls, may exhibit novel phenomena due to the combined effect of finite size and surface effects [1–12]. If the interactions between the fluid atoms and walls favor condensation at both walls, one observes "capillary condensation" [1,4,10,12], i.e., the gas condenses to the liquid at a pressure p that is lower than the pressure p_{coex} for phase coexistence in the bulk. While this phenomenon has been known for a long time, recent simulations [5] of two-dimensional (2D) lattice gas models with opposing one-dimensional boundaries, as well as phenomenological theories [6–9] suggest a new type of transition. Modeling the fluid by a lattice gas model and using the translation into the language of an Ising magnet (empty sites correspond to spin up, full sites to spin down), we find that the opposing walls translate into surface magnetic fields H_1 of equal magnitude but opposite sign. For this model a very puzzling and controversial [8] behavior was predicted from a mean-field theory [6]: For any finite distance D between the plates there is a *single* phase transition belonging to the universality class of the 2D Ising model but at a temperature $T_c(D)$ close to the wetting transition temperature $T_w(H_1)$ of the semi-infinite 3D Ising model with a surface field H_1 [13], i.e.,

$$\lim_{D\to\infty} T_c(D) = T_w(H_1) \,. \tag{1}$$

Note that $T_w(H_1)$ may be very far away from the bulk critical point T_{cb}. Equation (1) is extremely surprising, since in more standard finite size effects in thin films (such as capillary condensation, for instance [4]), one always has a convergence to the critical temperature T_{cb} of the bulk, $T_c(D \to \infty) \longrightarrow T_{cb}$. In fact, for the present case of opposing walls, a sharp 3D Ising transition must also appear in the system for a temperature $T = T_{cb}$ in the limit $D \to \infty$, but it disappears for finite D (i.e., it is *rounded*, qualitatively similar to systems which are finite in all their linear dimensions [14]). At this rounded transition an interface between the coexisting phases is predicted to appear gradually. For $T > T_c(D)$ this interface (which on average runs parallel to the walls) is expected to fluctuate freely in the center of the thin film, while for $T < T_c(D)$ it becomes localized at (or "bound to") one of the two walls.

Now the situation of two walls with fields $H_1 < 0, H_D = -H_1$ is certainly very special, but it can be readily generalized to arbitrary ratios of H_1/H_D (Fig. 1) [15]. The transition then occurs at a nonzero bulk field $H > 0$ (in fluid language this means $p < p_{\text{coex}}$), and $T_c(D)$ can exceed $T_w(H_1)$. The Ising model can also be used to describe phase separation of binary (AB) mixtures, and we speculate that closely related wall effects occur for much wider classes of phase transitions. For instance, liquid crystals, mesophases in microemulsions, and block copolymer systems, etc, are known to be very sensitive to wall effects; thus, our simple model is a generic case for an interface localization-delocalization transition in confined geometry.

In previous work [16,17] the wetting transition of simple cubic Ising models with exchange J between nearest neighbors was studied and T_w was estimated for a range of values of H_1/J by Monte Carlo methods. With a slight modification of the program the present problem can be studied as well [18], and Fig. 2 shows the predicted phenomena qualitatively. The magnetization profile smoothly develops an interface as one cools the system from $T > T_{cb}$ to $T < T_{cb}$: The surface fields induce a local magnetization near the walls (a negative one at the left wall and a positive one at the right wall) also for $T \gg T_{cb}$. But we expect that the layer magnetizations

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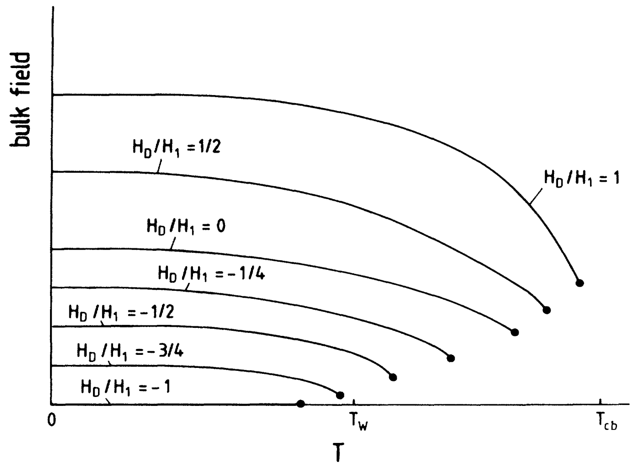

FIG. 1. Qualitative phase diagram of a 3D Ising system in a thin film of thickness D where surface fields $H_1 < 0$ and H_D act on the surface planes. The bulk critical temperature (T_{cb}) and the wetting transition of the semi-infinite system $\{T_W(H_1)\}$ are indicated. The curves show the (first-order) transition (from gas to fluid), which occurs for nonzero (negative) bulk field if $H_D/H_1 > -1$, while the dots show the critical points of the thin film. For $H_D/H_1 = 1$ one has the situation usually considered in capillary condensation [4,14].

m_n decay exponentially $\{m_n \propto -|H_1| \exp(-n/\xi_b)$ for $n \ll D/2$ and $m_{D-n} \propto +|H_1| \exp[-(D-n+1)/\xi_b]$ for $D - n \ll D/2$, ξ_b being the bulk correlation length of the 3D Ising model$\}$, as long as $D/2 \gg \xi_b$; the two walls are essentially noninteracting. Near T_{cb}, when $D \approx 2\xi_b$, the curvature in the center of the profile changes and a well-developed interface in the center of the film takes form. A study of other quantities [15] also corroborates the conclusion that there is no transition near T_{cb} for any finite D. For $T_c(D)$ near $T_w(H_1)$, however, one now observes a symmetry breaking in the thin film: The interface between the phases with negative and positive magnetizations is no longer located in the center, rather being bound either to the left or to the right wall [there is an exact degeneracy between these cases for $H_d = -H_1$ as shown in Fig. 2(b)]. While for $D = 20$ $T_c(D)$ and $T_w(H_1)$ cannot be clearly distinguished due to our rather large error bars, for $D = 8$ and $D = 6$ we have clearly observed that $T_c(D) < T_w(H_1)$, in agreement with Fig. 1 (and the theoretical prediction [6,9] for critical wetting).

An accurate characterization of the transition at $T_c(D)$ is difficult since the fluctuating, weakly confined interface for $T_c(D) < T \lesssim T_{cb}$ causes the existence of a huge correlation length in the directions parallel to the walls. Parry and Evans [9] predict that this length $\xi_{||}$ varies exponentially with thickness $\xi_{||} \propto \exp(D/4\xi_b)$, and hence susceptibilities such as $\chi_{nn} \propto (\partial m_n/\partial H_n)_T$ (H_n is a field acting on the nth layer only) should [20] vary as $\chi_{nn} \propto \xi_{||}^2$, for n near the center of the film. (We emphasize that ξ_b is the true correlation range in a lattice direction.) Figure 3 shows that an exponential variation is indeed observed—

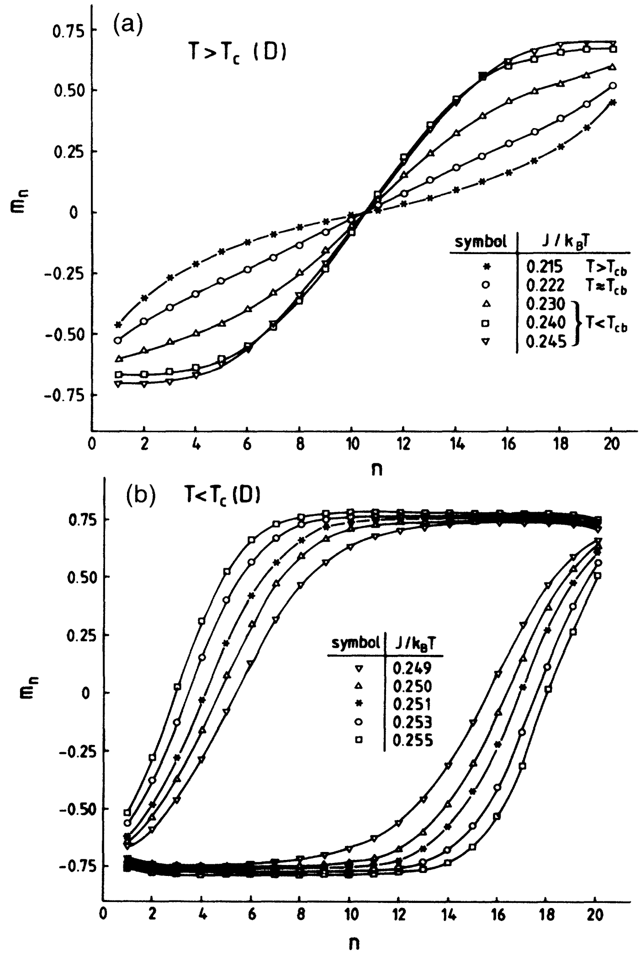

FIG. 2. Layer magnetization m_n plotted versus layer index n for an Ising lattice of linear dimension $L \times L \times D$ with thickness $D = 20$, $L = 128$, and two free $L \times L$ surfaces on which fields $H_1/J = -0.55$, $H_D/J = +0.55$ act. Part (a) refers to $T > T_c(D)$, part (b) to $T < T_c(D)$, with $J/k_B T_c(D) = 0.2475 \pm 0.0015$, while [19] $J/k_B T_{cb} = 0.221\,659 \pm 0.000\,003$. Curves are only drawn to guide the eye. All lengths are quoted in units of the lattice spacing.

although the slopes of the straight lines deviate strongly from corresponding estimates [15,21] of the predicted values $1/2\xi_b(T)$. For example, $J/k_B T = 0.232$ the length ℓ extracted from the estimate $\ln\chi_{nn}/D \approx 1/2\ell$ exceeds ξ_b by a factor of 1.79. Assuming that this characteristic length ℓ rather than the bulk correlation length ξ_b needs to be used in the constant w controlling the exponents of critical wetting [2,16,17], the discrepancy between simulations [16,17] and renormalization group predictions [22] possibly could be largely reduced. This discrepancy (which is possibly due to fluctuation effects) needs further study. In any case, the large values of $\xi_{||}$ imply that near $T_c(D)$ extremely large $L \gg \xi_{||}$ are needed to see the asymptotic critical behavior, and, due to the associated critical slowing down, and enormous statistical effort is

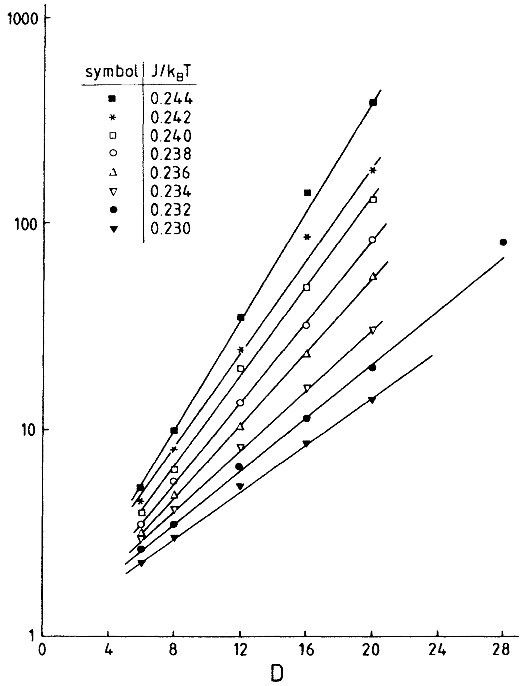

FIG. 3. Semilogarthmic plot of the maximum value of the layer susceptibility $\chi_{nn}^{\max}$ versus thickness D. Straight lines indicate the exponential variation. Note that the profile of χ_{nn} was symmetrized with respect to the midpoint $n_{\rm mid} = (D+1)/2$, in order to improve the accuracy.

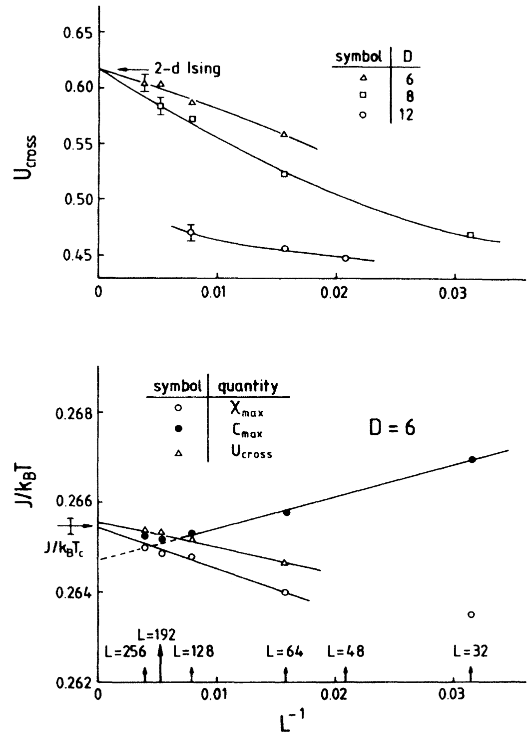

FIG. 4. Cumulant crossing values $U_{\rm cross}$ vs L^{-1} (upper part), for $D = 6$, 8, and 12. Arrow shows the value of the 2D Ising universality class. Curves are a guide to the eye only. Where not shown the error bars are smaller than the size of the symbols. Lower part shows (for $D = 6$ only) extrapolations of the temperatures of cumulant intersections as well as of the susceptibility and specific heat maxima. Arrow (with error bars) marks the final estimate of $J/k_BT_c(D)$, while straight lines indicate possible extrapolations.

needed. Thus, even using a very efficient vectorized, multispin coding program, we could only get accurate information about the critical behavior for rather thin films, $D \leq 12$ (Fig. 4).

For the largest systems with $L = 256$ as many as 5.4×10^6 Monte Carlo steps/site were used for computing averages, and even this statistical effort yielded results of moderate quality. Taking the total magnetization per spin of the film M [which is zero for $T > T_c(D)$, cf. Fig. 2(a), but nonzero for $T < T_c(D)$, cf. Fig. 2(b)] as the order parameter of the transition at $T_c(D)$, we analyze the moments $\langle |M| \rangle, \langle M^2 \rangle$, the susceptibilities $k_BT\chi = L^2D\langle M^2 \rangle$, $k_BT\chi' = L^2D(\langle M^2 \rangle - \langle |M| \rangle^2)$, the cumulant $U_L = 1 - \langle M^4 \rangle / 3\langle M^2 \rangle^2$, and the specific heat for a variety of sizes L near $T_c(D)$, desiring to perform a finite size scaling analysis. For 2D Ising criticality, all cumulants U_L should intersect at [14] $T_c(D)$ at a universal value [23] $U_L(T_c(D)) = U* = 0.615$. However, due to crossover between wetting criticality [24] and Ising criticality, we do not see this Ising behavior. Instead, the cumulants cross at temperatures $T_c^{\rm eff}$ that depend systematically on L, as do the corresponding crossing points $U_{\rm cross}(L)$ [defined by $U_L = U_{L/2} = U_{\rm cross}(L)$]. Extrapolating $U_{\rm cross}(L)$ versus $1/L$ (Fig. 4), one can see a convergence towards the Ising value for $D = 6$ and $D = 8$, while for $D = 12$ much larger values of L would presumably be needed to establish the Ising character of the transition.

Because of these crossover problems, $T_c(D)$ can also be estimated only roughly. Extrapolating the temperature of the cumulant crossing and the temperature of specific heat and susceptibility peaks versus $L^{-1/\nu(2D)} = L^{-1}$ [remember $\nu(2D) = 1$ in the Ising model], we obtain $J/k_BT_c(D = 6) = 0.2655 \pm 0.0002$ (Fig. 4). For $D = 6$ sizes $L \gtrsim 192$ are already needed to reach the asymptotic Ising region. While for $D = 6$ log-log plots of $\langle |M| \rangle_{T=T_c}$ vs L and $k_BT\chi(T_c)$, $k_BT_c\chi'_{\max}$ are roughly compatible with the expected power laws [$\langle |M| \rangle_{T=T_c} \propto L^{-\beta(2D)/\nu(2D)} = L^{-1/8}$, $\chi(T_c) \propto \chi'_{\max} \propto L^{\gamma(2D)/\nu(2D)} = L^{7/4}$, see Fig. 5], our data for $D = 6$, 8, and 12 are compatible with Eq. (1) [$J/k_BT_c(D = 8) = 0.2578 \pm 0.0002$, $J/k_BT_c(D = 12) = 0.2505 \pm 0.0005$, while [16,17] $J/k_BT_w(H_1/J = 0.55) = 0.250 \pm 0.005$]. For $D = 12$ one sees rather different "effective exponents," although there is also a mild curvature of the log-log plot [15]. More powerful techniques are clearly required in order to deal with this kind of simulation data in a crossover region.

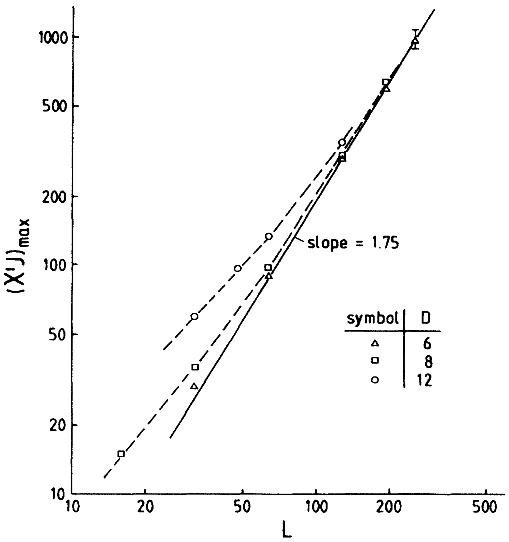

FIG. 5. Log-log plot of the maximum of the finite lattice susceptibility vs L for different film thicknesses D. The straight line has the slope of the 2D Ising model $\gamma = 1.75$. The dashed lines are simply guides to the eye. Where not shown the error bars are smaller than the size of the symbols.

In conclusion, we have clarified the phase transition behavior of thin films with competing walls. Indeed, the interface localization-delocalization transition as predicted by Parry and Evans [6,9] is the correct scenario. The exponential increase of the correlation length with thickness (cf. Fig. 3) does not allow us to study the critical behavior for larger D, however. We expect that in real systems (where D may be much larger than ξ_b) $\xi_{\parallel}$ could become of macroscopic size, and then finite size rounding will again be a problem. From the exponential increase of the response function χ_{nn} with thickness we have extracted a new length ℓ characterizing Ising interfaces, which possibly clarifies the controversies about critical wetting.

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