PHYSICAL REVIEW B VOLUME 31, NUMBER 7 1 APRIL 1985

First-order transition in systems of finite thickness

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(Received 5 July 1984)

Film systems, limited by two parallel disrupting surfaces and undergoing a first-order bulk transition, are shown to possess a number of specific features essentially governed by the ratio of the film thickness L to the "characteristic" length L_0 of the transition. For disordering boundaries, it is found that (1) the transition temperature scales as L^{-1} for $L/L_0 \gg 1$, (2) the continuous transition of the surface order parameter, predicted to occur in semi-infinite systems, transforms into a weak first-order transition, and (3) below a critical thickness, no transition occurs. Comparisons with experimental systems are discussed.

In studies of critical behavior in "finite" systems, the concept of finite-size scaling has provided a powerful tool to predict the characteristics of the transition in the limit of large finite systems, once the infinite case is known.[1-3] For example, systems bounded with some scale L in one direction but infinite in the others (so-called films) can be viewed as bridging the gap between d- and $(d-1)$-dimensional behavior.[4-7] Another type of such interdimensional system is an infinite pile of $(d-1)$-dimensional layers coupled by a tunable interaction which yields so-called d–$(d-1)$ anisotropy crossover.[8-10]

Much less attention has been paid to a first-order phase transition which, in such film systems, is expected to be strongly dependent on the presence of two surface boundaries. Of particular interest is the case of systems, exhibiting a phase transition in d dimensions which disappears or changes character in $d-1$ dimensions. This can occur, for instance, when $d=3$ and the group of symmetry under which the Hamiltonian is invariant is continuous, as is the case for the melting transition.[11]

By varying the width of the film, one may expect a continuous crossover from $(d-1)$-dimensional (small L) to d-dimensional behavior (large L). Examples of relevant physical systems are multilayer adsorbates of simple atoms or molecules on smooth substrates, antiferromagnetic crystal films, free-standing thin liquid-crystal films, lipid monolayers at an air (alkane)-water interface or lipid membranes in which the scale L is proportional to the hydrocarbon chain length of the lipid molecules. It has recently been shown within mean-field theory that for semi-infinite systems which undergo a first-order bulk transition, the surface order parameter may nevertheless exhibit a continuous transition.[12] Here, I consider the influence of a second interface, and I show that as a consequence of the disrupting effect of the two boundary surfaces, the transition temperature is different from that of the infinite or semi-infinite case. I find that, with disordering boundaries, (i) the transition temperature is lowered and follows a L^{-1} power law for "large" L, (ii) contrary to the semi-infinite case, the surface order parameter undergoes a weak first-order transition with a jump scaling as $L^{-1/2}$, and (iii) for finite thickness no transition occurs below a critical width L_c which depends on the disordering strength of the boundaries.

Consider a d-dimensional film system bounded by two $(d-1)$-dimensional parallel surfaces separated by a distance L, large compared to the microscopic structure. The one-component order parameter M depends on z, the coordinate perpendicular to the two surfaces.

Generalizing the semi-infinite case,[12] I write the generic form of the Landau free-energy functional as

$$F\{M\} = \int_0^L dz \left[\frac{1}{2} \left(\frac{dM}{dz} \right)^2 + f(M) + \delta(z) f_1(M) + \delta(z-L) f_2(M) \right] . \tag{1}$$

$f(M)$ is the bulk free energy for a homogeneous field configuration M, and $f_1(M)$ and $f_2(M)$ are the surface contributions describing the influence of the two walls on the order-parameter field. In the mean-field approximation, the order-parameter profile is determined by the Euler-Lagrange equation which yields

$$\frac{d^2M}{dz^2} = \frac{df}{dM} , \tag{2}$$

with the boundary condition

$$\left. \frac{dM}{dz} \right|_{z=0,L} = \pm \left. \frac{df_{1,2}}{dM} \right|_{M_{0,L}} , \tag{3}$$

where $M_0 = M(z=0)$ and $M_L = M(z=L)$.

Order-parameter profiles, which obey (2) and (3) and yield the absolute minimum of the free energy, describe the equilibrium thermodynamic state of the system. As will be discussed below, the features of the systems considered are qualitatively independent of the specific form of the bulk free energy $f(M)$. However, to be specific, let us consider the case of a system exhibiting a bulk tricritical point

$$f(M) = \tfrac{1}{2} a(T) M^2 - \tfrac{1}{4} u M^4 + \tfrac{1}{6} v M^6 . \tag{4}$$

Here, I am concerned with $u > 0$, which leads to a first-order bulk transition at $a = a^* = \frac{3}{16} u^2/v$. At $T = T^*$ (with $T - T^*$ proportional to $a - a^*$), the bulk order parameter jumps by the amount $(3u/4v)^{1/2}$.

For the surface contributions $f_1(M)$ and $f_2(M)$, one can take[12,13]

$$f_{1,2}(M)=\tfrac{1}{2}a_{1,2}M^2 \ , \tag{5}$$

which reflects the disordering effects of the boundaries. In order to extract the relevant parameter of the problem, I introduce the dimensionless variables

$$x=\frac{z}{L},\ \ l=L\Big/\left(\frac{v}{u^2}\right)^{1/2},\ \ \phi=\left(\frac{v}{u}\right)^{1/2}M \ ,\quad \tau=a\Big/\frac{u^2}{v},\ \ \tau_{1,2}=a_{1,2}\Big/\left(\frac{u^2}{v}\right)^{1/2} . \tag{6}$$

With (4), (5), and (6), the free-energy functional becomes

$$F\{\phi\}=\frac{u^2}{v^{3/2}}l\left\{\int_0^1 dx\left[\frac{1}{2l^2}\left(\frac{d\phi}{dx}\right)^2+\tilde{f}(\phi)\right]+\frac{1}{2}\frac{\tau_1}{l}\phi_0^2+\frac{1}{2}\frac{\tau_2}{l}\phi_1^2\right\} \ , \tag{7}$$

where $\phi_0=\phi(x=0)$, $\phi_1=\phi(x=1)$, and

$$\tilde{f}(\phi)=\tfrac{1}{2}\tau\phi^2-\tfrac{1}{4}\phi^4+\tfrac{1}{6}\phi^6 \ . \tag{8}$$

Scaling introduces a characteristic length scale $L_0=(v/u^2)^{1/2}$, which defines two regimes: (i) $L >> L_0$, "thick" films far from the tricritical line $(u=0)$ where L_0 diverges, and (ii) $L \lesssim L_0$, "thin" films near the tricritical point.

Note that no loss of generality follows from the particular form chosen for $f(M)$ [Eq. (4)]. For example, a system with a bulk critical point characterized by the free-energy density

$$f(M)=\tfrac{1}{2}a(T)M^2-\tfrac{1}{3}bM^3+\tfrac{1}{4}uM^4 \tag{9}$$

also possesses a natural length scale $L_0=(u/b^2)^{1/2}$ which diverges on the critical line $(b=0)$. Since, for a given system, the characteristics of the transitions are governed by the dimensionless parameter $l=L/L_0$, any form of the free energy, for which a characteristic length can be defined, will yield the same qualitative features. The behavior of the system as a function of the temperature emerges on examination of Eq. (7). For very large $L\,(l\rightarrow\infty)$, the total free energy F approaches that of the free-energy density $f(M)$ times the width l. As expected, the transition is then affected very little and the effects of the two walls become independent so that the problem reduces to the analysis presented in Ref. 12. For finite but still large l, the presence of boundaries and of the gradient term introduces additional contributions to the free energy. For all temperatures, the order parameter profile $\phi(x=z/L)$ has two solutions which satisfy the set of Eqs. (2) and (3) and yield an extremum for $F\{\phi\}$. As the temperature is lowered below the transition temperature $\tau^*(l)$, the trivial solution $\phi(x)=0$ no longer yields the absolute minimum of $F\{\phi\}$. The system condenses in an ordered phase whose profile $\phi(x)$ strongly depends on the disrupting effect of the boundaries, as illustrated in Fig. 1. The l dependence of the transition temperature $\tau^*(l)$ is determined as follows. Integration of Eq. (2) and use of (6) yields, for the generic symmetric case,

$$\frac{d\phi}{dx}=\sqrt{2}l[\tilde{f}(\phi)-\tilde{f}(\phi_{1/2})]^{1/2},\ \ \phi_{1/2}=\phi(x=\tfrac{1}{2}) \ , \tag{10}$$

which is the equation for the order-parameter profile. Therefore, the boundary conditions (3) can be written as

$$\tilde{f}(\phi_{1/2})=\tilde{f}(\phi_0)-\tfrac{1}{2}\tau_1^2\phi_0^2 \ . \tag{11}$$

For a given $\phi_{1/2}$, $\phi(x)$ is given by (10) in terms of an implicit elliptic integral. Inserting the profile $\phi(x)$ into (7) yields the extremum of the total free energy as a function of $\phi_{1/2}$. Then the stable phase is determined by minimization of F with respect to $\phi_{1/2}$; in general, this cannot be performed analytically. However, in the asymptotic regime $l >> 1$, the leading behavior of the total free energy $F\{\phi\}$ can be obtained explicitly. One could argue that, because of the finite thickness of the disordered phase wetting the boundaries, the contribution of the bulk to $F\{\phi\}$ is proportional to l and can be expressed as $\kappa l\tilde{f}(\phi_{1/2})$ where κ is a constant of order unity. This argument is valid as long as the layer of the disordered phase does not pervade the film, but becomes questionable in the light of the semi-infinite case where the width of the disordered layer diverges at $\tau=\tau_\infty^*$ like $\ln(\tau_\infty^*-\tau)$. Nevertheless, substitution of the asymptotic expression of the solution of (10) into (7) confirms the linear l dependence of the bulk contribution to $F\{\phi\}$. This means that the logarithmic divergence is weak and vanishes in the finite thickness case: at the transition, only a small layer of disordered phase wets the walls, as illustrated in Fig. 1.[14] So $F\{\phi\}$ can be written as the sum of the bulk term $\kappa l\tilde{f}(\phi_{1/2})$ and of two positive contributions, the gradient term and the surface energy whose leading behaviors for $l >> 1$ are independent of l.

Since for $l >> 1$, $\phi_{1/2}\approx\phi_B$ (where ϕ_B is the bulk order-parameter value), $\tilde{f}(\phi_{1/2})$ scales as $\tau-\tau_\infty^*$, for small $\tau-\tau_\infty^*$. Then $F\{\phi\}$ will vanish at a lower temperature $\tau=\tau^*(l)$

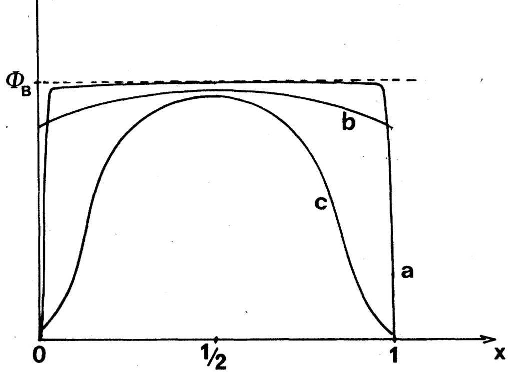

FIG. 1. Order-parameter profile $\phi(x)$: (a) large l, $\tau_1 > \tau_\infty^{*1/2}$; (b) small l, $\tau_1 << \tau_\infty^{*1/2}$; (c) small l, $\tau_1 > \tau_\infty^{*1/2}$.

given by

$$\tau_\infty^* - \tau^*(l) \sim \frac{1}{l} \ . \tag{12}$$

At this temperature $\tau^*(l)$, the disordered phase $[\phi(x)=0]$ condenses to the ordered phase.

This result can be compared with the same result for second-order transitions[3,4] and reflects simply the L^{-1} dependence of the relative weight of surface to bulk contributions.

A decrease in the transition temperature $\tau^*(l)$ with diminishing width l is found in many physical systems as, for example, in multilayer adsorbates on graphites,[15] paraffins,[16,17] and liquid crystals.[18]

However, in order to observe the l^{-1} power law, the system must be in the $l=L/L_0 >> 1$ asymptotic regime. This condition should be met in lipid bilayer systems made of highly flexible hydrocarbon chains whose lengths are of the order of 12–22 C–C bonds and for which the typical correlation length L_0 can be estimated to be of the order of a carbon-carbon link length. In such systems, the power law (12) was found experimentally.[19]

The displacement of the transition temperature given by Eq. (12) has an interesting consequence as to the nature of surface transitions. For strong disordering boundaries (namely, $\tau_1 > \tau_\infty^{*1/2}$) and semi-infinite systems, a continuous surface transition was predicted.[12] In the film system, the free-energy density $\tilde{f}(\phi_{1/2})$ in the middle of the film no longer vanishes at the shifted transition temperature $\tau^*(l)$. Thus, Eq. (11), yielding the surface order parameter ϕ_0 as a function of $\phi_{1/2}$, implies that the surface order parameter ϕ_0 undergoes a jump proportional to $l^{-1/2}$. In other words, due to the finite width l of the film, the continuous transition of the surface order parameter ϕ_0 transforms into a weak first-order transition.

For arbitrary l, the picture holds, at least qualitatively. As l decreases, the transition temperature lowers but corrections to the l^{-1} power law become important, reflecting the increase of the thickness of the layer of the disordered phase between the surface and the ordered phase, as shown in Fig. 1. However, a new phenomenon occurs when the thickness of the film becomes of the order of the natural length scale, i.e., $l \lesssim 1$. To illustrate this regime, I first consider the simple case of weak disordering boundaries: i.e., $\tau_1 << 1$.

Then Eq. (11) implies that $\phi_{1/2}-\phi_0$ is small and equal to, say, $\epsilon\phi_{1/2}$, where ϵ is a small parameter, itself a function of τ_1 and $\phi_{1/2}$. Introducing the new function $K(x)$ defined by

$$\phi(x)=\phi_{1/2}[1-\epsilon K(x)]$$

and expanding Eq. (10) to first order in ϵ, one obtains, for small l, the parabolic profile

$$\phi(x)=\phi_{1/2}[1-\epsilon(1-2x)^2] \ , \tag{13}$$

as shown in Fig. 1.

Substitution of (13) into (7) yields the total free energy which is found to stay positive at all positive temperatures if the width l of the film is less than a critical length $l_c \sim \tau_1$. In other words, for thin films with width $l < l_c$, no transition occurs. This result holds for arbitrary value of τ_1 with a critical length which is an increasing function of τ_1 and goes to a constant of the order of the characteristic length scale for strong disordering boundary parameters ($\tau_1 >> 1$). For l marginally higher than l_c, the layer of the disordered phase at the surface pervades the whole film, as shown in Fig. 1.

Such a behavior has been observed in the rotational transition in adsorbed methane films[20] for which heat-capacity measurements suggest that the order-disorder transition is absent when the adsorbed film is less than ~3–4 layers thick.

This disappearance of the bulk first-order phase transition in very thin films is also reminiscent of the change in nature and in range of transition temperature of the melting transition when going from a three- to a two-dimensional system.[21,22]

The results reported here correspond to disordering boundaries but we could have considered alternatively the influence of a local chemical potential or surface field and also of ordering boundaries by replacing expression (5) with $f_1(M)=\frac{1}{2}a_1(M-M_1)^2-H_1M$. It is easy to show that for a finite range of values of M_1, the presence of the gradient term in the total free energy induces an increase in the transition temperature for decreasing thickness. The transition occurs from a disordered phase surrounded by two layers of ordered phase wetting the boundaries to an ordered phase pervading the whole system. This effect has been observed in liquid-crystal films.[23]

The mean-field approach used here does not take into account the effect of fluctuations which can be very important in low-dimensional systems. A step beyond the classical approximation towards fluctuation theory should include corrections to the mean-field profile $\phi(x)$ and the evaluation of their contribution to the partition function. We are presently developing this approach.

Note added. After this work was submitted, I became aware that similar results appear in Phys. Rev. B **29**, 5213 (1984) by Lipowsky and Gompper (LG). The mathematical analysis developed in the two papers is mean field and thus similar. LG discuss the case $f(\phi)=\frac{1}{2}a\phi^2-\frac{1}{3}b\phi^3+\frac{1}{4}c\phi^4$, whereas I study $f(\phi)=\frac{1}{2}a\phi^2-\frac{1}{4}u\phi^4+\frac{1}{6}v\phi^6$. However, as stressed in the text, qualitative differences in the predictions of the two models should not exist, a result which is confirmed by comparing the two papers. LG postpone the exposition of their analysis to a work to be published, whereas this paper is self-contained and some details on the treatment are given. The conclusions of the two works are essentially identical except that I dwell on the significance of the absence of transition in thin films and discuss its experimental relevance, an aspect just touched upon in Ref. 21 of LG's paper. LG discuss more thoroughly the dependence on dimensionality ($d=2$ or $d=3$) of the thickness of disordering layer and transverse correlation lengths, whereas this work focuses more on dimensional crossover behaviors.

I am grateful to J. P. Boon and N. Ostrowsky for stimulating discussions and a critical reading of the manuscript.

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[1] M. E. Fisher, in *Critical Phenomena,* proceeding of the International School of Physics Enrico Fermi, Course No. LI, edited by M. S. Green (Academic , New York, 1970).

[2] E. Brezin, J. Phys. (Paris) **43**, 15 (1982).

[3] C. Domb and J. L. Lebowitz, *Phase Transitions and Critical Phenomena* (Academic, New York, 1983), Vol. 8.

[4] M. N. Barber and M. E. Fisher, Ann. Phys. **77**, 1 (1973); Phys. Rev. A **8**, 1124 (1973).

[5] W. Wazilewski, Phys. Lett. **93A**, 354 (1983).

[6] W. Korneta and Z. Pytel, Phys. Lett. **94A**, 305 (1983); **98A**, 379 (1983).

[7] J. P. Clerc, G. Giraud, S. Alexander, and E. Guyon, Phys. Rev. B **22**, 2489 (1980).

[8] C. Y. Weng, R. B. Griffiths, and M. E. Fisher, Phys. Rev. **162**, 2 (1967).

[9] E. Guyon, J. P. Clerc, G. Giraud, and J. Roussenq, J. Phys. (Paris) **42**, 1553 (1981).

[10] B. Gavish and Y. Imry, J. Chem. Phys. **65**, 139 (1976).

[11] N. D. Mermin, Phys. Rev. **176**, 1 (1968).

[12] R. Lipowsky, Phys. Rev. Lett. **49**, 1575 (1982).

[13] D. M. Kroll and R. Lipowsky, Phys. Rev. B **28**, 6435 (1983).

[14] Using the L^{-1} shift of the transition temperature obtained in Eq. (12) in the $\ln(\tau_\infty^* - \tau)$ dependence of the disordered layer yields a maximum value for the disordered layer which scales as $\ln(L)$, which is very small compared with the width L of the film.

[15] M. N. Barber, Phys. Rep. **59**, 4 (1980).

[16] M. G. Broadhurst, J. Chem. Phys. **36**, 2578 (1962).

[17] A. Holz, J. Naghizadeh, and D. T. Vigren, Phys. Rev. B **27**, 512 (1983).

[18] D. J. Bishop, W. D. Sprenger, and R. Pindak, Phys. Rev. Lett. **49**, 1861 (1982).

[19] D. Sornette and N. Ostrowsky, in *Physics of Amphiphiles, Micelles, Vesicles and Microemulsions,* edited by V. Degiorgio and M. Corti (North-Holland, Amsterdam, in press).

[20] A. D. Migone, M. H. W. Chan, and J. R. Boyer, Physica B **108**, 787 (1981).

[21] See, for example, D. R. Nelson and B. I. Halperin, Phys. Rev. B **19**, 2457 (1979).

[22] D. R. Nelson, in *Fundamental Problems in Statistical Mechanics V,* edited by E. G. D. Cohen (North-Holland, Amsterdam, 1980).

[23] J. Prost (personal communication).