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Irrelevance of bulk symmetry to critical wetting

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We consider a q-state Potts model below its critical temperature, which is in contact with a wall. The bulk is in one of the q phases while the wall favors one of the others. We show that if the critical wetting exponents are universal, independent of the wall, then they are superuniversal, independent of q and thus of the bulk symmetry. The order parameter of the wetting transition can be taken to be of one component, the thickness of the wetting layer. Although this derivation is within mean-field theory, we believe the result to be true in all dimensions.

Studies of wetting almost invariably[1] employ a model of the bulk in which there are two phases, A and B. Given that the bulk is in state A while a surface favors B, one examines the thickness l of the film of B as bulk coexistence between A and B is approached. The thickness at coexistence is finite below a wetting temperature T_w and infinite above. If l at coexistence increases continuously as T_w is approached, the transition, denoted critical wetting, has associated with it various exponents which describe, *inter alia*, the divergence of l with temperature

$$l \sim (T_w - T)^{\beta}$$

and the singularity in the surface specific heat

$$C \sim (T_w - T)^{-\alpha} .$$

One might expect that in models in which there are more than two bulk phases which are related by some symmetry, these exponents would depend upon that symmetry. For example, if the bulk were in one of the ordered states, A, of a q-state Potts model while the surface favored another such state, B, then the exponents governing the critical wetting of the surface by B might well be different from that of the two-component system due to the presence of the other components $C, D, \ldots$, just as the exponents governing the bulk transition are known to be different. However, it is believed that, within mean-field theory which should show such an effect, there is no such difference. This belief rests on the construction of effective one- (order-parameter) component theories which are essentially symmetry independent.[2-4] Although such theories are incapable of addressing some issues which arise in systems with a multicomponent order parameter,[3] they are thought to provide correctly the critical exponents associated with interfacial transitions. We consider below the multicomponent theory and show that if the exponents are universal, independent of wall potentials, then they are indeed superuniversal, independent of the symmetry. Thus, these systems can all be characterized by a single-component order parameter l specifying the thickness of the phase favored by the surface. Although our demonstration for short-ranged forces proves the point only above the upper critical dimension for such forces (Ref. 5) $d^* = 3$, we believe that it is true in all dimensions, a point to which we return later. In order to determine the exponents for the case in which the bulk has a Potts symmetry, it is convenient to remind the reader how they are obtained for the case in which the bulk exhibits Ising symmetry. One begins with a Landau free energy (per unit surface)

$$F \equiv F_B + F_S , \tag{1}$$

where

$$F_B = \int_0^{\infty} dz \left[\frac{1}{2} \left[\frac{dM}{dz} \right]^2 + U(M,T) \right] . \tag{2}$$

$M(z)$ is a one-component order parameter, the particle density, and $U(M,T)$ is a function with two equal minima: one at $M_G(T) < 0$, which represents the gas, the other at $M_L(T) > 0$, which represents the liquid. Surface contributions, which need not concern us, are given by F_S. The functional F_B is to be minimized with respect to variation of $M(z)$ subject to the boundary conditions that the bulk is in the gas phase,

$$M(\infty) = M_G , \tag{3}$$

and a condition at the surface which we need not make explicit. The problem is easily visualized in terms of its dynamical analogue, in which the action

$$F_B = \int_0^{\infty} dz \left[\frac{1}{2} \left[\frac{dM}{dz} \right]^2 - V(M,T) \right] \tag{4}$$

describes the motion of a particle moving in the potential $V = -U$, which has two maxima. The particle, whose coordinate at time z is $M(z)$, is constrained by Eq. (3) to arrive on top of the gas hill as $z\to\infty$. It begins at some point $M(0)$ determined by the initial conditions. As T approaches the wetting temperature T_W, the coordinate of the liquid hill, M_L, approaches the initial position $M(0)$. The particle begins with more potential and less kinetic energy, so the time spent in the vicinity of the liquid hill is greater. This corresponds to a thicker film in the original problem. As the critical exponents describe the divergence of this time, it is not surprising that they can be extracted by simply investigating the motion in the vicinity of M_L. Then we can write

$$V(M,T)\simeq-\tfrac{1}{2}k^2[M-M_L(T)]^2 \ . \tag{5}$$

With this choice of the zero of potential energy, the boundary condition (3) implies that the total energy of the system is zero. Thus,

$$\frac{1}{2}\left[\frac{dM}{dz}\right]^2-\frac{k^2}{2}(M-M_L)^2=0 \ , \tag{6}$$

so that

$$M(z)=M_L+[M(0)-M_L]e^{kz} \ . \tag{7}$$

The thickness of the film, l, can be obtained by defining $M(l)$ to be any fixed value of M with

$$M_G<M(l)<M_L \ .$$

From Eq. (7), the "time" l that it takes to obtain this position is given by

$$l(T)=k^{-1}\ln\left[\frac{M_L(T)-M(l)}{M_L(T)-M(0)}\right] . \tag{8}$$

The liquid density M_L is a smooth function of temperature. It coincides with $M(0)$ at T_W, so that, near T_W,

$$M_L-M(0)=ct \ , \tag{9}$$

where $t=(T_W-T)/T_W$ and c is a constant. Thus, from Eq. (8), one finds that the thickness diverges with temperature like

$$l\sim-\ln t \ , \tag{10}$$

which implies that $\beta=0$. The other exponents can be obtained from the surface free energy, given by (1) and (2), minus the free energy of a uniform bulk system of the same volume. However, with our choice of the zero of potential, this term vanishes so that the surface free energy is just given by F. Furthermore, whereas the surface term F_S is important in determining whether the wetting transition is first order or continuous,[5,6] if the latter, it does not, in general,[7] affect the exponents of the transition. Thus, it is sufficient to examine F_B of (2) or (4). Using conservation of energy and the explicit solutions (7), we find that the motion of the particle in the vicinity of the liquid hill contributes to F_B a term of the form

$$F_B(T,l)\sim[M_L(T)-M(0)]^2 \ , \tag{11}$$

or, using (8) to eliminate the initial conditions,

$$F_B(T,l)\sim[M_L(T)-M(l)]^2e^{-2kl} \ . \tag{12}$$

The inverse susceptibility χ^{-1} is obtained as $\chi^{-1}=\partial^2F(T,l)/\partial l^2$, which vanishes like t^{γ}. This has the same singular behavior as $\partial^2F_B/\partial l^2$, which, from (12), has the same behavior as F_B itself. Thus, on using the smooth temperature dependence of M_L given by (9), we obtain, from (11) and (12),

$$F_B\sim t^2 \ , \tag{13}$$

$$\chi^{-1}\sim t^2 \ , \tag{14}$$

which identifies $\alpha=0$ and $\gamma=2$. Lastly, one defines the correlation length ξ which describes the decay of the excess surface density-density correlation function in the direction parallel to the substrate. This length diverges as $t^{-\nu}$ with ν given, in mean-field theory, by $\gamma/2=1$.

Now consider the case of a three-state Potts model in contact with a wall. The state of the system is described by an order parameter with two components $M_1(z)$ and $M_2(z)$ which vary with the distance from the wall. The free energy can be written as in (1) with

$$F_B=\int_0^\infty\left[\frac{1}{2}\left[\frac{dM_1}{dz}\right]^2+\frac{1}{2}\left[\frac{dM_2}{dz}\right]^2-V(M_1,M_2,T)\right] . \tag{15}$$

The potential V has three symmetrically placed maxima which represent the three possible bulk phases. We now deal with the potential motion of a particle in two dimensions. The motion is subject to the boundary condition that at infinite time z the particle arrives at one of the bulk hills, A, which fixes the energy, and an initial condition which states that particle starts in the vicinity of one of the other bulk hills, B, which is favored by the wall. We locate this latter hill at the coordinates $(M_1,M_2)=(M_B,0)$. The others are at $(-M_B/2,\sqrt{3}M_B/2)$ and $(-M_B/2,-\sqrt{3}M_B/2)$. As before, the critical exponents emerge from an analysis of the motion of the particle in the vicinity of the maximum favored by the walls, where the potential can be approximated as

$$V(M_1,M_2,T)\simeq-\frac{k_1^2}{2}[M_1-M_B(T)]^2-\frac{k_2^2}{2}M_2^2 \ . \tag{16}$$

We now assume that the exponents of the wetting transition are universal, i.e., do not depend on the wall potential, and therefore one can make any convenient choice of initial conditions. For definiteness, we make the choice that $M_1(0)$ is given to be positive but less than M_B, $dM_1(0)/dz=0$, and $M_2(0)=0$. Then the fact that the total energy of the particle is zero implies that

$$dM_2(0)/dz=k_1[M_1(0)-M_B] \ .$$

The solutions of the equations of motion, which arise from minimizing F_B with respect to M_1 and M_2, are

$$\begin{aligned} M_1(z)-M_B&=[M_1(0)-M_B]\cosh(k_1z) \ , \\ M_2(z)&=(k_1/k_2)[M_1(0)-M_B]\sinh(k_2z) \ . \end{aligned} \tag{17}$$

The density of the three components n_A,n_B,n_C are obtained from the order-parameter components according to

$$n_A=\tfrac{1}{3}(1-M_1+\sqrt{3}M_2)\ ,$$
$$n_B=\tfrac{1}{3}(1+2M_1)\ ,$$
$$n_C=\tfrac{1}{3}(1-M_1-\sqrt{3}M_2)\ ,$$

so that the excess density of component B favored by the surface is

$$\begin{aligned} n_B^{\text{ex}} &= \tfrac{2}{3}\int_0^\infty dz[M_1(z)-M_1(\infty)] \\ &= \tfrac{2}{3}\int_0^\infty dz[M_1(z)+\tfrac{1}{2}M_B]\ , \end{aligned} \tag{18}$$

where the fact that the M_1 coordinate of the A or C hill is $-M_B/2$ has been used. The thickness of the film, l, is defined by setting $M_1(l)$ to be any fixed value between $-M_B/2$ and M_B. Equation (18) shows that the excess surface density and l so defined are linearly related for large l. From (17) we find, for large l,

$$l \simeq k_1^{-1}\ln\left|2\frac{[M_B-M_1(l)]}{[M_B-M_1(0)]}\right| . \tag{19}$$

As M_B is a smooth function of temperature which coincides with $M_1(0)$ at T_W,

$$M_B-M_1(0)\simeq ct\ , \tag{20}$$

from which we find that the thickness of the film diverges as

$$l\sim -\ln t\ , \tag{21}$$

so that $\beta=0$ as before.

The free energy F_B is again obtained by using the conservation of energy to write the integrand of (15) as $-2V$ and then employing the form of V given in (16) and the explicit solution of (17). The motion in the vicinity of the bulk hill favored by the surface contributes to F_B a term of the form

$$F_B(T,l)\sim[M_B-M_1(0)]^2\ , \tag{22}$$

which, from (19), can be written

$$F_B(T,l)\sim 4[M_B-M_1(l)]^2e^{-2k_1l}\ . \tag{23}$$

This form is independent of our convenient choice of initial conditions, and follows from the form of the potential of (16). Provided that the exponents are independent of the surface terms, the singular part of the inverse susceptibility can be obtained from two differentiations of F_B with respect to l, which vanishes like F_B itself. The smooth dependence of M_B on T leads to $\alpha=0, \gamma=2, \nu=1$, as in the case with Ising symmetry.[5] The generalization to an arbitrary number q of Potts states is immediate. Thus, we obtain our result that in the critical wetting of the interface between a wall and one Potts phase by another such phase[8] favored by the wall, the exponents of the transitions are independent of the number of possible Potts phases, q, and thus of the bulk symmetry.

A few observations are in order. First, we have assumed that the exponents are universal, independent of the wall potential.[9] When this is so, we have found that they are superuniversal, independent of q, a result which is in agreement with that of one-component theories.[2–4] Second, the fact that our result depends only on the quadratic form of the potential in a space of dimensionality equal to that of the number of bulk order-parameter components indicates that the result applies to other symmetries in which the Landau potential has minima of such form. Third, the quadratic form presumes short-range forces so that the mean-field demonstration only proves the point above the upper critical dimension (Ref. 5) $d^*_{\text{bulk}}=3$. However, we believe that the result holds for all dimensions. Below d^*_{bulk} the exponents in common are simply different from their common mean-field values. This belief is supported by results on the chiral Potts model in two dimensions,[10] which, in spite of its different symmetry, undergoes a critical interfacial wetting transition with exponents identical to that of the Ising model in two dimensions.[11]

Lastly, our result does not imply that the bulk symmetry cannot affect the wetting behavior at all. That it can do so is demonstrated by the $Z(N)$ model. If a wall favors the state 1 while the bulk is in a state of order $n/2$ with n large, then it is easy to show that the interface is always wet at zero temperature. Furthermore, in contrast to the Potts case in which only one macroscopic region of B intervenes between the wall and the bulk phase A, in the $Z(n)$ case there are, in general, several macroscopic regions of phases $n=1,2,3$, etc. intervening between the wall and the bulk. What our result does say, even in such a case, is that if a critical wetting occurs in which one region which is microscopically thick at low temperatures becomes macroscopic continuously with an increase in temperature, then the critical exponents of that transition, if independent of the wall potential, are also independent of the bulk symmetry and identical to those of an Ising model in the same dimension.

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