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Critical adsorption: The renormalization-group approach

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A wall having unequal interactions with the two components of a binary mixture is responsible for critical adsorption. We have analyzed with the renormalization-group formalism the scaling laws which govern this phenomenon. Furthermore, we have computed, within the ϵ-expansion formalism, the universal order-parameter profile for a range of possible values of the wall parameters (surface field and decoupling factor).

Recent experiments on binary mixtures[1] have revealed the existence of a new critical phenomenon occurring near the wall of the container. This phenomenon, *the critical adsorption,* is induced by the difference in attraction (or repulsion) of the two species by the wall. When the temperature approaches the bulk critical value from above ($T \gtrsim T_c$) a nonzero concentration (order parameter m) profile appears in the system. It is the existence of this profile $m(z) = \langle \phi(z) \rangle$ which has been demonstrated experimentally. (The wall conicides with the $z = 0$ plane.)

The presence of the wall affects the behavior of the system in two different ways[2]:

(i) First, as we have said, the wall modifies the chemical potential for the two species. In magnetic language this is equivalent to introducing the field h_1 on the surface. This provokes a perturbation which can spread inside the system, if T is close to T_c.

(ii) The second effect is due to the semi-infinite geometry of the system. The absence of molecules of the mixture from one-half space (say, $z < 0$) changes the interaction on the surface. Using the magnetic analogy one can describe this change by introducing a new interaction term $c\phi^2$ on the surface,[3] where c has a positive value. In general there is no reason for the parameter c to vanish when T approaches T_c; thus the surface does *not* become critical simultaneously with the bulk. Because of this effect the surface tends to decouple from the rest of the system.

These two effects are, in fact, in competition: If $c > 0$ (the case called *"ordinary transition"*[3]) the perturbation due to h_1 cannot "propagate" when the temperature approaches T_c. There is no critical profile: $m(z) = 0$, for z bigger then a few molecular distances a_0. Only if the field h_1 is big enough to overcome the decoupling effect can one observe critical adsorption. This is the situation in the above-mentioned binary-mixture experiments.

One can also imagine a different situation in other physical systems, in which c is small because of a supplementary enhancement of the interparticle interactions on the surface. In this case (called the *special transition*[3]; $c \approx 0$) the critical adsorption can take place even for h_1 not so large.[4]

In this paper we use the renormalization-group approach to describe the critical adsorption. In 1978 Fisher and de Gennes proposed[5] scaling laws for the order-parameter profile $m(z)$. We shall discuss the domain of validity of these laws for the ordinary transition and show how to modify them for the special transition. We shall derive a formula for the universal scaling profile to first order in $\epsilon = 4 - d$.

We shall study its behavior and, in particular, the crossover from the special to the ordinary transition. The profile has a power-law behavior at large z, which is identical to that which appears in the ordinary transition. However, near the special transition, the existence of additional length scales modifies this profile for smaller values of z.

MEAN-FIELD THEORY FOR THE ORDER-PARAMETER PROFILE

The Landau free energy consists of bulk terms

$$\mathcal{H}_{\text{bulk}} = \int_0^\infty dz \int d^{d-1}x \left[\tfrac{1}{2} \nabla \phi^2 + \tfrac{1}{2} t \phi^2 + \frac{u_0}{4!} \phi^4 \right] \quad (1)$$

plus a surface free energy

$$\mathcal{H}_{\text{surf}} = \int d^{d-1}x \left(\tfrac{1}{2} c_0 \phi^2 - h_1^0 \phi \right)_{z=0} . \quad (2)$$

We assume here that the wall-sample interactions are short ranges. (Long-range interactions of van der Waals type will be discussed in Ref. 6.)

The minimization of this free energy leads to the differential equation

$$\frac{\partial^2 \phi}{\partial z^2} + t\phi + \frac{u_0}{6} \phi^3 = 0 \quad (3)$$

with the boundary condition

$$\left(c_0 \phi - h_1^0 - \frac{\partial \phi}{\partial z} \right)_{z=0} = 0 . \quad (4)$$

For z much larger than the bulk correlation length ξ, the order parameter falls off exponentially.

The interesting region is thus $z \lesssim \xi$, and therefore we will study directly the critical profile $t \equiv (T - T_c)/T_c = 0$, $\xi = \infty$. The solution is then simply

$$\phi = \left(\frac{12}{u_0}\right)^{1/2} \frac{1}{z + z_0} \tag{5}$$

with

$$z_0 = \frac{c_0 + [c_0^2 + 4h_1^0 (u_0/12)^{1/2}]^{1/2}}{2h_1^0 (u_0/12)^{1/2}} . \tag{6}$$

One can see in this simple solution the two regimes.

(i) Ordinary transition. The parameter c_0, which has the dimension of an inverse length, is not small at T_c. It is given as the inverse of some characteristic interatomic length scale a_0. Then since c_0 is large, z_0 is also large in general and it means that there is no penetration of the surface effects: The order-parameter profile is very small. The only way of getting a finite profile for large c_0 is to impose a strong surface field h_1^0. Then z_0 itself will be of the order of a few interatomic distances a_0 and the profile is proportional to $1/z$ or all distances down to the immediate vicinity of the wall.

(ii) Special transition. If c_0 and h_1^0 both remain small in a_0^{-1} units, then z_0 is a large length scale (compared to a_0) and the profile falls off as $1/z$ only for $z >> z_0$. However, it remains finite in the vicinity of the wall. We shall see that this last feature is modified when fluctuations are taken into account.

RENORMALIZATION-GROUP EQUATIONS

As shown by Wilson, the Landau free energy is a Hamiltonian which enters into the statistical sum of Boltzmann factors over all the order-parameter distributions. The scaling limit of this theory (zero lattice spacing or interatomic distance limit) has been described by **Symanzik**[7] **and Diehl and Dietrich**[8] **and** we are not going to repeat their analysis in detail. Let us simply recall that the free wall of semi-infinite geometry introduces a new short-distance singularity of the Green's function $G(x,x')$: It is now singular when x coincides with either x' or with the image of x' with respect to the wall (i.e., when x and x' are close to the wall). Consequently, correlation functions with arguments near the suface acquire a new multiplicative renormalization factor Z'_ϕ. Furthermore, new linear and logarithmic divergences are caused by the surface "temperature" term $c_0\phi^2|_{z=0}$, which are cancelled, respectively, by $\phi\partial_z\phi|_{z=0}$ and $\phi^2|_{z=0}$ counterterms. We have used the minimal subtraction scheme and the first counterterm has vanishing coefficients. Then there is a simple multiplicative renormalization of c_0.

Consequently in terms of the renormalized field Φ the Hamiltonian reads

$$\mathcal{H} = \int_0^\infty dx \int d^{d-1}x \left\{ \tfrac{1}{2} Z_\phi (\nabla\Phi)^2 + \tfrac{1}{2} Z_{\phi^2} t\Phi^2 + \mu^{4-d} \frac{g}{4!} Z_1 \Phi^4 \right\} \tag{7}$$

with the boundary condition

$$\left(-Z_\phi \frac{\partial\Phi}{\partial z} - \frac{h_1}{\sqrt{Z'_\phi}} + cZ_c\phi \right)_{z=0} = 0 \tag{8}$$

(μ is an arbitrary finite inverse length scale).

A differential renormalization-group equation follows by the standard procedure from these results. If we look simply at the order-parameter profile $m(z;t,c,h_1,g,\mu)$ the integration of the renormalization-group equation gives the flow equation

$$m(z;t,c,h_1;g,\mu) = \zeta(\lambda)\, m(z;t(\lambda),c(\lambda),h_1(\lambda);g(\lambda),\lambda\mu) \tag{9}$$

in which the parameter transformations under rescaling are given as usual by the equation $\lambda(dg(\lambda)/d\lambda) = \beta(g(\lambda))$,

$$\lambda \frac{dh_1}{d\lambda} = \tfrac{1}{2} h_1(\lambda) \left(\beta(g) \frac{\partial}{\partial g} \ln Z_\phi Z'_\phi \right)_{g(\lambda)} , \quad \text{etc.}, \ldots .$$

We use in addition canonical dimensional analysis and choose the rescaling factor λ as $\lambda = (z\mu)^{-1}$; when z, the distance to the wall, is large compared to the microscopic length μ^{-1}, we obtain the relation

$$m(z;tc,h_1;g,\mu) \underset{z\mu >> 1}{=} z^{-1/2(d-2+\eta)} m(1; tz^{1/\nu}, cz^{1+\eta_c}, h_1 z^{\Delta 1/\nu}; g^*, 1) \tag{10}$$

in which g^* is the infrared stable fixed point and

$$\eta_c = \left(\beta(g) \frac{d}{dg} \ln Z_c \right)_{g^*} ,$$

$$\frac{2\Delta_1}{\nu} = \left(d - \beta(g) \frac{d}{dg} \ln Z_\phi Z'_\phi \right)_{g^*} .$$

This establishes the scaling law

$$m(z;t,c,h_1) = z^{-\beta/\nu} F\left(\frac{z}{\xi}, z h_1^{\nu/\Delta_1}, c h_1^{-(\nu/\Delta_1)(1+\eta_c)} \right) \tag{11}$$

which generalizes the de Gennes-Fisher[5] scaling law. The critical profile ($t = 0$) satisfies the same relation with $z/\xi = 0$. This scaling law shows that there are

two new length scales in the special transition problem, namely, l_{h_1} proportional to $h_1^{-\nu/\Delta_1}$ and l_c proportional to $c^{-1/(1+\eta_c)}$. For the ordinary transition l_{h_1} and l_c are of the order of molecular distances and $m(z) = m_0 z^{-\beta/\nu}$.[9] This is the case of *strong adsorption* limit discussed in Refs. 9 and 6, which has been realized experimentally.[1] For the special transition the critical profile is a function with two length scales. If $z \gg l_{h_1}$, l_c, again $m(z)$ falls off as $z^{-\beta/\nu}$. Close to the wall for $z \ll l_{h_1}$, l_c (but $z \gg \mu^{-1}$ the microscopic length scale), the scaling law (11) is not sufficient to make any conclusion since we have no indication *a priori* on the possible short-distance singularities of the function F. A short-distance expansion of the operator $\phi(x)$ for $x=(z,\vec{x}_\perp)$ next to the wall consists at leading order simply of the relation

$$\phi(z,\vec{x}_\perp) \underset{z\to 0}{\sim} s(z)(\phi(0,\vec{x}_\perp))_R \ , \tag{12}$$

in which $s(z)$ is a c-number function and $(\phi(0,\vec{x}_\perp))_R$ is the surface operator with its genuine renormalization which makes its correlation functions finite. This leads as usual to a differential renormalization-group equation for $s(z)$ from which we obtain that

$$m(z) \underset{\substack{z\ll l_{h_1}\\ z\ll l_c}}{\sim} z^\theta \tag{13}$$

with

$$\theta = (d-\eta-2\Delta_1/\nu) \ . \tag{14}$$

At lowest order in ϵ, the exponent θ vanishes. We did verify that in mean-field theory the special transition critical profile $m(0)$ is finite. However, at first order in ϵ, $\theta = -\epsilon/6 + O(\epsilon^2)$ and the profile diverges close to the wall (of course it is cut off again at atomic distances).

In order to obtain the full crossover between the large and small z regimes, which is in fact the crossover between the normal and special transition profiles, we have performed an explicit calculation at T_c, to first order in ϵ. The calculation is extremely tedious and full of technical difficulties overcome by proper surface-operator renormalization. The details will be presented in a longer publication. We give here just the result for the critical profile

$$m(z;c,h_1) = z^{-\beta/\nu} F(\zeta = z h_1^{\nu/\Delta_1}, \gamma = c h_1^{-(\nu/\Delta_1)(1+\eta_c)}) \ , \tag{15}$$

$$F(\zeta,\gamma) = F_0(\zeta,\gamma) + \epsilon F_1(\zeta,\gamma) \ . \tag{16}$$

Mean-field theory gives

$$F_0(\zeta,\gamma) = \zeta/\zeta + \zeta_0(\gamma) \tag{17}$$

in which

$$2\zeta_0(\gamma) \equiv \gamma + (4+\gamma^2)^{1/2} \ . \tag{18}$$

Our calculation leads to

$$F_1(\zeta,\gamma) = -\frac{1}{2}\frac{\zeta}{\zeta+\zeta_0}\ln\zeta + \frac{\zeta}{\zeta_0}\left[\left(\ln\frac{2}{\zeta_0}-\frac{1}{2}\right)\left(-\frac{x}{2}+\frac{x^2}{3(2+\gamma\zeta_0)}\right)\right] + I(\zeta,\gamma) \tag{19}$$

in which $I = I_1 + I_2$, where

$$I_1(\zeta,\gamma) = -\frac{2}{3}\frac{\zeta}{\zeta_0}\int_0^\infty dk\left[\alpha(k)\left(\frac{k(5\gamma\zeta_0+22)+6(\gamma\zeta_0+3)}{4k^3(2+\gamma\zeta_0)}x^3 - e^{-2k(\zeta/\zeta_0)}\frac{k^2x+5kx^2+6x^3}{4k^3}\right)\right.$$
$$\left. + \frac{x^2}{4(2+\gamma\zeta_0)}\left(\alpha(k)\frac{2k+11+\zeta_0\gamma}{k} - \frac{2k+1-3\gamma\zeta_0}{k+1}\right)\right] \ , \tag{20}$$

$$I_2(\zeta,\gamma) = \frac{1}{4(2+\gamma\zeta_0)}x^2[e^{-2} - (\gamma\zeta_0+11)\mathrm{Ei}(-2) + 3(\gamma\zeta_0+1)(\mathfrak{C}+\ln 2) - 14\gamma\zeta_0 - 9] + \tfrac{3}{4}x\left(\ln\frac{x}{2} - \mathfrak{C} + 6\right) \ , \tag{21}$$

and $\mathfrak{C}$ is Euler's constant. Here x stands for

$$x = (\zeta/\zeta_0+1)^{-1}$$

and

$$\alpha(k) \equiv e^{-2k}$$
$$+ \frac{k^3-(\gamma\zeta_0+3)k^2+3(\gamma\zeta_0+2)k-3(\gamma\zeta_0+2)}{k^3+(\gamma\zeta_0+3)k^2+3(\gamma\zeta_0+2)k+3(\gamma\zeta_0+2)} \ . \tag{22}$$

Remark: The integral over k is convergent for small k since

$$\alpha(k) \underset{k\to 0}{\sim} k^5$$

and for large k because

$$\alpha(k) \underset{k\to\infty}{\sim} 1 - \frac{2}{k}(\gamma\zeta_0+3) \ .$$

It is easy to verify that from this expression one recovers the expected large-z and small-z behavior. For large ζ

$$F_0(\zeta) \underset{\zeta\gg\zeta_0}{\simeq} 1$$

and $F_1(\zeta)$ vanishes as $\log\zeta/\zeta$. Therefore $m(z)$ indeed falls off as $z^{-\beta/\nu}$ [see Eq. (15)]. For small ζ,

$$F_0(\zeta,\gamma) \underset{\zeta\ll\zeta_0}{\simeq} \zeta/\zeta_0$$

and

$$F_1(\zeta,\gamma) \underset{\zeta\ll\zeta_0}{\simeq} -\frac{2}{3}\left(\frac{\zeta}{\zeta_0}\right)\ln\left(\frac{\zeta}{\zeta_0}\right) .$$

Therefore we find, within the ϵ-expansion formalism, the expected behavior

$$m(z) \underset{z\,\text{small}}{\sim} z^{-\epsilon/6} . \tag{23}$$

Hence $\theta=-\epsilon/6+O(\epsilon^2)$, as predicted. A numerical study of the profile for various values of the scaling parameters ζ and γ is planned to be included in a detailed version of this work.

We have computed the critical order-parameter profile as a function of the distance to the wall for all values of the surface field h_1 and of the surface decoupling factor c. From the present experimental standpoint the physical distance to the wall is always large compared to the lengths related to h_1 and c and one should observe a profile which varies simply as $z^{-\beta/\nu}$ up to the bulk correlation length ξ. In other physical systems with small effective c parameters (such as ferromagnets with enhanced surface exchange interactions) one should expect to observe a more complicated profile with a succession of length scales up to the correlation length.

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