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Amplitude of the surface tension near the critical point

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In the vicinity of a critical point, along the coexistence curve for a liquid and its vapor (or for a binary mixture below the consolute point), the surface tension vanishes as $\sigma=\sigma_0(1-T/T_c)^\mu$, whereas the correlation length diverges as $\xi=\xi_0^-(1-T/T_c)^{-\nu}$. Widom's scaling law relates μ to ν as $\mu=(d-1)\nu$ ($d\leq 4$ is the dimensionality). Consequently, the combination of amplitudes $(\sigma_0/kT_c)(\xi_0^-)^{d-1}$ is universal; the first two terms of the ϵ expansion for this quantity are computed in this work.

I. INTRODUCTION AND RESULTS

Below the Curie point of an Ising ferromagnet, or equivalently below the consolute point of a binary mixture of two fluids, the two pure phases of the system may coexist in the absence of any symmetry breaking field, if the boundary conditions are set up appropriately. Let us consider for definiteness a sample contained in a vertical cylinder of height L and cross-sectional area A; if the spins point down in the $z=-L/2$ plane and up in the $z=L/2$ plane, an interface appears between the two pure phases of opposite magnetization. The corresponding surface tension σ is defined in terms of the free energy per unit area as

$$\sigma=(F_{\uparrow\downarrow}-F_{\uparrow\uparrow})/A \quad , \tag{1}$$

in which the arrows specify the boundary conditions in the planes $z=L/2$ and $z=-L/2$, respectively. This surface tension vanishes at the critical point with an exponent μ defined as

$$\sigma(\tau)=\sigma_0\tau^\mu, \quad \tau\equiv(T_c-T)/T_c \quad . \tag{2}$$

Widom's scaling law[1] relates μ to the correlation length exponent ν. Specifically, if one writes

$$\xi(\tau)=\xi_0^-\tau^{-\nu} \quad , \tag{3}$$

Widom's law states that

$$\mu=(d-1)\nu \quad , \tag{4}$$

in which d is the dimension of space (assumed here to be smaller than four). It has been further argued by Fisk and Widom[2] and recognized later as an aspect of the "two-scale factor universality"[3] that there exists a universal combination of critical amplitudes involving the surface tension amplitude σ_0. Indeed, it is now understood that there is a universal amplitude ratio corresponding to any critical exponent equality.[4] The simplest way to define this universal combination is to notice that we expect the free energy of the interface per unit area (divided by kT) multiplied by an area defined by the correlation length to be both temperature independent and universal in the vicinity of T_c. We thus consider the quantity ω defined as

$$(4\pi\omega)^{-1}=\frac{\sigma(\tau)\xi^{d-1}(\tau)}{kT_c} \quad ; \tag{5}$$

it is both temperature independent [from the scaling law (4)], universal, and equal to

$$(4\pi\omega)^{-1}=\frac{\sigma_0}{kT_c}(\xi_0^-)^{d-1} \quad . \tag{6}$$

The reason for choosing this rather odd normalization of ω (with this factor 4π) is related to the previous work on the wetting transition[5] in which it was shown that the actual numerical value of ω, defined by Eq. (5), plays a key role in understanding the nature of critical wetting. We report in this work a calculation of ω within the ϵ expansion[6] ($\epsilon\equiv 4-d$). Our calculation is similar to that of a quantity C_0 performed by Ohta and Kawasaki.[7] There are nevertheless a few reasons to report our result. First, in order to deduce ω from C_0 we need a number of other amplitude ratios (defined in Ref. 4), the relation being

$$\omega=\frac{1}{16\pi C_0}\left(\frac{r^-}{r^+}\right)\left(\frac{A^-}{A^+}\right)\frac{R_c}{(R_\xi^-)^d} \quad . \tag{7}$$

These other amplitudes are all available from Ref. 4; however, for reasons that we do not understand, when we use the various ϵ expansions for these quantities, we do not obtain a result for ω in agreement with ours.[8] Second, the calculation of the one-loop correction to mean-field theory involves the Fredholm determinant of a Schrödinger operator which is known in closed form and this makes our calculation much simpler.

Our result, to second order in ϵ, is

$$\omega=\frac{2\pi}{3}\epsilon\left[1-\epsilon\left(\frac{47}{54}+\frac{1}{2}\ln(4\pi)-\frac{1}{2}\gamma-\frac{5\pi\sqrt{3}}{18}\right)\right]+O(\epsilon^3) \tag{8}$$

(γ is Euler's constant $=0.5772\ldots$).

Setting ϵ equal to one in ω (or in $1/\omega$) yields estimates which vary from 1.39 to 1.57. Experimental data on σ_0 and on the amplitude ξ_0^+ of the correlation length above T_c are available in a few binary mixtures.[9] With use of theoretical estimates on ξ_0^+/ξ_0^- (Ref. 10) they lead to semiexperimental values of ω in the range 1.2 to 1.5. The ϵ expansion (8) for ω is thus giving a 10 to 20% accuracy (which is sufficient to decide that ω lies in the interesting range 0.5 to 2 for the critical wetting work reported in Ref. 5).

II. RENORMALIZATION-GROUP APPROACH

The vicinity of the critical point is described by a Landau-Wilson continuum model[11] with an energy functional written in terms of a one-component order parameter $\phi_0(x)$ in an arbitrary external field $h_0(x)$:

$$\beta H=\int d^dx[\tfrac{1}{2}(\vec{\nabla}\phi_0)^2-\tfrac{1}{2}\tau_0\phi_0^2+\tfrac{1}{4}g_0\phi_0^4-h_0(x)\phi_0(x)] \ . \tag{9}$$

In order to obtain the free energy we must calculate the partition function

$$\exp W\{h_0\}=\int D\phi_0 e^{-\beta H} \ , \tag{10}$$

and the Legendre transform $\Gamma\{\phi_0\}$ of $W\{h_0\}$ defined by

$$\phi_0(x)=\frac{\delta W}{\delta h_0(x)},\qquad \Gamma\{\phi_0\}=-W\{h_0\}+\int d^dx h_0(x)\phi_0(x) \ . \tag{11}$$

In zero field the free energy is given by

$$F/kT=\Gamma\{\phi_0^c\} \ , \tag{12}$$

in which $\phi_0^c(x)$ is the solution of

$$h_0(x)\equiv\frac{\delta\Gamma}{\delta\phi_0(x)}=0 \ . \tag{13}$$

Boundary conditions must be supplemented to Eq. (13). For up-up (or down-down) boundary conditions at $z=-L/2$ and $z=L/2$, respectively, $\phi_0^c(x)$ is uniform and equal to the spontaneous magnetization M_0. For down-up boundary conditions, $\phi_0^c(z,\vec{x}_\parallel)$ is independent of $\vec{x}_\parallel$ but vary with z between $-M_0$ and M_0. The surface tension is finally given by

$$\sigma/kT=[\Gamma\{\phi_0^c(z)\}-\Gamma\{M\}]/A \ . \tag{14}$$

In order to go beyond the mean-field theory, it is, as usual, much simpler to use renormalized perturbation theory[11] in which one deals immediately with the scaling limit

$$\beta H=\int d^dx\left[\tfrac{1}{2}Z(\vec{\nabla}\phi)^2-\tfrac{1}{2}\tilde{Z}\tau\phi^2+\frac{g\mu^{4-d}}{4!}Z_1\phi^4\right] \tag{15}$$

(in which μ is an arbitrary inverse length scale, so that g is dimensionless). We have used the minimal subtraction renormalization scheme in which the Z's are power series in g with coefficients containing only multiple poles in ϵ (but no finite part).

The renormalization-group (RG) equations for any RG-invariant physical quantity x, such as the surface tension or the correlation length, read

$$x(\tau,g,\mu)=x(\tau(\lambda),g(\lambda),\lambda\mu) \ , \tag{16}$$

in which λ^{-1} is an arbitrary length-scale dilatation. In particular, the product $(\sigma/kT)\xi^{d-1}$ satisfies (16) and is dimensionless. Consequently, using the RG and dimensional analysis, we have

$$\left[\frac{\sigma}{kT}\xi^{d-1}\right](\tau,g,\mu)=\left[\frac{\sigma}{kT}\xi^{d-1}\right]\left[\frac{\tau(\lambda)}{\lambda^2\mu^2},g(\lambda),1\right] \ . \tag{17}$$

Choosing λ such that $\tau(\lambda)/\lambda^2\mu^2=1$, [i.e., $\lambda\sim(\mu\xi)^{-1}$], $g(\lambda)$ is driven to its fixed point value g^*, and we obtain

$$\left[\frac{\sigma}{kT}\xi^{d-1}\right](\tau,g,\mu)=\left[\frac{\sigma}{kT}\xi^{d-1}\right](1,g^*,1) \ . \tag{18}$$

The right-hand side of (18) is a pure number, a function of ϵ only, and thus this establishes both Widom's scaling law (4) and the universality of ω.

III. EXPANSION IN POWERS OF ϵ OF THE SURFACE TENSION

At the mean-field level ($\epsilon=0$) we have

$$\Gamma^{\mathrm{MF}}\{\phi\}=\int d^4x[\tfrac{1}{2}(\vec{\nabla}\phi)^2-\tfrac{1}{2}\tau\phi^2+(1/4!)g\phi^4] \ . \tag{19}$$

This gives the spontaneous magnetization

$$M^{\mathrm{MF}}=(6\tau/g)^{1/2} \ , \tag{20a}$$

and for the coexistence problem, the equation for ϕ^c_{MF} is

$$-\frac{d^2\phi^c_{\mathrm{MF}}}{dz^2}-\tau\phi^c_{\mathrm{MF}}+\tfrac{1}{6}g(\phi^c_{\mathrm{MF}})^3=0 \ , \tag{20b}$$

with the boundary condition $\phi^c_{\mathrm{MF}}(\pm\infty)=\pm M^{\mathrm{MF}}$. The solution of (20b) is the well-known kink

$$\phi^c_{\mathrm{MF}}=M^{\mathrm{MF}}\tanh[\sqrt{\tau/2}(z-z_0)] \tag{21}$$

in which, from translational invariance, z_0 is arbitrary. Noting that

$$\Gamma^{\mathrm{MF}}_{\uparrow\downarrow}-\Gamma^{\mathrm{MF}}_{\uparrow\uparrow}=A\int_{-\infty}^{+\infty}dz\left[\frac{1}{2}\left(\frac{d\phi^c}{dz}\right)^2+\frac{1}{4!}g[(\phi^c)^2-(M^{\mathrm{MF}})^2]^2\right] \ , \tag{22}$$

elementary quadratures yield

$$\frac{\sigma^{\mathrm{MF}}}{kT}=\frac{1}{A}(\Gamma_{\uparrow\downarrow}-\Gamma_{\uparrow\uparrow})^{\mathrm{MF}}=\frac{4\sqrt{2}}{g}\tau^{3/2} \ . \tag{23}$$

One-loop corrections (first order in ϵ*).* We have now to include one-loop diagrams and one-loop counterterms. For the counterterms at this order, we note[11] that

$$Z=1,\quad \tilde{Z}=1+\frac{1}{2\epsilon}u,\quad Z_1=1+\frac{3}{2\epsilon}u \ , \tag{24}$$

in which

$$u\equiv gS_d\equiv g\frac{2\pi^{d/2}}{\Gamma(d/2)(2\pi)^d} \ .$$

This gives

$$\frac{\sigma}{kT}=\frac{4\sqrt{2}}{g}\tau^{3/2}+\frac{u}{\epsilon}\int_{-\infty}^{+\infty}dz\left[-\tfrac{1}{4}\tau(\phi^{c2}-M^2)+\frac{g}{16}(\phi^{c4}-M^4)\right]+\frac{1}{2A}\ln\det\left[\frac{-\nabla^2-\tau+g\phi^{c2}}{-\nabla^2-\tau+gM^2/2}\right] \ . \tag{25}$$

Two remarks are in order:

(i) When we expand loopwise the functional $\Gamma\{\phi\}$ up to first order, $\Gamma=\Gamma_{\mathrm{MF}}\{\phi\}+\Gamma_1\{\phi\}$, and solve for the zero-field profile $(\delta\Gamma/\delta\phi)\{\phi^c\}=0$, the solution ϕ^c is also shifted from its mean-field value (21), $\phi^c_{\mathrm{MF}}\rightarrow\phi^c=\phi^c_{\mathrm{MF}}+\phi^c_1$. Therefore we have to consider $\Gamma_{\mathrm{MF}}\{\phi^c\}+\Gamma_1\{\phi^c\}$; however, in the loop expansion, this gets replaced by $\Gamma_{\mathrm{MF}}\{\phi^c_{\mathrm{MF}}\}+\Gamma_1\{\phi^c_{\mathrm{MF}}\}$, since by definition

$$\frac{\delta\Gamma_{\mathrm{MF}}}{\delta\phi}\Big|_{\phi^c_{\mathrm{MF}}}=0 \ .$$

Hence we do not need to compute the change from the mean-field order-parameter profile (21).

(ii) When we expand the field ϕ about the mean-field solution ϕ_{MF}^c [(21)], the Gaussian part of these fluctuations yields a determinant which appears in (25). This determinant has a zero eigenvalue corresponding to the insensitivity of the energy to a change of z_0, the interface location. In principle, we should allow for fluctuations of ϕ only in directions transverse to this mode $(\partial\phi_c/\partial z)$. However, in this problem, we can ignore this zero-mode problem completely because it does not give any singular contribution to (25). Indeed, the lowest eigenvalue of the determinant $\epsilon_0(q_\parallel)=q_\parallel^2$ vanishes when $\vec{q}_\parallel$, the wave vector of the fluctuations of the interface parallel to the z plane, vanishes; however, it gives a contribution to (25) which, for low $q_\parallel$, behaves as $\int d^{d-1}q_\parallel \ln q_\parallel^2$, which is finite.

We now give the main element of the calculation. The determinant which appears in (25) may be easily diagonalized, as far as the direction parallel to the $z=0$ plane are concerned, by Fourier transformation, i.e.,

$$I\equiv\ln\det\left(\frac{-\nabla^2-\tau+g\phi_c^2(z)/2}{-\nabla^2-\tau+gM^2/2}\right)=A\int\frac{d^{d-1}q_\parallel}{(2\pi)^{d-1}}\ln\det\left(\frac{-d^2/dz^2+q_\parallel^2-\tau+3\tau\tanh^2(z\sqrt{\tau}/2)}{-d^2/dz^2+q_\parallel^2-\tau+3\tau}\right)\ , \tag{26}$$

in which we have used explicitly (20) and (21). Using the identity $\tanh^2z\equiv1-1/\cosh^2z$, we now have to consider a one-dimensional Schrödinger operator in the attractive potential $-1/\cosh^2z$. The corresponding Fredholm determinant is known in closed form:[12]

$$\det\left(\frac{-d^2/dz^2-6\omega^2/\cosh^2(\omega z)+\omega^2\rho^2}{-d^2/dz^2+\omega^2\rho^2}\right)=\frac{(\rho-1)(\rho-2)}{(\rho+1)(\rho+2)}\ . \tag{27}$$

We are dealing here with the case $\omega=\sqrt{\tau/2}$,

$$\rho=\left(\frac{2}{\tau}q_\parallel^2+4\right)^{1/2}\ .$$

Therefore we end up with the explicit integral for I:

$$\frac{1}{A}I=\int\frac{d^{d-1}q_\parallel}{(2\pi)^{d-1}}\ln\frac{\left[\left(\frac{2}{\tau}q_\parallel^2+4\right)^{1/2}-2\right]\left[\left(\frac{2}{\tau}q_\parallel^2+4\right)^{1/2}-1\right]}{\left[\left(\frac{2}{\tau}q_\parallel^2+4\right)^{1/2}+2\right]\left[\left(\frac{2}{\tau}q_\parallel^2+4\right)^{1/2}+1\right]}\ . \tag{28}$$

We, therefore, see explicitly in (28) that the zero of the determinant at $q_\parallel=0$ does not prevent the integral to converge for small $q_\parallel$. A tedious, but straightforward, calculation yields

$$\frac{1}{A}I=\tau^{(d-1)/2}S_{d-1}\frac{3\sqrt{2}}{2\epsilon}\left(1+\frac{\epsilon}{2}\ln2-\frac{\pi\sqrt{3}}{18}\epsilon+O(\epsilon^2)\right)\ . \tag{29}$$

The $1/\epsilon$ pole of I/A cancels exactly the $1/\epsilon$ parts given by the counterterms, since elementary quadratures yield

$$\int_{-\infty}^{+\infty}dz\left(-\tfrac14\tau(\phi_c^2-M^2)+\frac{g}{16}(\phi_c^4-M^4)\right)=-\frac{3\sqrt{2}\tau^{3/2}}{g}\ , \tag{30}$$

where we have used

$$\frac{S_{d-1}}{S_d}=4\left(1+\frac{\epsilon}{2}(1-2\ln2)\right)+O(\epsilon^2)\ . \tag{31}$$

Using, in addition,

$$g^*S_d=\tfrac{2}{3}\epsilon+\tfrac{34}{81}\epsilon^2+O(\epsilon^3)\ , \tag{32}$$

we find

$$\frac{\sigma(\tau)}{kT}=\frac{\sigma_0}{kT_c}\tau^{3/2-\epsilon/4}+O(\epsilon^2)\ , \tag{33}$$

with

$$\frac{\sigma_0}{kT_c}=\frac{4\sqrt{2}}{g^*}\left[1+\frac{\epsilon}{4}\left(1-\ln2-\frac{\pi\sqrt{3}}{9}\right)\right]\ . \tag{34}$$

It is eady to verify that $\frac{3}{2}-\epsilon/4=\nu(d-1)+O(\epsilon^2)$.

IV. CORRELATION LENGTH BELOW T_c

The calculation of the correlation function is completely standard.[11] At one-loop order below T_c one obtains for the inverse correlation function at momentum p

$$\Gamma^{(2)}(p)=p^2-\tau\left(1+\frac{u}{2\epsilon}\right)+\frac{gM^2}{2}\left(1+\frac{3u}{2\epsilon}\right)+\frac{g}{2}\int\frac{d^dq}{(2\pi)^d}\frac{1}{(q^2-\tau+gM^2/2)}-\frac{g^2M^2}{2}\int\frac{d^dq/(2\pi)^d}{(q^2-\tau+gM^2/2)[(p+q)^2-\tau+gM^2/2]}$$

$$=p^2-\tau+\tfrac12gM^2+\tfrac14u(\tfrac12gM^2-\tau)\ln(\tfrac12gM^2-\tau)+\tfrac14ugM^2\left(1+\int_0^1dx\ln[p^2x(1-x)-\tau+\tfrac12gM^2]\right)\ . \tag{35}$$

The correlation length is defined by the closest pole of the correlation function in momentum space, namely,

$$\Gamma^{(2)}\left(\frac{i}{\xi}\right)=0\ .$$

This yields

$$\xi(\tau)=\tau^{-1/2-\epsilon/12}\xi_0^-=\xi_0^-\tau^{-\nu}\ , \tag{36}$$

with

$$\xi_0^-=2^{-1/2}\left[1+\epsilon\left(-\tfrac{1}{12}\ln2+\tfrac14-\frac{\pi\sqrt{3}}{12}\right)\right]\ . \tag{37}$$

An elementary calculation, using (37), (34), and (32), and the ϵ expansion of S_d,

$$S_d=\frac{1}{2^{d-1}\pi^{d/2}\Gamma(d/2)}$$

$$=\frac{1}{8\pi^2}\left[1+\epsilon\left(\tfrac12\ln4\pi+\tfrac12-\frac{\gamma}{2}\right)\right]+O(\epsilon^2)\ ,$$

leads to the final result (8).

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