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Equivalence of different definitions of the surface tension

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Recently Brézin and Feng and independently Pant reported renormalization-group calculations of a universal amplitude ratio involving the surface tension, σ, defined as the free-energy difference produced by appropriate boundary conditions. Here we comment on an equivalent result obtained, within the same one-loop framework, using an alternative definition of σ involving the free-energy increment due to a macroscopic distortion of a flat interface.

There has been considerable interest recently in evaluations of universal ratios involving the surface tension near the critical point. Reanalysis by Moldover[1] of the existing experimental data suggests approximately a factor of 2 discrepancy with theoretical calculations of the ratio $U_\sigma = \sigma\xi^{(d-1)}/k_B T_c$, where σ is the surface tension and ξ the (bulk) correlation length. Experimental approaches have involved inelastic light scattering from the interface and capillary rise techniques, while the theoretical investigations have included renormalization-group ϵ expansions[2] and Monte Carlo simulations.[3]

The theoretical calculations noted have focused directly (or indirectly) on the difference between the free energies of the system with an interface and in a homogeneous phase at the same temperature. The experiments, on the other hand, measure something more akin to the response of the flat interface to perturbations which bend or distort it. These two approaches to the surface tension are presumably equivalent,[4] although it is difficult to demonstrate it explicitly. The renormalization-group ϵ-expansion approach presents the opportunity to demonstrate that results are equivalent order by order, and, here, we briefly comment on the lowest-order fluctuation calculation.

The standard surface tension definition arising from the free-energy difference is, essentially,[5]

$$\sigma_1 = [F^{+-}(T) - F^{++}(T)]/A \ , \tag{1}$$

where A is the area of the flat interface at rest and F^{+-}, F^{++} refers to the system's free energies with and without boundary conditions inducing an interface between two coexisting homogeneous phases. ϵ-expansion calculations noted in Ref. 2 have used this definition, as have the Monte Carlo simulations of Ref. 3.

A second definition imagines a system with an interface and asks for the incremental free energy associated with a distortion of the flat interface. This leads to

$$\sigma_2 = \frac{1}{2(d-1)} \int_{-\infty}^{+\infty} dz_1\, dz_2\, M'(z_1) M'(z_2) \times \nabla_q^2 \Gamma^{(2)}[q;z_1,z_2|M(z)]|_{q=0} \ , \tag{2}$$

which is the Triezenberg-Zwanzig formula.[6] A recent derivation has been given by Weeks, Bedeaux, and Zielinska,[7] and further background can be found in the monograph by Rowlinson and Widom.[4] In this formula, $M(z)$ is the exact equilibrium order parameter profile for the system with the flat interface (centered nominally at $z=0$). $\Gamma^{(2)}$ is (in the language of fluids) the direct correlation function *in the inhomogeneous system* [not simply the homogeneous system's direct correlation function with $M(z)$ replacing M_B, the constant value of the bulk order parameter] and is a functional of $M(z)$. More specifically, $\Gamma^{(2)}$ is the matrix inverse of the exact two-point correlation function

$$G(\rho-\rho';z,z') = \langle s(\rho,z)s(\rho',z')\rangle - M(z)M(z') \ , \tag{3}$$

where the position x is decomposed as $x=(\rho,z)$; z is measured in the direction perpendicular to the plane of the interface and there is assumed translational invariance in the $(d-1)$-dimensional ρ space. In Eq. (2), $\Gamma^{(2)}$ has been Fourier transformed with respect to ρ, so that q is the $(d-1)$-dimensional wave vector in the plane of the interface.

For the standard Ginzburg-Landau model defined by the reduced Hamiltonian

$$H = \int d^dx \left\{ \tfrac{1}{2}(\nabla s)^2 + \tfrac{1}{2} r_0 s^2 + \frac{1}{4!} u_0 s^4 \right\} \ , \tag{4}$$

the interfacial profile is known to one-loop order.[8] Using minimal subtraction methods one has

$$M(z) = M_B \tanh\left[\frac{\kappa_R z}{2}\right] \left[1 - \frac{\pi\sqrt{3}}{18}\epsilon\, \mathrm{sech}^2\left[\frac{\kappa_R z}{2}\right] + O(\epsilon^2)\right] \ , \tag{5}$$

where $M_B = \sqrt{3}(2\tau)^\beta/u^{1/2} + O(\epsilon^2)$ is the full bulk order parameter and where

$$\kappa_R = (2\tau)^\nu \left[1 + \frac{1}{4}\left[\frac{\pi\sqrt{3}}{3} - 1\right]\epsilon + O(\epsilon^2)\right] \ , \tag{6}$$

with $\tau = 1 - T/T_c$ and with $\nu = \frac{1}{2} + \epsilon/12 + O(\epsilon^2)$ and $\beta = \frac{1}{2} - \epsilon/6 + O(\epsilon^2)$ the standard correlation length and order parameter exponents. As usual, $u \rightarrow u^* = 2\epsilon/3 + 34\epsilon^2/81 + O(\epsilon^3)$ is the renormalized coupling constant fixed point. Furthermore, the bare inverse correlation function $\Gamma^{(2)}$ is given, to order one loop, by

$$\Gamma^{(2)}[q;z_1,z_2|M(z)] = [q^2 - \partial_{z_1}^2 + r_0 + \tfrac{1}{2}u_0 M^2(z_1) + \tfrac{1}{2}u_0 G_0(x,x)]\delta(z_1-z_2) - \tfrac{1}{2}u_0^2 M_0(z_1) M_0(z_2) \int d^{(d-1)}p\, G_0(q-p;z_1,z_2) G_0(p;z_2,z_1) \ , \tag{7}$$

where

$$G_0(p;z_1,z_2)=\Sigma_\mu \frac{\zeta^{(\mu)}(z_1)\zeta^{(\mu)}(z_2)^*}{p^2+E^{(\mu)}} \quad (8)$$

is the propagator associated with the interface fluctuation operator and related eigenvalue equation[8]

$$[-\partial_z^2+r_0+\tfrac{1}{2}u_0M_0^2(z)]\zeta^{(\mu)}(z)=E^{(\mu)}\zeta^{(\mu)}(z) \ , \quad (9)$$

with $M_0(z)$ the zero-order profile. To zero-loop order (neglecting fluctuations), Eqs. (1) and (2) give

$$\sigma_1=\sigma_2=\sigma^{MF}=k_BT_c\int_{-\infty}^{+\infty}dz\,[M_0'(z)]^2=k_BT_c\frac{4\sqrt{2}}{u}\tau^{3/2}, \quad (10)$$

which yields the van der Waals surface tension exponent $\mu=\frac{3}{2}$. To order one loop, Eq. (2), together with Eqs. (5),(6), and the renormalized version of (7), yield, after a laborious but straightforward calculation,

$$\sigma_2=\sigma_0\tau^\mu \ , \quad (11)$$

with $\mu=(d-1)\nu=\frac{3}{2}-\epsilon/4+O(\epsilon^2)$, and

$$\frac{\sigma_0}{k_BT_c}=\frac{3\sqrt{2}}{4\pi^2\epsilon}\left[1+\left(\tfrac{1}{4}\ln(8\pi^2)+\frac{7\pi\sqrt{3}}{180}-\frac{41}{108}-\frac{1}{2}\gamma+\frac{2\pi}{9}\Gamma\right)\epsilon+O(\epsilon^2)\right] \ . \quad (12)$$

In this result, $\gamma=0.5772\ldots$ is Euler's constant, and, defining

$$I(\mu,\mu')=\int_{-\infty}^{+\infty}dz\,M_0(z)\zeta^{(0)}(z)\zeta^{(\mu)}(z)\zeta^{(\mu')}(z)^* \ , \quad (13)$$

$$\Gamma=\Sigma_{\mu,\mu'}u\frac{|I(\mu,\mu')|^2}{(E^{(\mu)1/2}+E^{(\mu')1/2})^3} \ . \quad (14)$$

Such integrals, $I(\mu,\mu')$, have already been encountered in our previous evaluation of the interface dispersion relation.[9] As above, $M_0(z)$ is the zero-order interfacial profile. Use of Eq. (12) and of the one-loop order bulk correlation length amplitude[10]

$$\xi_0=\frac{1}{\sqrt{2}}\left[1+\left(\frac{1}{4}-\frac{1}{12}\ln 2-\frac{\pi\sqrt{3}}{12}\right)\epsilon+O(\epsilon^2)\right]=\kappa_{R0}^{-1}+O(\epsilon^2) \ , \quad (15)$$

yields the universal ratio,

$$U_\sigma=\frac{\sigma_0\xi_0^{(d-1)}}{k_BT_c}=\frac{3}{8\pi^2\epsilon}\left[1+\left(\frac{10}{27}+\frac{1}{2}\ln(4\pi)-\frac{19\pi\sqrt{3}}{90}-\tfrac{1}{2}\gamma+\frac{2\pi}{9}\Gamma\right)\epsilon+O(\epsilon^2)\right] \ . \quad (16)$$

We have evaluated Γ numerically and found consistency with $\Gamma=9/(4\pi)-3\sqrt{3}/10$. This expression for Γ makes Eq. (16) identical to the result quoted by Brézin and Feng and by Pant in Ref. 2 using the definition of Eq. (1) for the surface tension, as well as Eq. (15) for ξ_0.

We have verified explicitly to $O(\epsilon)$ in the fluctuations within the renormalization-group framework that the two different definitions of the surface tension, Eqs. (1) and (2), lead to the same value of the universal ratio $U_\sigma=\sigma\xi^{(d-1)}/k_BT_c$. This yields a further verification of the equivalence of the two forms of the surface tension[4] and suggests that the discrepancy between theoretical and experimental estimates of U_σ (if it persists) has other origins.

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[10]This amplitude corresponds to the "true" correlation length, i.e., the rate of exponential decay of the pair correlation function.