Amplitude ratios at the extraordinary transition

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The amplitude ratio $Q=K_+/K_-$, for the leading singular terms in the excess free energy above and below the critical temperature at the *extraordinary* transition for the semi-infinite scalar ϕ^4 field theory, is studied using renormalization-group methods in dimension $d=4-\epsilon$. This is expected to be pertinent (at $d=3$) to a binary fluid mixture near its critical end point. We find that $Q\simeq -\sqrt{2}+1.521\epsilon+O(\epsilon^2)$, which is within 0.1% of that obtained from using *local free-energy functionals*. Similar agreement between these two methods is found for another amplitude relation involving the critical adsorption profile.

Consider the common experimental system of binary-fluid mixture held in a sealed container with its liquid phases in coexistence with its vapor phase α. At the *critical end point* for this system, corresponding to the consolute point ($T=T_c$) at liquid-vapor coexistence, the liquid phase becomes critical in the presence of a noncritical *spectator* phase, i.e., the vapor α. This will give rise to a singularity in the liquid-vapor interfacial tension, $\Sigma_\alpha(T)$, of the form[1–3]

$$\Sigma_\alpha(T)\sim\Sigma_0(T)+K_\pm|t|^\mu+\cdots \quad \text{as } T\to T_c\pm\ , \tag{1}$$

where $t=(T-T_c)/T_c$ and $\Sigma_0(T)>0$ is some analytic background term. The exponent μ for the leading singular term is predicted by scaling[2] to be given by $\mu=(d-1)\nu$ for $d\le 4$ and $\mu=\frac{3}{2}$ for $d>4$, where d is the bulk dimension of the system and ν is the usual correlation-length exponent for the critical phase. The critical amplitude ratio $Q\equiv K_+/K_-$ is expected to be universal.[3]

Similar behavior to (1) is also found for a fluid (e.g., single-component liquid-vapor system or, more generally, a system with order-parameter symmetry $n=1$) against a rigid wall near its bulk critical point. In this case $\Sigma_\alpha(T)$ would refer to the wall or *excess* free energy, usually denoted $f_s(T)$ in the literature of surface critical phenomena.[4] It has been suggested that Q for the wall system is identical to that of the previously described situation, so that the noncritical spectator phase may be replaced by an *effective* wall.[3] For fluid systems one usually finds preferential adsorption of one of the ordered phases against the wall (or spectator phase), which implies the presence of a symmetry-breaking field h_1 on the wall. Hence, at $T=T_c$, the bulk would order in the presence of an already ordered surface, and in accordance with accepted belief,[5] such a phase transition would be in the universality class of the *extraordinary* transition, as it is called in the nomenclature of surface critical phenomena.[4]

A recently proposed theory[3] predicted the values of Q for a range of universality classes, including that of the $n=1$ extraordinary transition of interest to this Brief Report. Among the methods used was a theory that introduced a local free-energy functional for the order-parameter profile which was adapted to incorporate nonclassical criticality. It therefore gave Q as a function of d for $2\le d\le 4$.[3(b)] Of course, for $d\ge 4$, Q reduces to its mean-field value $Q=-\sqrt{2}$.[1,3]

The purpose of this Brief Report is to compare predictions of this local-functional theory against those of renormalization-group methods involving an expansion in $\epsilon=4-d$. Results will be presented to $O(\epsilon)$ after a concise sketch of the basic method. Details of the calculation will be presented in a longer publication generalized for the n-vector model.[6]

A field-theoretical description for surface critical phenomena[4] starts from the semi-infinite Landau-Ginzburg-Wilson *effective* Hamiltonian $\mathcal{H}[\phi]$ for a bare scalar field $\phi=\phi(\mathbf{x}_\parallel,z)$, where $\mathbf{x}_\parallel$ is a $(d-1)$-dimensional vector parallel to the wall at $z=0$. The Hamiltonian is given by

$$\mathcal{H}[\phi]=\int_0^\infty dz\int d^{d-1}\mathbf{x}_\parallel\left\{\frac{1}{2}|\nabla\phi|^2+\frac{1}{2}[t_0+c_0\delta(z)]\phi^2+\frac{u_0}{4!}\phi^4-[h_0+h_{1,0}\delta(z)]\phi\right\}. \tag{2}$$

Unrenormalized correlation functions are obtained from functional derivatives of $\ln\int\mathcal{D}\phi\exp(-\mathcal{H}[\phi])$. Divergences in these are removed, as usual, from the reparametrization of the bare field ϕ and the bare parameters $(t_0,c_0,u_0,h_0,h_{1,0})$ in terms of the renormalized field ϕ_R and the renormalized parameters (t,c,u,h,h_1), respectively.[4] The *ordinary* transition occurs at $h=h_1=t=0$ and $c>0$ and is characterized by the bulk and surface ordering at the same temperature $t=0$. The *extraordinary* transition, where the bulk orders against an already ordered surface, occurs at $h=h_1=t=0$ and $c<0$. These transitions are separated by a multicritical point, the *special* transition, at $h=h_1=t=c=0$. Much is already known about ordinary and special transitions.[4] However, mainly because of technical difficulties caused by the presence of a nontrivial order-parameter profile $m(z)=\langle\phi(\mathbf{x}_\parallel,z)\rangle$ for both $t>0$ and $t<0$, considerably less is known about the extraordinary transition.[5,7–14]

As mentioned before, the extraordinary transition is pertinent to fluid systems since, if $h_1 \neq 0$ for any $c < \infty$ (indeed, for fluids one would expect $c > 0$), the leading singular terms in excess quantities would behave as if $h_1 = 0$ with $c < 0$. This can easily be seen at zero-loop (mean-field) order[5] and demonstrated more generally by considering the renormalization-group (RG) flows.[4,6] Henceforth, we shall therefore set $h = h_1 = 0$ with $c < 0$.

The amplitudes $K_\pm$ in (1) are most conveniently obtained from the excess internal energy

$$E_s(T) = \int_0^\infty dz[E(z) - E(\infty)] , \tag{3}$$

where $E(z) = \frac{1}{2}\langle \phi^2(\mathbf{x}_\parallel, z)\rangle$ is the energy density. The renormalized excess internal energy is related to $\Sigma_\alpha(T) \equiv f_s(T)$ through $E_s^R(T) = \partial\Sigma_\alpha/\partial t$, from which we can identify the amplitudes $K_\pm$ from the coefficients of $|t|^{\mu-1}$ in $E_s^R(T)$. In order to obtain $K_\pm$ to $O(\epsilon)$, one applies the *loop expansion*[15,4] to $m(z)$ and $E(z)$. This involves writing $m(z) = m^{[0]}(z) + m^{[1]}(z) + O(\text{2-loop})$ and $E(z) = E^{[0]}(z) + E^{[1]}(z) + O(\text{2-loop})$, where the numbers in the superscripts refer to the order in the loop expansion. When using *dimensional regularization,*[16] the one-loop terms will contain poles in ϵ as $\epsilon \to 0$. These poles are removed by renormalization of the bare quantities. Universal asymptotic behavior then follows from setting the parameters at their infrared-stable RG fixed-point values.

At zero-loop order (mean-field theory), $m^{[0]}(z)$ is determined by $\delta\mathcal{H}/\delta\phi = 0$ for $\phi = m^{[0]}(z)$. The resulting Euler-Lagrange equation, with a boundary condition at $z = 0$ involving $c_0 < 0$, can be solved to yield[17,7]

$$m^{[0]}(z) = 2\left[\frac{3t_0}{u_0}\right]^{1/2} \operatorname{csch}[(z+z_0)t_0^{1/2}] , \tag{4a}$$

for $0 < t_0 < |c_0|^2$, where $\tanh(t_0^{1/2}z_0) = t_0^{1/2}/|c_0|$, and

$$m^{[0]}(z) = \left[\frac{6|t_0|}{u_0}\right]^{1/2} \coth[(z+z_0)(|t_0|/2)^{1/2}] , \tag{4b}$$

for $t_0 < 0$ with

$$\sinh[(2|t_0|)^{1/2}z_0] = (2|t_0|)^{1/2}/|c_0| .$$

Since $E^{[0]}(z) = \frac{1}{2}[m^{[0]}(z)]^2$, the excess internal energy at zero loop, $E_s^{[0]}$, is[11]

$$E_s^{[0]} = \left[\frac{6}{u_0}\right](|c_0| - t_0^{1/2}) , \tag{5a}$$

for $0 < t_0 < |c_0|^2$, and

$$E_s^{[0]} = \frac{3|c_0|}{u_0}\left[1 + \left[1 + \frac{2|t_0|}{c_0^2}\right]^{1/2}\right] - \frac{3\sqrt{2}|t_0|^{1/2}}{u_0} , \tag{5b}$$

for $t_0 < 0$. Note that, even at zero loop, one finds nonanalytic corrections to scaling with leading behavior $\propto |t_0|/|c_0|$.[11] However, the leading singular terms ($\propto |t_0|^{1/2}$) are independent of c_0. Hence (as is generally true of excess quantities[13]), in order to determine the universal asymptotic properties, we can set c_0 at its infrared-stable RG fixed-point value c^* *before* taking $\epsilon \to 0$. Since for the extraordinary transition $c^* \to -\infty$, this will simplify the calculation of $m^{[1]}(z)$ and $E^{[1]}(z)$.

From the standard loop expansion,[15,4] $m^{[1]}(z)$ and $E^{[1]}(z)$ are given by

$$m^{[1]}(z) = -\frac{u_0}{2}\int_0^\infty dz'\, \tilde{G}^{[0]}(p=0;z,z')m^{[0]}(z') \times \int_p \tilde{G}^{[0]}(p,z',z') , \tag{6a}$$

$$E^{[1]}(z) = m^{[0]}(z)m^{[1]}(z) + \tfrac{1}{2}\int_p \tilde{G}^{[0]}(p;z,z) , \tag{6b}$$

where $\int_p \equiv S_{d-1}\int_0^\infty p^{d-2}dp/(2\pi)^{d-1}$, with S_d denoting the surface area of a unit d sphere and $\tilde{G}^{[0]}(p;z,z')$ is the zero-loop propagator Fourier transformed with respect to the $(d-1)$-dimensional $\mathbf{x}_\parallel$ coordinate, which is a Green's function for the Schrödinger equation

$$[-\partial_z^2 + p^2 + t_0 + u_0E^{[0]}(z)]\tilde{G}^{[0]}(p;z,z') = \delta(z-z') , \tag{7}$$

with boundary condition $(\partial_z - c_0)\tilde{G}^{[0]}(p;z,z') = 0$ for $z = 0$ and $z' > 0$. Clearly, $\tilde{G}^{[0]}(p;z,z') = \tilde{G}^{[0]}(p;z',z)$, and Eq. (7) can be solved[9,14] to yield, as $c_0 \to -\infty$ and for $z \geq z'$,

$$\tilde{G}^{[0]}(p;z,z') = \frac{g_0 A_+(p;\tilde{z})e^{-\omega_p\tilde{z}}[A_-(p;\tilde{z}')e^{\omega_p\tilde{z}'} - A_+(p;\tilde{z}')e^{-\omega_p\tilde{z}'}]}{2\omega_p(\omega_p^2-1)(\omega_p^2-4)} , \tag{8a}$$

where

$$A_\pm(p;\tilde{z}) = 3\coth^2\tilde{z} \pm 3\omega_p\coth\tilde{z} + \omega_p^2 - 1 , \tag{8b}$$

with $\tilde{z} = z/g_0$, $\tilde{z}' = z'/g_0$, $\omega_p^2 = g_0^2(t_0^2g_0^2 + p^2)$, and $g_0 = t_0^{-1/2}\,[=(2/|t_0|)^{1/2}]$ for $t_0 > 0$ $[t_0 < 0]$.

In order to calculate $E_s^{[1]}$, Eqs. (8) are substituted into (6) and then (3) and the resulting integrals in z, z', and p are performed. In doing so, one encounters divergent integrals. By using dimensional regularization,[16] these divergencies are isolated as simple poles in ϵ as $\epsilon \to 0$. The poles are then subtracted away by the usual multiplicative renormalizations[15,4]

$$t_0 = \tilde{\mu}^2 Z_t t + t_b, \quad u_0 = \tilde{\mu}^\epsilon 2^d \pi^{d/2} Z_u u , \\ E_s^R = \tilde{\mu}^{\epsilon-1} Z_t E_s , \tag{9}$$

where $\tilde{\mu}$ is the usual arbitrary inverse length scale and, since dimensional regularization is used, $t_b = 0$. Additive renormalization is not required for E_s.[13,18] The factors Z_t and Z_u, which are well known,[15] have the form $Z_i = 1 + a_i u/\epsilon + 0(u^2)$, leading to a pole in $E_s^{R[0]}$, which cancels exactly with the pole in $E_s^{R[1]}$. This then gives an expression for E_s^R valid to one-loop order.[6] Finally, to obtain universal critical properties, u is set at its infrared-stable RG fixed-point value $u^*=\frac{1}{3}\epsilon+O(\epsilon^2)$ for $\epsilon>0$.[15] Since the leading singular term in E_s^R is $\pm\mu K_\pm|t|^{\mu-1}$ as $t\to 0\pm$, with the scaling law $\mu=(d-1)\nu$ now confirmed to $O(\epsilon)$,[6] one immediately obtains the required quantity

$$Q\equiv\frac{K_+}{K_-}=-\sqrt{2}\left[1+\epsilon\left[\frac{1}{4}-\frac{5\pi}{36}-\frac{\pi}{6\sqrt{3}}+\frac{\ln 2}{4}+\frac{\ln(2-\sqrt{3})}{\sqrt{3}}\right]+O(\epsilon^2)\right]$$
$$=-\sqrt{2}+1.521\,257\,378\epsilon+O(\epsilon^2)\ . \qquad (10)$$

In order to compare (10) to results obtained from *local-functional theory,* we now briefly review the method developed by Fisher and Upton.[3,19] One starts by introducing a free-energy functional $\mathcal{F}_s[m]$, for the order-parameter profile $m(z)$, which is assumed to depend on $m(z)$ and $\dot{m}=dm/dz$, but not on higher derivatives. Therefore one writes

$$\mathcal{F}_s[m]=\int_0^\infty dz\,\mathcal{A}(m,\dot{m};T,h)+f_1(m_1;h_1,c)\ , \qquad (11)$$

where $m_1=m(z=0)$ and usually one takes $f_1=-h_1m_1+\frac{1}{2}cm_1^2$. Also, $\mathcal{A}(m_\infty,0)=0$, where $m_\infty=m(z=\infty)$. The equilibrium profile $m(z)$ is that which minimizes $\mathcal{F}_s[m]$ and $\Sigma_\alpha(T,h)=\min_{[m]}\mathcal{F}_s$. The familiar squared-gradient Landau theory corresponds to the choice $\mathcal{A}=\frac{1}{2}A_0\dot{m}^2+V(m)-V(m_\infty)$, where $V(m)=\frac{1}{2}tm^2+(1/4!)um^4-hm$. To go beyond mean-field theory, one chooses forms for $\mathcal{A}$ which incorporate nonclassical bulk critical exponents. Pioneering work in this direction was performed by Fisk and Widom[20] and, later, for $T=T_c$, by Fisher and de Gennes.[21] More recently, Fisher and Upton[3] considered a class of theories where $\mathcal{A}(m,\dot{m})=[1+\mathcal{G}(X)]W(m)$, with $W(m)=W(m;T,h)$ being related to the *bulk* free energy[3(b)] and $\min_m W(m)=0$ reproduces the bulk equation of state [so, clearly, $W(m_\infty)=0$]. The dimensionless quantity $X=X(m,\dot{m};T,h)$ is given by[3(b)] $X=\xi\dot{m}/\sqrt{2\chi W}$, where $\xi=\xi(m;T)$ is the correlation length and $\chi=\chi(m;T)$ the susceptibility of a system with homogeneous magnetization m. From the Euler-Lagrange equations that extremize (11) (and additional conditions to ensure thermodynamic consistency[3]), we find that the surface free energy $\Sigma_\alpha(T,h)$ is given by[3(b),19]

$$\Sigma_\alpha=\int_{m_\infty}^{m_1}dm(2\xi^2W/\chi)^{1/2}+f_1(m_1)\ . \qquad (12)$$

Thus we now have an expression for Σ_α in terms of bulk quantities which are relatively well understood. In particular, we require that W, χ, and ξ be analytic in the single-phase region of the phase diagram and have the appropriate scaling form in the vicinity of the critical point ($T=T_c$, $h=0$). A convenient way of achieving this is to use Schofield's linear parametric model[22] for the (bulk) equation of state. This is known to be consistent with the ϵ expansion to $O(\epsilon^2)$ inclusive.[23] Similar parametric models[24] have been constructed for $\xi(m;T)$ which are also consistent with ϵ expansion.[25] Hence, by substituting parametric model expressions into (12), one can derive an ϵ expansion for Q, which, to $O(\epsilon)$, was found to be[19,26]

$$Q=-\sqrt{2}+1.522\,96_2\epsilon+O(\epsilon^2)\ . \qquad (13)$$

This should be compared with (10).

One can also use these methods to study an amplitude relation involving the magnetization profile $m(z)$ at the critical point (with $h_1\neq 0$) where a phenomenon known as *critical adsorption* occurs.[21,8-10] Here scaling[21] predicts that $m(z)\approx P_c z^{-\beta/\nu}$ as $z\to\infty$ at $T=T_c$ and $h=0$, where β is the usual bulk (spontaneous) magnetization exponent. If, along the critical isotherm ($T=T_c$, $h\neq 0$) we have that $h\approx D|m_\infty|^\delta \mathrm{sgn}(m_\infty)$ and $\xi\approx f_c|h|^{-\nu/\beta\delta}$ (which defines the usual bulk amplitudes D and f_c and the bulk exponent δ), then the amplitude relation $R_P\equiv P_c^{\nu/\beta}D^{\nu/\beta\delta}/f_c$ should be universal. Local-functional methods leading to Eq. (12) predict a particularly simple expression for this, involving only the bulk exponents:

$$R_P=\frac{\beta}{\nu}\left[\frac{\delta(\delta+1)}{2}\right]^{1/2}\ . \qquad (14)$$

Given the known ϵ expansions for the bulk exponents,[15] local-functional theory predicts that $R_P=\sqrt{6}(1-0.208\dot{3}\epsilon)+O(\epsilon^2)$. This should be compared with the results of a field-theoretical calculation[6] [using Eq. (6a) at $t=0$], which gives $R_P=\sqrt{6}(1-0.207\,896\,745\epsilon)+O(\epsilon^2)$.

In conclusion, we have shown that phenomenological local-functional theories are consistent with the ϵ expansion, as derived from field theory, at $O(\epsilon)$ to within about 0.1%. The local-functional theory has the strength that it can be applied with relative ease to any dimension, including the physically interesting $d=3$ case, which was the focus of previous work.[3,19] In contrast, field-theory calculations are extremely difficult to perform beyond $O(\epsilon)$, and results presented here will not give reliable information about $d=3$. Note, in particular, that simply putting $\epsilon=1$ in either (10) or (13) gives $Q\simeq 0.1$, whereas it is believed, largely on the basis of local-functional theory,[3] that $Q\simeq -0.82\pm 0.01$ when $d=3$, with Q being a highly nonlinear function of d. Also, substituting modern estimates for the $d=3$ exponents[27] into (14) gives $R_P\simeq 1.93$. It would be interesting to see how this compares with experiment. However, an important conclusion to be drawn from the results near $d=4$ as presented here is that local-functional theory, as applied to the extraordinary transition, should be quite reliable and probably accurate to within a few percent.

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