Fluid Interface Tensions near Critical End Points

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Novel local free-energy functionals are presented, generalizing the de Gennes–Fisher critical-point ansatz, for obtaining fluid interface tensions near critical end points and critical wall tensions. Nonclassical exponents, proper analyticity in T, etc., are embodied. New "interpolated linear-model" and "trigonometric" parametric equations of state then lead to universal ratio estimates $K_+/K_- \simeq -0.83$, $(K_+ + K_-)/K \simeq 0.1_2$, for the amplitudes K of the critical and $K_\pm$ of the noncritical/wall tensions.

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It has been recently emphasized[1,2] that new critical singularities appear at a *critical end point* beyond those observable at a normal bulk critical point. Furthermore, these singularities should exhibit various universal features that are susceptible to experimental study.[1] An important example of a *nonsymmetric*[1,3] critical end point arises in binary fluid mixtures of small molecules.[4,5] A mixture of components, say B and C, often separates into a B-rich liquid phase, β, which coexists with a C-rich liquid phase, γ. In a sealed container both may coexist with a dilute vapor phase, α. At the critical end point, $T=T_e$, the *spectator* phase, α, remains noncritical, with a finite correlation length, while phases β and γ become critical; above T_e these merge into a single homogeneous liquid phase, $\beta\gamma$. Of particular interest[1,4,5] are the various interfacial tensions observable near T_e. Our purpose here is to outline new theoretical developments which enable one to estimate the singularities in these tensions and various novel universal amplitude ratios, and to report the first numerical results from such calculations. The theory significantly extends earlier work[6] pertaining to order-parameter profiles at criticality in semi-infinite and bounded systems and also describes criticality of wall free energies at the so-called extraordinary surface transition[1,7] (which, however, in the laboratory is more normal than the "ordinary" transition).

The interfacial tensions of concern are $\Sigma_{\alpha|\beta\gamma}(T)$, between phases α and $\beta\gamma$ above T_e, and $\Sigma_{\alpha|\beta}(T)$ and $\Sigma_{\beta|\gamma}(T)$ below T_e. Antonow's rule[4] will apply for the systems of interest, so, using β to label the "middle" phase, the remaining tension satisfies $\Sigma_{\alpha|\gamma}=\Sigma_{\alpha|\beta}+\Sigma_{\beta|\gamma}$. Now, when $t\equiv(T-T_e)/T_e\to 0-$, scaling gives[4]

$$\Sigma_{\beta|\gamma}(T)\approx K|t|^{\mu},\quad \mu=2-\alpha-\nu=2\beta+\gamma-\nu\,, \tag{1}$$

where α, β, γ, and ν denote the standard bulk critical exponents.[8] Following paper **I**,[1] we also have

$$\Delta\Sigma_{\alpha|\beta\gamma}(T),\Delta\Sigma_{\alpha|\beta}(T)\approx K_\pm|t|^{\mu}\,, \tag{2}$$

as $t\to 0\pm$, where the $\Delta\Sigma$ denote deviations from $\Sigma_0(T)>0$, a suitable background term analytic through T_e. The amplitude ratios

$$P=(K_+ + K_-)/K \text{ and } Q=K_+/K_- \tag{3}$$

should then be *universal* and characteristic of a critical end point.[1]

Mean-field theory for a single scalar order parameter, m, which should be valid for dimensions $d>4$, yields[1] $P=-\frac{1}{2}(\sqrt{2}-1)$ and $Q=-\sqrt{2}$. Note the negative signs which do not seem in accord with current data for real systems.[4,9] The evaluation of P and Q for $d=3$ (and, to cross-check theory, for continuous $d\geq 2$) is a major aim of our work. However, few models exhibiting critical end points are amenable to exact analysis even for bulk properties.[10] Renormalization-group $\epsilon=4-d$ expansions are possible in principle, but seem extremely hard to derive for this problem. Furthermore, reasonable accuracy for $d=3$ will require $O(\epsilon^2)$ if not $O(\epsilon^3)$ calculations.[1] Accordingly, we have instead explored generalizations of the classical square-gradient theory for critical interfaces[4] by constructing novel local free-energy functionals, $\mathcal{F}[m]$, which, **A**, embody the correct nonclassical critical exponents; **B**, reflect the properly analytic asymptotically scaled equation of state; **C**, imply a correctly decaying order-parameter profile in a semi-infinite system at criticality; and **D**,**E**, . . . , exhibit various desirable analytic and asymptotic features detailed below.

Pioneering work embodying **A** has been performed by Widom and co-workers[4,5,11] but is not adequate for our purposes. Thus, correction terms in (2) should be of order $|t|^{\mu+1}$ and $|t|^{\mu+\theta}$, where[12] $\theta\simeq 0.54$ for $d=3$; however, Ramos-Gomez and Widom[5] obtain, for reasons we find associated with the failure of **B**, *nonscaling* terms $O(|t|^{\gamma})$ which are surely erroneous and even dominate the scaling terms (2) when $d>3-\eta$.[8]

To construct a suitable $\mathcal{F}[m]$ recall,[1,4,5] first, that a full description of a critical end point requires a thermodynamic space of three fields, (T,g,h), where g is a nonordering field, like the pressure, which varies along the critical line $[h=0,\ T=T_c(g)]$ and carries the system through the end point at $(T_e,g_e,0)$ into the α phase,[1] while h is the ordering field conjugate to m so that $h=0$ specifies the $(\beta+\gamma)$ coexistence surface and its smooth extensions into the α and $\beta\gamma$ phases. Let $\Phi(T,g;h)\equiv F/k_BT$ be the true reduced free-energy density with conjugate $\tilde{\Phi}(m;T,g)$ that is well defined and *must be* analytic in T, g, and m within all single-phase regions.

We follow tradition by assuming, **Y**, that $\tilde{\Phi}(m)$ can be smoothly continued into all "metastable" and "unstable" two-phase and three-phase regions (but see further below). Then a plot of

$$W(m;T,g)=\tilde{\Phi}(m;T,g)-hm-\Phi(T,g;h)\geq 0 \quad (4)$$

vs m has the familiar single-, double-, or triple-well appearance[4,5] with minima $W=0$ at $m=m_\varphi(T,g;h)$, $\varphi=\alpha,\beta,\gamma,\beta\gamma$.

On expanding in $\Delta m=m-m_\varphi$ about any minimum one has

$$W(m)=\tfrac{1}{2}\chi_\varphi^{-1}\Delta m^2+\tfrac{1}{6}v_\varphi\Delta m^3+\tfrac{1}{24}u_\varphi\Delta m^4+\cdots, \quad (5)$$

the subscript denoting evaluation at m_φ of $\chi^{-1}(m;T,g)\equiv\partial^2W/\partial m^2$, the *local* inverse susceptibility, and of $v(m)=\partial^3W/\partial m^3$ and $u(m)=\partial^4W/\partial m^4$. One may regard $u(m)$ as a local, field-theoretic "renormalized coupling constant." We may suppose $m=0$ on the critical line and describe the (β,γ) coexistence curve by $m_0(T,g)\approx B(g)|\tilde{t}|^\beta$, where the nonlinear scaling field satisfies $\tilde{t}\approx t-q(g-g_e)$ with $qT_e=(dT_c/dg)_e$.

Next, we regard the bulk equilibrium correlation length, $\xi(m;T,g)$, as known in each noncritical single-phase state and as associated with the, **E**, exponential decay of the order-order correlation function. The single-phase correlation length varies analytically with m, T, and g and diverges (only) *on* the critical line. We further suppose, **Z**, that $\xi^2(m)/2\chi(m)$ can be continued smoothly as a positive function into all multiphase regions.

Correct nonclassical exponents, **A**, are now embodied in the scaling forms ($h=0$)

$$W\approx|m|^{\delta+1}Y_\pm(y),\quad \xi^2/2\chi\approx|m|^{-\eta\nu/\beta}Z_\pm(Y), \quad (6)$$

where $\pm$ refers to $\tilde{t}\gtrless 0$ and $y=m/m_0(T,g)$. As indicated, it is crucial to recognize, **B**, the analyticity of Φ and ξ. This enforces the asymptotic form

$$Y_\pm(y)\approx\frac{A_\pm|By|^{-\delta-1}}{(2-\alpha)(1-\alpha)}+\sum_{n=0}Y_{\infty,n}(\pm|y|)^{-n/\beta}, \quad (7)$$

as $y\to\infty$, where $A_\pm(g)$ are the specific-heat amplitudes;[1] $Z_\pm(y)$ must vary similarly but with no term in $A_\pm$. To accommodate the spectator phase *properly* (with m_α far from $m_e=0$), correction-to-scaling factors of the form $1+|m|^{\theta/\beta}Y_\pm^{(1)}(y)+\cdots$, etc., must be recognized. However, the quantitative behavior of the correction scaling functions $Y_\pm^{(j)}(y)$, etc., will not affect the leading end-point singularities.

If z measures distances normal to the mean interfacial plane(s) the local functional

$$\mathcal{F}[m(z)]=\int dz[\Phi(T,g;h)+\mathcal{A}(m,\dot{m};T,g,h)], \quad (8)$$

with $\dot{m}\equiv dm/dz$ and $\mathcal{A}(m,0)=W(m)$, reproduces the correct bulk equation of state. One may, further, allow for an *external wall* located, say, at $z=0$, by adding the usual boundary term[7] $f_1(m_1;h_1,T,g)$, in which $h_1>0$ represents a surface field coupled to $m_1\equiv m(z=0)$. We consider this in order to test the *hypothesis* $\mathbf{\Omega}$, introduced in paper **I**, which asserts that *the spectator phase α can be replaced, as $t\to 0$, by a rigid wall, ω.* If $\mathbf{\Omega}$ is valid, one can[1] deduce the exact behavior of the amplitude ratios $P(d)$ and $Q(d)$ at *and* near $d=2$; in addition, the task of ϵ expansion is greatly eased. Furthermore, it is of independent interest to treat various open wall-criticality problems: see, e.g., Refs. 4-7,13.

We now introduce postulates for $\mathcal{A}(m,\dot{m})$ which, we believe, represent significant improvements over previous proposals.[4-6,11] To start, recall the de Gennes-Fisher (dGF) ansatz[6] which applied only *at criticality* ($h=0$, $\tilde{t}=0$) where $W(m)\approx W_c|m|^{\delta+1}$. This featured[6] a locally varying correlation length $\xi[m(z)]\sim|m|^{-\nu/\beta}$ and a new exponent $2-\tilde{\eta}$; it can be written

$$\mathcal{A}(m,\dot{m})=W[1+J\mathcal{G}(\Lambda\dot{m})],\quad \mathcal{G}(-x)=\mathcal{G}(x), \quad (9)$$

with $\Lambda(m)=\xi(m)/m$, so that $x=\Lambda\dot{m}$ is scale free, $\mathcal{G}(x)=|x|^{2-\tilde{\eta}}$, and $J=k_0$, constant.[14] Note that for classical exponents, $\delta=3$, $\beta=\nu=\frac{1}{2}$, and $\tilde{\eta}=0$, the dGF form reduces to[14] $\mathcal{A}=W_cm^4+k_1\dot{m}^2$, which is mean-field theory. More generally, it meets the desiderata **A** and **B** and, in a semi-infinite (critical) system, it yields the decay **C**: $m_c(z)\sim z^{-\beta/\nu}$. Furthermore, for a critical *slab*, bounded between two parallel walls at separation L, it predicts,[6,15] **D**, a correction factor $1+k_2(z/L)^{d^*}+\cdots$ as $L\to\infty$, where[8] $d^*=(2-\alpha)/\nu$ (independently of $\tilde{\eta}$); this result is *not* a direct consequence of scaling. However, it has been verified (along with other predictions) by exact $d=2$ Ising calculations,[16(a)] by renormalization-group analysis[16(b)] ($d=4-\epsilon$), and by conformal covariance theory[16(c)] (general d).

In a finite critical slab with $+-$ (or $++$) boundary conditions the critical profile exhibits a zero (or a minimum)

$$m_c(z)=M_1(z-z_0)^{\lambda_1}[1+M_2(z-z_0)^{\lambda_2}+\cdots], \quad (10)$$

which, on general grounds, should be analytic, so that, **F**(**i**), $\lambda_1=1$ for a zero and $\lambda_1=0$ for a minimum, with, (**ii**), $\lambda_2=2$, $\lambda_4=4,\ldots$. Now **F**(**i**) is satisfied only if[14]

$$\tilde{\eta}=2\eta/(d^*+\eta), \quad (11)$$

which we will assume henceforth. Note, as previously unremarked, that $\mathcal{A}$ then reduces simply to[14] $W_c|m|^{\delta+1}+k_3|\dot{m}|^{2-\tilde{\eta}}$. However, the dGF ansatz does *not* (in general)[15] satisfy **F**(**ii**) which is a defect [even though $\lambda_1=0$ leads to $(\lambda_2-2)/\lambda_2=\eta/d^*$ which is small].

To *extend* the dGF ansatz *away* from criticality it is natural to simply replace W and ξ by their noncritical forms [as in (6)]. But one then finds that condition **E**, exponential decay, is violated! Instead, we introduce the "EdGF ansatz" via

$$J=1,\quad \Lambda^2(m;T,g,h)=\xi^2(m)/2\chi(m)W(m), \quad (12)$$

where T, g, and h are to be understood on the right-hand side, and we also require

$$\hat{\mathcal{G}}(1)=1 \text{ with } \hat{\mathcal{G}}(x)=x\,d\mathcal{G}/dx-\mathcal{G}(x)\,, \qquad (13)$$

$$\mathcal{G}(x)=G_0+G_\infty x^{2-\bar{\eta}}(1+j_1x^{-\tau}+j_2x^{-2\tau}+\cdots) \qquad (14)$$

as $x\to\infty$, where $\tau=2\beta/(\beta+\nu)$. In addition, one should demand, in accord with standard phenomenology,[4] that, **G**, *away* from criticality $\mathcal{A}(m,\dot{m})$ should have an expansion in powers of $\dot{m}^2$. Accordingly we suppose that

$$\mathcal{G}(x)=x^2+G_2x^4+G_4x^6+\cdots,\ \text{as } x\to 0\,. \qquad (15)$$

The resulting EdGF functional satisfies *all* of **A** to **G**. Clearly, the choice of $\mathcal{G}(x)$ satisfying (13)–(15) requires further discussion.[17] Remarkably, however, for an infinite or semi-infinite system, as needed for the end-point and wall problems, the wall/interfacial free energy is *independent* of the details of $\mathcal{G}$, being[17]

$$\Sigma/k_BT=\mathcal{G}_+\int_{m_\varphi}^{m_\psi}dm\,W(m)\Lambda(m)+f_1(m_1)\,, \qquad (16)$$

where $m_\varphi=m(z\to\infty)<m_\psi=m_1$ if there is a wall; otherwise $f_1\equiv 0$ and $m_\psi=m(z\to-\infty)$. The constant $\mathcal{G}_+\equiv 1+\mathcal{G}(1)$ cancels out of the ratios P and Q. Furthermore, the requirement of, **H**, thermodynamic consistency, with $\int_0^\infty[m(z)-m_\varphi]dz=-\partial\Sigma/\partial h$, requires, for the EdGF ansatz, the *extra* condition $\mathcal{G}(1)=1$ so that $\mathcal{G}_+=2$.

Now, on the basis of this EdGF functional we have (i) verified the forms (1) and (2) with the *expected* corrections—because of (7), Ramos-Gomez and Widom's[5] anomalous $|t|^\gamma$ term does *not* arise; (ii) established the *wall-equivalence hypothesis,* **Ω**, rather generally—this reinforces the discussions in paper **I**; (iii) shown that the *extra* term $K_lt^\mu\ln|t|$ appears in (2) whenever μ is an integer—this is confirmed by exact results for $d=2$ Ising models;[1] and (iv) estimated $P(d)$ and $Q(d)$ numerically, as described below.

Although *not* encountered in the wall or end-point problems, a defect of the EdGF ansatz appears under $+-$ boundary conditions in a *noncritical,* single-phase slab: A zero of $\Delta m(z)$ is *not* perfectly represented. Because of the factor W in (12), the analog of λ_1 in (10) is $1-\eta/(d^*+\eta)$ rather than precisely unity.

The following "generalized de Gennes–Fisher postulate" still satisfies **A–H** but is free of this blemish, generating, **J**, analytic profiles $m(z;T,g,h;L)$ in *all* noncritical regimes. To specify this GdGF ansatz, recall the "renormalized coupling constant" $u(m;T,g,h)$ introduced via (5), drop (13), and replace (12) by

$$J(m)=1/u(m)\chi^2(m)W(m),\quad \Lambda^2(m)=\tfrac{1}{2}u\chi\xi^2\,, \qquad (17)$$

while adding a term $G_l\ln|x|$ to (14) with $G_l=G_0+(\delta-1)(\delta-2)/\delta(\delta+1)$. A novel feature is that when $u\to 0$ the theory reduces to the Gaussian form in accord with renormalization-group precepts. The profile and interfacial/wall free energy are again given by quadratures, over $\xi(m)$, $u(m)$, $\chi(m)$, and $W(m)$, but the inverse of $\hat{\mathcal{G}}(x)$ now enters explicitly. One may devise[17] representations satisfying (14) and (15), but we have not, as yet, explored the GdGF ansatz quantitatively.

Of course, neither this nor the EdGF ansatz allow explicitly for *capillary waves* on a free interface which enter for $d\le 3$ and must affect the tails of the profile $m(z)$; and both entail the extensions, **Y** and **Z**, into the multiphase regions which probably have no strict statistical-mechanical meaning. It seems possible, nevertheless, that local formulations such as these, which embody many correct features, may, when judiciously fitted to exact results near $d=2$ and 4, yield reliable estimates for surface tensions and for constrained interface problems. To decide that issue requires quantitative studies to which we now turn.

For *numerical* purposes all exponents may be regarded as accurately known for $d\ge 2$. To ensure **B** a *parametric* representation of the scaling functions $Y_\pm$ and $Z_\pm$ is optimal: One introduces "polar" coordinates (r,θ) centered on the critical point $(t,h,m)=(0,0,0)$ and writes the equation of state as[18]

$$t=r\tilde{k}(\theta),\quad h=r^{\beta\delta}\tilde{l}(\theta),\quad m=r^\beta\tilde{m}(\theta)\,. \qquad (18)$$

Representations of $\chi(m)$ and $u(m)$ follow directly; $W(m)$ can be obtained by a quadrature. The Schofield-Litster-Ho linear model[18] sets $\tilde{m}=\tilde{m}_0\theta$, $\tilde{l}=\tilde{l}_0\theta(1-\theta^2)$, and $\tilde{k}=1-b^2\theta^2$; it proves exact to $O(\epsilon^2)$ and, with modern amplitude estimates,[19] works reasonably (in single-phase regions) even for $d\simeq 3$. Nevertheless, it does fail at $O(\epsilon^3)$ and current data warrant an improved form. For $Z_\pm$, series data[19] for $d=3$ and an $O(\epsilon)$ calculation[20] provide an adequate first parametric representation.

However, the two-phase region, needed to compute K in (1), requires special consideration since analytic continuation of linear-model (m,h) isotherms always fails *inside* the coexistence curve; usually, h becomes complex for $|m|<m^*<m_0$. To sidestep this, we have (a) explored some conceptually straightforward but somewhat *ad hoc,* polynomially *interpolated linear models:* We let $\bar{\theta}$ ($|\bar{\theta}|\le 1$) describe the interior of the coexistence curve where, by **Y**, we expect van der Waals "loops." Then we choose low-order polynomials $\bar{k}(\bar{\theta}),\bar{m}(\bar{\theta})$, continuous with $k(\theta)$ and $m(\theta)$ at $\theta=\bar{\theta}=\pm 1$. Finally, $\bar{l}(\bar{\theta})$ is an odd polynomial chosen so that $N=1,2,\ldots$ derivatives of the equation of state are continuous through the phase boundary. Reduction to mean-field theory (for all b) whenever $\beta=\frac{1}{2},\delta=3$ is embodied.[21] Beyond the choice of $\bar{k}$, $\bar{m}$, and N, no further data are required; however, the $(M\ge N+1)$th derivatives are discontinuous and increasing N must lead to unsatisfactory behavior.

To do better we have devised (b) *trigonometric models* in which θ is periodic. Putting $\sigma(\theta)\equiv(2/q)\sin\frac{1}{2}q\theta$,

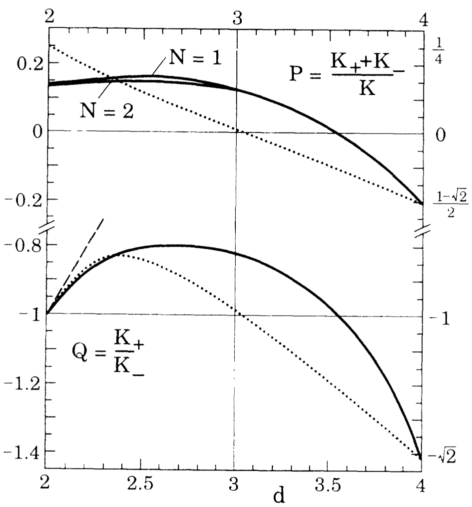

FIG. 1. Universal amplitude ratios for interfacial tensions near critical end points vs d: See text for details.

one can write

$$\tilde{k}(\theta)=1-b^2\sigma^2(\theta),\quad \tilde{m}(\theta)=\tfrac{1}{2}\tilde{m}_0\sigma(2\theta)\,, \tag{19}$$

$$j(\theta)\equiv\tilde{l}/\tilde{m}=j_0[1-b^2\sigma^2(\theta)+c\sigma^2(2\theta)]\,, \tag{20}$$

with $q,c>0$. On using classical exponents $\beta=\frac{1}{2}$, $\delta=3$, this reduces to mean-field theory (for all b,c,q).[21] On letting $q\to 0$ the linear model is reproduced (provided $c<\frac{1}{4}b^2$); taking $q=o(\epsilon)$, this yields exact results to $O(\epsilon^2)$. On the other hand, the extra parameters c and q allow[17] more precise representations beyond $O(\epsilon^2)$ and for $d=2$ and 3. Finally, the trigonometric models *automatically* generate the desired, analytically continued van der Waals loops.

Exploration of these parametric representations is underway[17] but here we report our first calculations of the end-point amplitude ratios based on (i) the EdGF functional combined with (ii) the linear model, using the Schofield-Litster-Ho choice[18] $b^2=(\gamma-2\beta)/\gamma(1-2\beta)$, and (iii) the interpolated linear model with $N=1$ and 2. Exponents versus d are matched to exact $d=2$ results, modern $d=3$ estimates,[19] $\gamma=1.2395$ and $\nu=0.632$, and $O(\epsilon^3)$ results. Figure 1 shows a plot of $P(d)$ and $Q(d)$; the dotted curves indicate the leading-order approximants derived in paper **I**. Note that $P_2\equiv P(d=2)=\frac{1}{4}$ is exact.[1] The dashed line depicts the exact gradient[1] $Q_2'\equiv(dQ/d\mu)_{d=2}=\pi$. Our calculations yield $P_2\simeq 0.14$ and $Q_2'\simeq 2.77$ but such discrepancies are to be expected since the linear model is known to be poor for $d=2$. However, near $d=3$ where $Q\simeq -0.823$, the accuracy should be better. Indeed, for $d=3$ we have also fitted b and the correlation-length parameters *directly* to recent amplitude estimates[15] and find $Q\simeq -0.83$, $P\simeq 0.1_2$, and thus expect Fig. 1 to be accurate to within a few percent for $d\gtrsim 2.7$. Further work[17] should check this.

In summary, we have presented two novel free-energy functionals for near-critical fluids which embody many desirable features not realized previously. In combination with new parametric representations of the critical equation of state, including the interior of the two-phase region, these yield quantitative estimates for universal amplitude ratios describing fluid interfacial tensions near a critical end point and the extraordinary surface transition.

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