# Surface Amplitude Ratios near a Critical End Point

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We provide the first experimental test of the universality of a *surface amplitude ratio* near a critical end point by measuring the modified critical adsorption amplitude ratio, $R_{MA}$, for the liquid mixtures aniline+cyclohexane and isobutyric acid+water. Our results thus far support the universality hypothesis with $R_{MA}=1.3\pm0.1$. The universality of $R_{MA}$ would imply that the surface tension amplitude ratio $Q$ is universal in agreement with the predictions of Fisher and Upton; however, a precise connection relating $R_{MA}$ to $Q$ is not currently available.

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Recently there has been increasing interest in the calculation of universal amplitude ratios *at surfaces* in either confined geometries [1] or near critical end points [2]. Of particular interest to us are the predictions of Fisher and Upton [2] who extended some earlier ideas of Ramos-Gomez and Widom [3]. The noncritical liquid/vapor surface tension of a critical binary liquid mixture is predicted to behave as

$$\sigma_\pm=\sigma_c+At+K_\pm t^\mu . \tag{1}$$

The subscripts + and − refer respectively to quantities either above or below the critical temperature $T_c$, $t=|T-T_c|/T_c$ is the reduced temperature, while $\mu$ is the exponent which characterizes the critical surface tension. The surface tensions $\sigma_+$ and $\sigma_-$ remain nonzero and finite as the bulk liquid traverses a second-order phase transition; they have a continuous first derivative and a common value of $\sigma_c$ at $T_c$. The term linear in $t$ is the noncritical contribution to the surface tension while the critical contribution, with $t^\mu$ dependence, originates from the fact that Antonow's rule holds not only at $T_c$ but also in the vicinity of $T_c$. Fisher and Upton [2] predict that the surface amplitude ratio $Q=K_+/K_-$ should be universal with a value of −0.82 for a critical binary liquid mixture. This prediction for the value of $Q$ was based upon the "extended-de Gennes–Fisher ansatz" [2] which sufficiently far from criticality takes the expected form [4] for the excess surface free energy density,

$$\psi=W(m)+\tfrac{1}{2}A\left(\frac{dm}{dz}\right)^2,\quad A=\frac{\xi^2}{\chi}\sim|m|^{-\eta\nu/\beta}, \tag{2}$$

with a local excess potential $W(m)$, plus a squared-gradient term in the order parameter $m$. Here $\xi$ is the bulk correlation length and $\chi$ is the bulk susceptibility while $\eta$, $\nu$, and $\beta$ are the usual critical exponents.

The critical contribution to the noncritical surface tension in (1) is very difficult to determine above the large noncritical background and despite very precise surface tension measurements [5] remains unconfirmed near an "ordinary" critical end point. In the recent very accurate measurements of Pegg *et al.* [6] the essential form of (1) was confirmed *in the vicinity* of a tricritical point where the surface tension $\sigma_c$ is much smaller; their measurements are consistent with a negative value for $Q$, however, its magnitude was not determined.

Another surface amplitude ratio which is expected to be universal, and which should be related to $Q$, is the ratio of the amplitudes of the critical adsorption above and below $T_c$, which we denote by $R_A=m_{0+}/m_{0-}$. This follows from the van der Waals relation between the surface tension and the order-parameter profile, $m(z)$ [4],

$$\sigma=\int A\left(\frac{dm(z)}{dz}\right)^2 dz . \tag{3}$$

In this paper we present the first experimental test of the universality of a surface amplitude ratio near a critical end point by measuring the modified critical adsorption amplitude ratio $R_{MA}$ using ellipsometry. $R_{MA}$ is related to $R_A$ via the equation $R_{MA}=R_AU$, where $U$ is a universal multiplicative constant, $U=\int P_+(x)dx/\int P_-(x)dx$, and $P_\pm(x)$ is the surface scaling function defined below in Eq. (4). $R_{MA}$ has not yet been calculated theoretically; it can undoubtedly be calculated from the theory of Fisher and Upton [2,7]. At the conclusion of this paper we discuss the connection between the amplitude ratios $R_A$ and $Q$.

Fisher and de Gennes [8] proposed that the critical adsorption profile at a critical end point varies as

$$m_\pm(z)=m_{\text{bulk}}+m_{0\pm}t^\beta P_\pm(z/\xi_\pm),\quad z\geq 0 . \tag{4}$$

Here $P(x)$ is a surface scaling function where $P(x)\sim e^{-x}$ as $x\to\infty$ and $P(x)\sim x^{-\beta/\nu}$ as $x\to 0$; $P(x)$ has a different form above and below $T_c$ as indicated by the + and − subscripts.

Liu and Fisher [9] have proposed and tested several scaling functions in the one-phase region. We will consider the exponential Padé model with

$$P(x)=\left(\frac{1+c(1-e^{-x})}{1-e^{-x}}\right)^{\beta/\nu}e^{-x} \tag{5}$$

in this paper. The crossover from algebraic to exponential decay is tuned by the value of the parameter $c$.

Critical adsorption near a critical end point has been studied extensively using a variety of experimental probes [10], the exponential decay of the scaling function has been verified beyond doubt [9,11], and there is evidence of the power-law behavior for small $x$ [9,11]. Phase-modulated ellipsometry [12] is a particularly effective method for probing the order-parameter profile; a procedure established by Beaglehole [13] is to monitor the ellipticity at the Brewster angle where for thin profiles (compared with the wavelength of light, λ) the signal is described by the Drude equation [14]

$$\bar{\rho} = \mathrm{Im}(r_p/r_s)|_{\theta_B} = \frac{\pi}{\lambda}\frac{(\varepsilon_v+\varepsilon_L)^{1/2}}{\varepsilon_v-\varepsilon_L}\int\frac{[\varepsilon(z)-\varepsilon_L][\varepsilon(z)-\varepsilon_v]}{\varepsilon(z)}dz\,, \quad (6)$$

where $\varepsilon(z)$ is the dielectric profile which varies from $\varepsilon_v$, the vapor dielectric constant, to $\varepsilon_L$, the bulk liquid dielectric constant. For thicker profiles Maxwell's equations have to be solved numerically for the $p$-wave ($r_p$) and $s$-wave ($r_s$) complex reflection amplitudes [9,15]. We will assume, as have Liu and Fisher [9], that the dielectric profile $\varepsilon(z)$ is directly proportional to the order-parameter profile $m(z)$.

For critical liquid mixtures, in which the less dense pure liquid has the lower liquid/vapor surface tension, critical adsorption will occur both above and below $T_c$ without the presence of an interfering wetting layer in the two-phase region. We have chosen to study the critical mixtures aniline+cyclohexane [16] (AC) and isobutyric acid+water (IW) because they have convenient critical temperatures (~30 °C) which readily allow measurements over many decades in reduced temperature in both the one- and two-phase regions. The ellipsometer was a conventional phase-modulated ellipsometer based upon the design of Beaglehole [13] and incorporating a high stability birefringence modulator [17]. Our measurement procedure typically consisted of waiting from 2 to 6 h after thermal equilibrium had been established and then collecting twenty measurements over the succeeding 2 h. Data which showed any systematic trends or excessive noise in either $T$ or $\bar{\rho}$ were omitted. The longer wait periods were used close to $T_c$. Occasionally the sample was shaken to ensure that the same results were obtained with and without mixing. The temperature stability during the 2-h measurement period was ±0.5 mK while the variation in $\bar{\rho}$ was $\pm 2\times 10^{-5}$. However, a more realistic estimate of the error in $\bar{\rho}$, as determined from the reproducibility of the measurements, is $\pm 5\times 10^{-5}$. This value has been used in the calculations below. During the month over which measurements were collected the critical temperature for AC drifted down by 3 mK from an initial value of 29.760±0.001 °C while for IW the critical temperature was determined to be 26.025±0.005 °C.

Far from the critical temperature the Drude equation (6) holds where $\varepsilon(z) \approx \varepsilon_L - \Delta\varepsilon(z)$, $z > 0$, and $\Delta\varepsilon(z) = Cm_0 t^{\beta} P(z/\xi)$ is a small perturbation compared with $\varepsilon_L - \varepsilon_v$; the proportionality constant $C$ is expected to depend upon the optical contrast of the two liquid components. Therefore,

$$\bar{\rho} \approx \bar{\rho}_{\mathrm{BG}} + \frac{\pi}{\lambda}\frac{(1+\varepsilon_L)^{1/2}}{\varepsilon_L} Cm_0\xi_0 t^{\beta-\nu}\int_0^{\infty} P(x)\,dx\,, \quad (7)$$

where $\bar{\rho}_{\mathrm{BG}}$ is a noncritical background (due to the noncritical correlation length $\xi_{\mathrm{NC}}$ in the vapor), which is expected to be reasonably temperature independent [9], and the integral over $P(x)$ is a constant universal number. In this approximation $\bar{\rho}$ is proportional to the excess adsorption $\Gamma = \int [m(z) - m_{\mathrm{bulk}}]dz \sim t^{\beta-\nu}$. A plot of $\log\bar{\rho}$ against $\log t$ should have a slope of $\beta - \nu \sim -0.3$ provided the background term is small and provided the approximation used in deriving (7) is valid. For the AC data [Fig. 1(a)], sufficiently far from $T_c$, we obtain a slope of $\sim -0.3$ in both the one- and two-phase regions; the

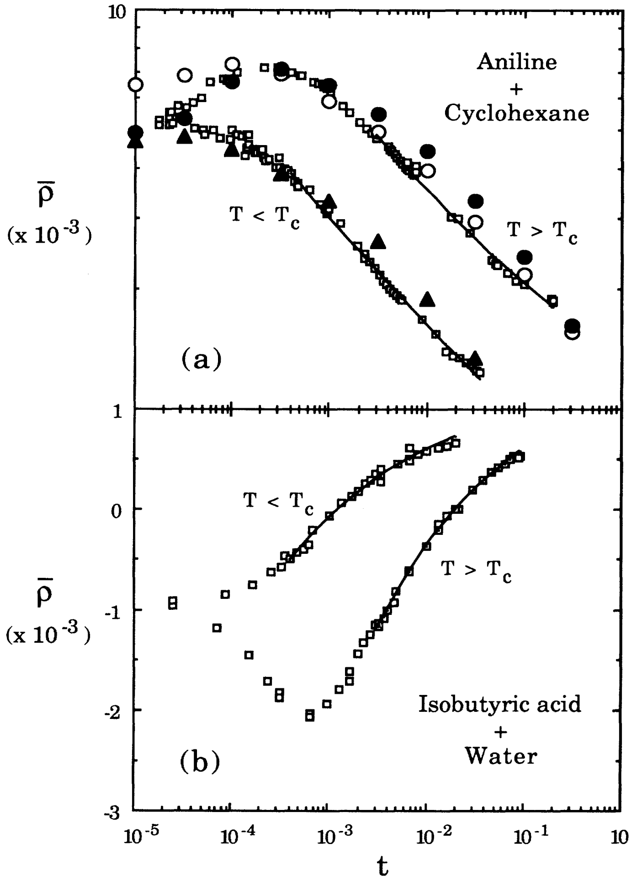

FIG. 1. Ellipsometric measurements at the noncritical interface of the critical binary liquid mixtures (a) aniline+cyclohexane and (b) isobutyric acid+water. Experimental data (open squares). Exponential Padé model for $T > T_c$: $Cm_0 = 0.4$, $c = 0.7$ (open circles) and $Cm_0 = 0.3$, $c = 5.0$ (solid circles); and for $T < T_c$: $Cm_0 = 0.3$, $c = 0.7$ (solid triangles). Nonlinear least-squares fit by Eq. (7) (solid line)—see text for details.

slight curvature in the data is due to the background term $\bar{\rho}_{\text{BG}}$ and the temperature dependence of $\varepsilon_L$. In Fig. 1(b) we plot the IW data on a log-linear graph. This mixture is almost index matched, hence the magnitude of the $\bar{\rho}$ change is smaller. The change in sign of $\bar{\rho}$ can be understood from (6). Water is depleted from the surface region on approaching $T_c$; the critical portion of the dielectric profile (where $\varepsilon > \varepsilon_v, \varepsilon_L$) dominates the profile making $\bar{\rho}$ negative. The amplitudes $m_{0+}$ and $m_{0-}$ have been determined using two independent methods.

*Method 1.*—Far from $T_c$ we have fitted Eq. (7) to the data using a nonlinear least-squares fit. The results are listed in Table I with $\beta - \nu$ either fixed at the theoretical value of $-0.304$ (Ref. [18]) or used as an adjustable parameter. For the AC data we have chosen $\xi_{0+} = 0.23$ nm [19,20], $\xi_{0+}/\xi_{0-} = 1.96$ (Ref. [21]), and used the refractive-index data analysis of Beysens, Bourgou, and Calmettes [19]. (In the two-phase region, where $\varepsilon_L \sim t^{\beta}$, the volume-fraction data analysis of Beysens, Bourgou, and Calmettes was converted to the temperature-dependent dielectric constant using the Lorenz-Lorentz relation [22].) The experimentally determined values for $\beta - \nu$ in both the one- and two-phase regions (Table I) are in excellent agreement with the theoretical value of $-0.304 \pm 0.005$; this good agreement indicates that the corrections to scaling are small and that the critical adsorption profile has precisely the form given in (4). In analyzing the IW data we have used $\xi_{0+} = 0.363$ nm [19] and the refractive-index data from Ref. [23]. With $\beta - \nu$ fixed at the theoretical value we obtain for the modified adsorption amplitude ratio $R_{MA}$ a value of $1.27 \pm 0.07$ for AC and $1.45 \pm 0.20$ for IW. These values are in agreement within experimental error thus supporting the universality hypothesis for $R_{MA}$. The solid lines in Figs. 1(a) and 1(b) indicate the least-squares fit to the data (open squares) with $\beta - \nu$ fixed at $-0.304$ and with $Cm_0 \int P(x)dx$ and $\bar{\rho}_{\text{BG}}$ given in Table I.

*Method 2.*—The second method for determining $m_0$ is to calculate $\bar{\rho}$ by numerically integrating Maxwell's equations using the scaling function suggested by Liu and Fisher (5) assuming that the dielectric constant is directly proportional to the order parameter. We have taken account of the noncritical liquid/vapor correlation length $\xi_{\text{NC}}$ by splicing the adsorption profile smoothly (in both value and slope) to a hyperbolic tangent function as described by Liu and Fisher [9]. The exponential Padé scaling function (5) has been fitted to the AC data with $\xi_{\text{NC}} = 0.2$ nm. This function qualitatively describes the data over the whole temperature range. The circles and triangles in Fig. 1(a) indicate the fit to the experimental data for various values of $Cm_0$ and $c$. There is considerable variation in the value of $Cm_0$ determined using this method. We expect that method 1 will give the more accurate value for $Cm_0$ because it only assumes that the adsorption profile has the form specified in (4) without assuming a particular model for $P(x)$.

The universality of $R_A$ is related to the universality of $Q$ via Eq. (3). Unfortunately Eq. (4) for the critical adsorption cannot be merely substituted into (3) in order to find a direct connection between $R_A$ and $Q$. The reason is, to quote Fisher and Upton [7], Eq. (4) is an asymptotic scaling law correct for large $z$ and small $t$ ($z \to \infty$, $t \to 0\pm$) while the integral for the surface tension (3) covers the whole $z$ range ($z \geq 0$) at fixed $t$. Such a substitution would lead to a positive value for $Q$ whereas Fisher and Upton [7] and Pegg *et al.* [6] obtain a negative value. Thus, at present the amplitude ratio $R_{MA}$ which is measured experimentally cannot be directly compared with the surface tension amplitude ratio $Q$ calculated by Fisher and Upton.

In conclusion, our results support the universality of the modified adsorption amplitude ratio $R_{MA}$ with a value of $\sim 1.3 \pm 0.1$. By implication the surface tension amplitude ratio $Q$ is expected to be universal as predicted by Fisher and Upton [2]. We are planning further experiments on liquids mixtures with greater optical contrast than IW in order to provide a more stringent test of universality. There still remain some unresolved theoretical questions, namely, the value of $R_{MA}$ and the interrelationship between $R_A$ and $Q$.

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TABLE I. Nonlinear least-squares fit to ellipsometric data far from $T_c$. (Quoted errors are 3 standard deviations.)

| | | Reduced temperature range | $10^{-3}\bar{\rho}_{\text{BG}}$ | $Cm_0\int P(x)dx$ | $\beta-\nu$ | Reduced $\chi^2$ |
|---|---|---|---|---|---|---|
| Aniline + cyclohexane | One-phase region | $t > 0.003$ | $0.56 \pm 0.09$ | $0.79 \pm 0.02$ | $-0.304$ (fixed) | 1.3 |
| | | $t > 0.003$ | $0.5 \pm 0.2$ | $0.9 \pm 0.2$ | $-0.30 \pm 0.02$ | 1.5 |
| | Two-phase region | $t > 0.0004$ | $0.20 \pm 0.07$ | $0.62 \pm 0.02$ | $-0.304$ (fixed) | 1.1 |
| | | $t > 0.0004$ | $0.1 \pm 0.4$ | $0.7 \pm 0.3$ | $-0.29 \pm 0.05$ | 1.1 |
| Isobutyric acid + water | One-phase region | $t > 0.003$ | $1.57 \pm 0.09$ | $-0.29 \pm 0.02$ | $-0.304$ (fixed) | 0.2 |
| | Two-phase region | $t > 0.0004$ | $1.26 \pm 0.09$ | $-0.20 \pm 0.02$ | $-0.304$ (fixed) | 0.7 |

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[1] J. L. Cardy, Phys. Rev. Lett. **65**, 1443 (1990); M. Krech and S. Dietrich, Phys. Rev. Lett. **66**, 345 (1991).
[2] M. E. Fisher and P. J. Upton, Phys. Rev. Lett. **65**, 2402 (1990); **65**, 3405 (1990).
[3] F. Ramos-Gomez and B. Widom, Phys. Rev. B **27**, 180 (1983); B. Widom, Chem. Soc. Rev. **14**, 121 (1985).
[4] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford Univ. Press, London, 1982), Chap. 3.
[5] N. Nagarajan, W. W. Webb, and B. Widom, J. Chem. Phys. **77**, 5771 (1982); I. L. Pegg, Ph.D. thesis, Department of Chemistry, University of Sheffield, 1982 (unpublished).
[6] I. L. Pegg, M. C. Goh, R. L. Scott, and C. M. Knobler, Phys. Rev. Lett. **55**, 2320 (1985).
[7] M. E. Fisher and P. J. Upton (private communication).
[8] M. E. Fisher and P.-G. de Gennes, C. R. Acad. Sci. Paris B **287**, 207 (1978).
[9] A. J. Liu and M. E. Fisher, Phys. Rev. A **40**, 7202 (1989).
[10] See S. Dietrich, in *Phase Transitions and Critical Phenomena,* edited by C. Domb and J. Lebowitz (Academic, London, 1987), Vol. 12, Sec. IX B.
[11] J. W. Schmidt, Phys. Rev. A **41**, 885 (1990); M. Schlossman, X.-L. Wu, and C. Franck, Phys. Rev. B **31**, 1478 (1985); R. Sussmann and G. H. Findenegg, Physica (Amsterdam) **156A**, 114 (1989).
[12] D. Beaglehole, in *Fluid Interfacial Phenomena,* edited by C. A. Croxton (Wiley, New York, 1986).
[13] D. Beaglehole, Physica (Amsterdam) **100B**, 163 (1980).
[14] P. Drude, *The Theory of Optics* (Dover, New York, 1959).
[15] M. Born and E. Wolf, *Principles of Optics* (Pergamon, Oxford, 1980), Sec. 1.6; B. M. Law and D. Beaglehole, J. Phys. D **14**, 115 (1981); B. M. Law, Ph.D. thesis, Department of Physics, Victoria University of Wellington, New Zealand, 1985 (unpublished).
[16] This mixture has been studied previously by D. Beaglehole [J. Chem. Phys. **73**, 3366 (1980)]. Our results differ significantly from Beaglehole's; we attribute this difference to his procedure of continuous cooling while collecting data.
[17] Beaglehole Edgar Instruments, 22 Messines Road, Wellington, New Zealand.
[18] M. E. Fisher and J.-H. Chen, J. Phys. (Paris) **46**, 1645 (1985).
[19] D. Beysens, A. Bourgou, and P. Calmettes, Phys. Rev. A **26**, 3589 (1982).
[20] P. Calmettes, I. Lagues, and C. Laj, Phys. Rev. Lett. **28**, 478 (1972).
[21] E. Brezin, J. C. Le Guillou, and J. Zinn-Justin, Phys. Lett. **47A**, 285 (1974); H. B. Tarko and M. E. Fisher, Phys. Rev. Lett. **31**, 926 (1973); A. J. Liu and M. E. Fisher, Physica (Amsterdam) **156A**, 35 (1989).
[22] See, for example, R. F. Kayser, Phys. Rev. B **34**, 3254 (1986).
[23] W. V. Andrew, T. B. K. Khoo, and D. T. Jacobs, J. Chem. Phys. **85**, 3985 (1986); see also J. G. Shanks, Ph.D. thesis, Department of Physics and Astronomy, University of Maryland, College Park, 1986 (unpublished).