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Critical Adsorption at the Liquid/Vapor Surface of Multicritical Mixtures

B. M. Law, C. M. Sorensen and F. Zhou

Department of Physics, Kansas State University, Manhattan, KS 66506

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ABSTRACT

Preferential adsorption at the liquid/vapor surface of a critical binary liquid mixture gives rise to a position dependent order parameter $\varphi(z)$. Near an ordinary critical point the excess adsorption, $\Gamma = \int_0^\infty \varphi(z) - \varphi_{bulk}\, dz$, diverges as $\sim t^{\beta-\nu}$ where $t = |1 - T/T_c|$ is the reduced temperature and β and ν are the usual critical exponents.

Bulk multicritical points will modify critical adsorption due to exponent renormalization. The critical binary liquid mixture D_2O + 3-methylpyridine exhibits a closed-loop coexistence curve with the two phase region existing between upper (T_{UC}) and lower (T_{LC}) critical temperatures. On addition of ordinary water, T_{UC} and T_{LC} approach each other and coalesce for a specific mole fraction of H_2O where the closed-loop coexistence curve has shrunk to a point at $T_{DCP}=T_{UC}=T_{LC}$. At this double critical point (DCP) the exponents β and ν are expected to be renormalized to 2β and 2ν. We compare ellipsometric measurements of the adsorption near this double critical point with the same phenomena near an ordinary single critical point. Surprisingly we find that near the DCP $\Gamma \sim t^{-1.0}$ experimentally, rather than $\sim t^{-0.6}$ expected theoretically. The measured Γ dependence is believed to be due to β not renormalizing

in the one phase region; however an adequate theoretical interpretation of this effect is at present lacking.

INTRODUCTION

Critical adsorption at the interface between a critical and a non-critical phase has been extensively studied since its prediction by Fisher and de Gennes in 1978. In a critical liquid mixture the liquid component with the lowest surface free energy is adsorbed at the non-critical surface thus leading to an order parameter which varies with distance away from the surface, $\varphi(z)$. The excess adsorption $\Gamma = \int[\varphi(z) - \varphi_{bulk}]\, dz \sim t^{\beta-\nu}$ diverges on approaching the critical temperature T_c where β and ν are the usual critical exponents and $t = |T_c\text{-}T|/T_c$ is the reduced temperature.

In this paper we present a simple, model independent, scheme for obtaining information on critical adsorption from ellipsometric data near an ordinary critical point. This analysis scheme works very well for binary liquid mixtures and gives agreement with theory for the divergence of the excess adsorption. Near a double critical point the exponents β and ν are expected to be renormalized to 2β and 2ν. We study critical adsorption near a double critical point, for the first time, and discuss the surprising divergence $\Gamma \sim t^{-1.0}$ that is measured experimentally.

CRITICAL ADSORPTION NEAR AN ORDINARY CRITICAL POINT

The liquid/vapor surface of a critical liquid has a very asymmetric order parameter profile. In the vapor phase the order parameter approaches the liquid phase over a non-critical correlation length $\xi_{NC} \sim$ 0.2nm while in the liquid phase the order parameter exhibits a power law decay $(z/\xi)^{-\beta/\nu}$ for length scales less than the critical correlation length, ξ, and thereafter decays exponentially to the bulk (Fisher and de Gennes, 1978). The order parameter profile can be represented in the following form:

$$\varphi(z) = \begin{cases} \sim e^{z/\xi_{NC}} , & z < 0 \\ \varphi_{bulk} + \varphi_0 t^{\beta} P\left(\frac{z}{\xi}\right) , & z \geq 0 \end{cases} \qquad (1)$$

where we have assumed that the vapor phase occupies the half-space $z < 0$ while the liquid phase occupies the half-space $z \geq 0$. The surface scaling function $P(x) \sim x^{-\beta/\nu}$ as $x \rightarrow 0$ and $P(x) \sim e^{-x}$ as $x \rightarrow \infty$ while φ_0 is the amplitude of the critical adsorption.

Liu and Fisher (1989) have re-analysed the critical adsorption data of Schmidt (1990) and Schlossman, Wu and Franck (1985). They qualitatively confirm equation (1) although critical adsorption is still an active field of research as an appropriate model for P(x) which describes the cross-over from power law to exponential behavior and which gives quantitative agreement with all available experimental results is lacking (Law, 1991). The most common methods for studying P(x) have been the optical methods of reflectometry (Schlossman, Wu and Franck, 1985) and ellipsometry (Schmidt, 1990; Sussmann and Findenegg, 1989). In general it has not been possible to invert the experimental data to find P(x). Instead the consistency of a particular model surface scaling function P(x) has been tested by numerically integrating Maxwell's equations with the assumed form for P(x); the resulting reflection amplitudes are then compared with the experimental results. In this paper we will concentrate on those aspects of critical adsorption near an ordinary critical point which are well understood and which are model independent. This will enable us to interpret key features of critical adsorption near a double critical point.

A particularly convenient technique for studying surface structure is phase-modulated ellipsometry (Beaglehole, 1986). At the Brewster angle, ellipsometry measures the ratio of the p-wave (r_p) to s-wave (r_s) complex reflection amplitudes where for thin profiles (compared with the wavelength of light, λ) the signal is given by the Drude equation (Drude, 1959)

$$\bar{\rho} = \mathrm{Im}\left(\frac{r_p}{r_s}\right)\Big|_{\theta_B} = \frac{\pi}{\lambda}\frac{\sqrt{\varepsilon_v + \varepsilon_L}}{\varepsilon_v - \varepsilon_L}\int \frac{(\varepsilon(z) - \varepsilon_L)(\varepsilon(z) - \varepsilon_v)}{\varepsilon(z)}\,dz \qquad (2)$$

where $\varepsilon(z)$ is the dielectric profile which varies from ε_V, the vapor dielectric constant, to ε_L, the bulk liquid dielectric constant. For thicker profiles Maxwell's equations have to be solved numerically (Born and Wolf, 1980; Law and Beaglehole, 1981; Liu and Fisher, 1989). We will assume, as have Liu and Fisher (1989), that the dielectric profile $\varepsilon(z)$ is directly proportional to the order parameter profile $\varphi(z)$.

Far from the critical temperature the Drude equation (2) holds where $\varepsilon(z) \approx \varepsilon_L - \Delta\varepsilon(z)$, $z > 0$ and $\Delta\varepsilon(z) = m_0 t^{\beta} P(z/\xi)$ is a small perturbation compared with $\varepsilon_L - \varepsilon_V$. The constant $m_0 = C\varphi_0$, where C is proportional to the optical contrast of the liquids. Therefore we find from (2) that

$$\bar{\rho} \approx \bar{\rho}_{BG} + \frac{\pi}{\lambda}\frac{\sqrt{1+\varepsilon_L}}{\varepsilon_L} m_0 \xi_0 t^{\beta-\nu} \int_0^{\infty} P(x)\,dx \tag{3}$$

where $\bar{\rho}_{BG}$ is a noncritical background (due to the noncritical correlation length, ξ_{NC}, in the vapor), which is expected to be reasonably temperature independent, ξ_0 is the correlation length amplitude, and the integral over P(x) is a constant universal number. In this approximation $\bar{\rho}$ is proportional to the excess adsorption $\Gamma = \int[\varphi(z) - \varphi_{bulk}]\,dz \sim t^{\beta-\nu}$. A plot of $\log\bar{\rho}$ against log t should be a straight line with a slope of $\beta-\nu \sim -0.3$ provided the background term is small and provided the approximations used in deriving (3) are valid.

A conventional computer controlled phase-modulated ellipsometer, based upon the design of Beaglehole (1980), was used to obtain the $\bar{\rho}$ measurements. Our measurement procedure

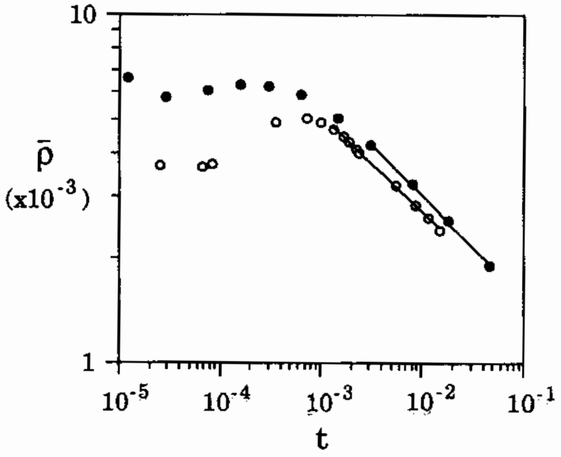

Fig. 1. Ellipsometric data near an ordinary critical point for the liquid mixtures C_6H_{12}+CH_3OH (open circles) and C_7H_{14}+C_7F_{14} (solid circles). The solid line is a nonlinear least squares fit to (3) with the parameters given in Table 1.

typically consisted of waiting for 2 hours after thermal equilibrium had been established and then collecting 20 measurements over the succeeding 2 hours. Data which showed any systematic trends or excessive noise in either T or $\bar{\rho}$ were omitted. The temperature stability during the 2 hour measurement period was ±0.5 mK while the variation in $\bar{\rho}$ was $\pm 2\text{x}10^{-5}$ (~2%). However a more realistic estimate of the error in $\bar{\rho}$, as determined from the reproducibility of the measurements, is $\pm 5\text{x}10^{-5}$ (~5%). This value has been used in the calculations below.

A critical mixture of cyclohexane (C_6H_{12}) plus methanol (CH_3OH) was prepared in a dry nitrogen gas atmosphere from ACS grade chemicals without further purification. The critical mole fraction was $X_{C_6H_{12}} = 0.516$ while the critical temperature was determined to be $T_c = 45.76 \pm 0.02^\circ C$. In Fig. 1 we plot the data for $C_6H_{12}+CH_3OH$ and methylcyclohexane (C_7H_{14}) plus perfluoromethylcyclohexane (C_7F_{14}) from Schmidt (1990) on a log-log plot. Sufficiently far from T_c the data is approximately linear -- the slight curvature in the data is due to $\bar{\rho}_{BG}$ and the temperature dependence of ε_L. A nonlinear least squares fit to equation (3) (solid line) gives the results in Table 1 where we have used $\xi_0 = 0.324$nm and the refractive index data from Houessou et al. (1985) in fitting $C_6H_{12}+CH_3OH$ and the data of Schmidt (1990) in fitting $C_7H_{14}+C_7F_{14}$. The experimental measurements for $\beta - \nu$ (Table 1) are in excellent agreement with the theoretical value of

TABLE 1

Fitting parameters in eq. (3) for $\bar{\rho}$.

System range	Temp $(\text{x}10^{-3})$	$\bar{\rho}_{BG}$	$m_0 \int P\, dx$	$\beta - \nu$	Reduced χ^2
$C_6H_{12}+CH_3OH$ (this work)	$t \geq 0.0011$	0.2 ± 0.4	0.5 ± 0.2	-0.29 ± 0.04	0.5
$C_7H_{14}+C_7F_{14}$ (Schmidt, 1990)	$t \geq 0.002$	0.0 ± 0.3	0.7 ± 0.2	-0.29 ± 0.03	4.3
$D_2O+C_6H_7N+H_2O$ (this work)	$t \geq 0.04$	0.1 ± 0.2	-0.19 ± 0.06	-1.02 ± 0.08	0.3

Quoted errors are three standard deviations.

-0.304±0.006 (Fisher and Chen, 1985). In a previous publication (Law, 1991) we also demonstrated that, for aniline/cyclohexane and isobutyric acid/water, equation (3) describes the $\bar{\rho}$ behavior sufficiently far from T_c in both the one- and two-phase regions. We should emphasis however that (3) was derived from the order parameter profile given in (1) which assumes that the surface scaling function is only a function of z/ξ; hence this analysis gives no information as to whether P(x) crosses over from a power law decay to an exponential decay. Such information is contained in the higher order terms of $\bar{\rho}$ whose analysis requires the numerical integration of Maxwell's equation for a particular model P(x).

CRITICAL ADSORPTION NEAR A DOUBLE CRITICAL POINT

Bulk multicritical points will modify critical adsorption due to exponent renormalization. The critical binary liquid mixture heavy water (D_2O) + 3-methylpyridine (C_6H_7N) exhibits a closed-loop coexistence curve with the two phase region existing between upper (T_{UC}) and lower (T_{LC}) critical temperatures. On addition of ordinary water T_{UC} and T_{LC} approach each other and coalesce for a specific mole fraction of H_2O where the closed-loop coexistence curve has shrunk to a point at $T_{DCP}=T_{UC}=T_{LC}$ (Fig. 2). At this double critical point (DCP) the

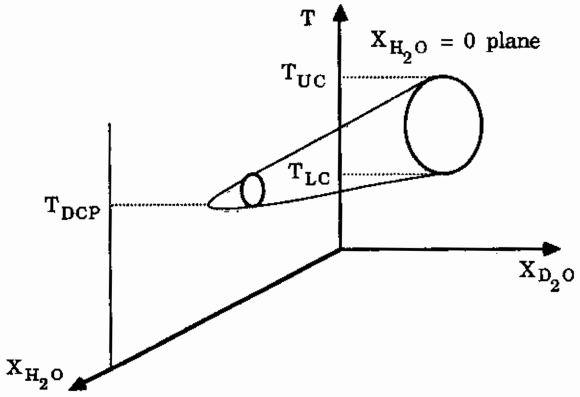

Fig. 2. Diagram showing the closed-loop phase diagram for $D_2O+C_6H_7N$ and the line of critical points ending at the double critical point (DCP) at a temperature $T_{DCP} = T_{UC} = T_{LC}$ as H_2O is added to the system.

exponents β and ν are renormalized to 2β (Sorensen, 1988) and 2ν (Sorensen and Larsen, 1985; Johnson et al., 1985) respectively, therefore we expect from equation (3) that the slope will double to 2β-$2\nu \approx -0.6$. Cross-over behavior is expected for systems which exhibit closed-loop phase diagrams. For example, on approaching the lower critical temperature the exponents are doubled for temperatures T with $T_{LC} - T >> T_{UC} - T_{LC}$; this behavior crosses over to ordinary critical point exponents when $T_{LC} - T << T_{UC} - T_{LC}$ as now T_{LC} behaves like an ordinary critical point. This system, which exhibits a line of critical points ending at the DCP, is particularly interesting to study as a universal surface scaling function should globally describe adsorption for all mole fractions of H_2O.

In preparing a double critical mixture of $D_2O+C_6H_7N+H_2O$ the C_6H_7N was distilled over CaH_2 and collected over a molecular sieve. The H_2O was distilled and deionized while the D_2O was used as received from Aldrich Chemical Company and had an isotropic purity of 99.8%. Two stock solutions 30.0% by weight of C_6H_7N in either H_2O or D_2O were made. By mixing these solutions various ratios of H_2O to D_2O could be obtained while keeping the weight fraction of C_6H_7N constant (although the mole fraction varied). Mixing and filling operations were performed volumetrically under dry nitrogen gas. The line of upper and lower critical points and hence the double critical point were determined. We found that T_{DCP} = 76.70±0.05°C and

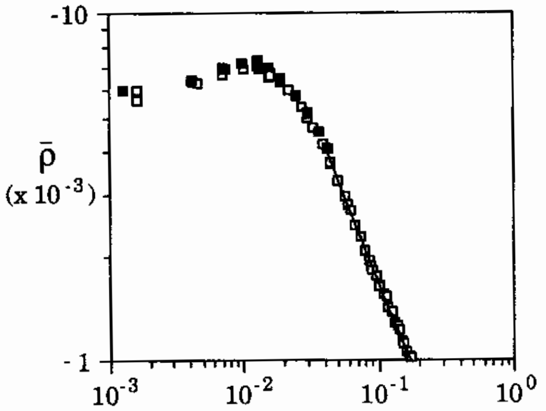

Fig. 3. Ellipsometric data near a double critical point for the liquid mixture $D_2O+C_6H_7N+H_2O$ with the composition given in the text (open squares, $T < T_c$; solid squares, $T > T_c$). The solid line is a nonlinear least squares fit to (3) with the parameters given in Table 1.

$X_{DCP(D_2O)} = 0.0780 \pm 0.0003$. A solution which skimmed past the DCP in the one-phase and which had mole fractions of $X_{H_2O} = 0.848$, $X_{D_2O} = 0.0748$ and $X_{C_6H_7N} = 0.0772$ was prepared. In Fig. 3 we present the $\bar{\rho}$ results for this system. A nonlinear least squares fit to (3) (solid line) gives the results listed in Table 1. Surprisingly we find that the slope is -1.02±0.08 rather than ~ -0.6. An explanation for this behavior could be that β is not renormalized in the one phase region; however an adequate theoretical interpretation of this effect is at present lacking.

DISCUSSION

We have demonstrated that sufficiently far from an ordinary critical point $\Gamma \sim \bar{\rho} \sim t^{\beta-\nu}$ where $\beta-\nu \approx -0.29 \pm 0.04$. This behavior agrees with theoretical predictions. Near a double critical point we find that $\bar{\rho} \sim t^{x}$ where $x = -1.02 \pm 0.08$ while theory would predict that $x = 2\beta - 2\nu \approx -0.6$. A conjecture that would explain the measured exponent would be if β did not double in the one phase region. This conjecture however raises a disturbing inconsistency for the heat capacity exponent, α. From the hyperscaling relation $2-\alpha = d\nu$ we find $\alpha = -1.78$ (using $\nu \rightarrow 2\nu$) which is in agreement with the theoretical prediction (Walker and Vause, 1983) whereas from the scaling relation $2-\alpha = 2\beta + \gamma$ we find $\alpha = -1.06$ (using $\beta \rightarrow \beta$ and $\gamma \rightarrow 2\gamma$, Johnston et al. (1985)). Further theoretical and experimental work is required to elucidate the source of this discrepancy.

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