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Universal surface scaling function for critical adsorption

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We present an accurate determination of the one- and two-phase universal surface scaling function which describes critical adsorption at noncritical interfaces of critical binary liquid mixtures in the strong surface field limit. The 95% confidence levels for this function are also determined. This function quantitatively describes ellipsometric critical adsorption data for three upper critical and one lower critical binary liquid mixtures. [S1063-651X(99)04705-4]

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For a binary liquid mixture, or even for a nominally pure liquid (which necessarily possesses some impurities), adsorption of the liquid component (or impurity) possessing the lowest surface free energy occurs at all liquid/vapor and liquid/solid interfaces. This preferential adsorption is also found in the two-phase region of the liquid mixture, provided a layer does not form at the interface [1]. The composition in the vicinity of the interface will therefore vary with distance z away from the interface. Concomitant with this composition variation mechanical properties, such as the local viscosity and the mutual diffusion coefficient, will vary with distance z near the interface. We therefore expect the flow properties in porous media (important in oil extraction processes), the spreading properties of droplets, surface chemical reactions such as electrolysis and catalysis, and the permeability of membranes to be significantly influenced by the presence of adsorption [2]. Adsorption also plays an important role in other areas of physics, such as the aggregation of colloidal particles [3]. Before a quantitative understanding of the influence of adsorption on these diverse processes can be obtained, the local variation in the composition with distance z due to this preferential adsorption must be more completely understood.

The adsorption profile exhibits surprising universal features near the *critical point* of the binary liquid mixture [4] and it is in this region of the phase diagram where adsorption is most well understood. The adsorption is described by the Fisher–de Gennes (FdG) scaling theory [4] where a surface field h_1 determines the composition of the first molecular layer immediately adjacent to the surface. The adsorption structure varies away from the surface over a distance of the order of the bulk correlation length, $\xi_\pm = \xi_{0\pm} t^{-\nu}$, where the reduced temperature $t = |T_c - T|/T_c$, $\nu(=0.632$ [5]) is a bulk critical exponent, and the $+$ $(-)$ subscript refers throughout this publication to quantities in the one- (two-) phase region of the liquid mixture. The distance $\xi_\pm$, over which the adsorption structure is correlated, obviously diverges as the critical temperature T_c is approached. The local adsorption at a distance $z(>0)$ from the surface (at $z=0$) is governed by the local order parameter $m(z,t) = \varphi_L(z,t) - \varphi_L(+\infty,0)$ where $\varphi_L(z,t)$ is the local volume fraction of the lighter liquid component (L) and $\varphi_L(+\infty,0)$ is its critical volume fraction. FdG predict that $m_\pm(z,t) = M_- t^\beta G_\pm(z/\xi_\pm, h_1 t^{-\Delta_1})$, where $\Delta_1(\approx 0.5$ [6]) and β $(=0.328$ [5]) are critical exponents and the term $M_- t^\beta$ describes the shape of the coexistence curve for the binary liquid mixture. The function $G_\pm(x,y)$ is predicted to be *universal* with differing forms in the one- and two-phase regions. The functional form for $G_\pm(x,y)$ is not well understood and only recently have experiments been designed to examine the dependence upon the surface field h_1 [7]. In this paper we are only interested in a limiting case of this function, for *strong* h_1 fields, where sufficiently close to T_c the first few monolayers at the liquid/vapor surface are completely saturated with the preferred component so that $m_\pm(z,t)$ simplifies to

$$m_\pm(z,t) = M_- t^\beta P_\pm(z/\xi_\pm), \tag{1}$$

where $P_\pm(x) \equiv P_\pm = G_\pm(x,\infty)$ is again a *universal function* which assumes differing forms in the one- and two-phase regions. This simpler situation is believed to occur most frequently in nature. $P_\pm$ is predicted to exhibit a power law decay at small $x(\ll 1)$ which crosses over to an exponential decay at large $x(\gg 1)$ [8].

It is extremely important to prove the existence of the surface scaling functions $G_\pm$ and $P_\pm$ because these functions form the very foundations on which surface critical phenomena are built. Although FdG postulated their existence many years ago it is not self-evident (at least to an experimentalist) that such functions can be found because surface critical phenomena must compete with nonuniversal long-range surface forces. In fact, up until now there is no evidence that a single universal function can be found which will quantitatively describe critical adsorption for many different systems. A number of different techniques have been used to study critical adsorption at liquid surfaces. None of these techniques directly measures the local order parameter profile $m(z,t)$. Instead an integral over $m(z,t)$ is measured and therefore it is difficult to obtain direct estimates of the functional form for $P_\pm$. A neutron reflectometry experiment [9] has confirmed the power law behavior of P_+ at small x while analysis of a number of optical experiments has (i) verified the z/ξ dependence of $P_\pm$ [10], (ii) measured various integrals over $P_\pm$ [11,12], and (iii) determined various universal numbers which enter P_+ [8,12,13]. However, the form for P_+ determined from several different experiments [12] differs by more than 100% at intermediate values of

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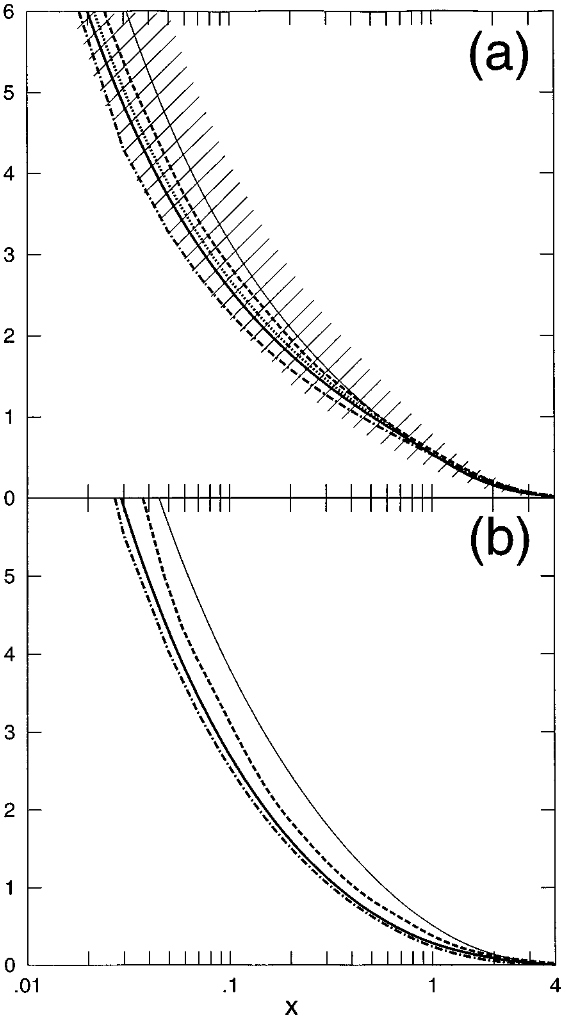

FIG. 1. Surface scaling functions $P_+(x)$ and $P_-(x)$. Models: $P1$ (heavy solid line), RG (dashed-dotted line), and MC (dashed line). The 95% confidence levels for the $P1$ model (Table I) would be barely discernible and have been omitted for clarity. In (a) we additionally have the EP model (dotted line) and the experiment of Zhao *et al.* [9] (light solid line), while the shaded region represents the variation in the $P_+(x)$ functions determined from various experiments by Flöter and Dietrich [12]. In (b) the $P_-(x)$ function determined by Flöter and Dietrich for the experiment of Ref. [28] is also shown (light solid line).

$x(\sim 1)$ (Fig. 1, shaded region) and therefore these experimental determinations of P_+ cannot be claimed to fulfill the universality requirement of P_+.

It is very important to quantitatively determine the functional form for $P_\pm$ because this functional form will not only allow us to more clearly understand the local mechanical properties (e.g., local viscosity and mutual diffusion coefficient) in the vicinity of an interface but $P_\pm$ also forms a ''limiting function'' for many other important situations near a critical point of a binary liquid mixture. Specifically, (i) the functional form of $G_\pm(x,y)$, where the surface field h_1 is no longer large, can obviously never be quantitatively understood until the simpler function $P_\pm$ is determined precisely, (ii) finite-size effects in critical films [4,14] cannot readily be understood until the semi-infinite system, where $P_\pm$ is applicable, has been determined, and (iii) an understanding of $P_\pm$ is required before nonplanar geometries (e.g., spheres [15] applicable to colloidal particles) can be quantitatively understood. The purpose of this publication is therefore to demonstrate that one can find a universal function $P_\pm(x)$ which describes a number of different ellipsometric critical adsorption experiments. The universal functional form for $P_\pm(x)$ is determined to within a few percent and is compared with a number of other determinations for $P_\pm$.

According to our definition for the local order parameter, $m(z,t)$, the universal surface scaling function $P_\pm$ must take the limiting forms $P_+(\infty)=0$ and $P_-(\infty)=1$ in the bulk liquid so that the order parameter is either zero or describes the shape of the coexistence curve in, respectively, the one- or two-phase regions. At criticality, where $t=0$, we expect the adsorption to remain finite (and nonzero) so that $m(z,0)$ must lose its dependence upon the reduced temperature t; this requirement implies that the small $x(\ll 1)$ behavior for the surface scaling function must be $P_\pm(x)\cong c_\pm x^{-\beta/\nu}$ where c_+ and c_- are universal numbers [4]. In general, this is the first term in an asymptotic expansion for small x where [16]

$$P_\pm(x)=c_\pm x^{-\beta/\nu}+c_{1\pm}x^{(1-\beta)/\nu}+c_{2\pm}x^{(2-\beta)/\nu}+\cdots \tag{2}$$

and $c_{1\pm}$ etc. are universal numbers. Additionally, second order phase transitions are continuous at T_c, therefore, we must have $P_+(x)=P_-(x)$ at $t=0$ which requires that [16]

$$c_+/c_-=(\xi_{0+}/\xi_{0-})^{-\beta/\nu}, \tag{3}$$

where the correlation length amplitudes have a universal ratio $R_\xi=\xi_{0+}/\xi_{0-}\simeq 1.96$ [17]; a similar condition also holds between c_{1+} and c_{1-}, etc. At large $x(\gg 1)$ the $P_\pm$ functions exhibit exponential decay which takes the general form [8]

$$P_\pm(x)=P_\pm(\infty)+P_{\infty\pm}e^{-x}+P_{1\pm}e^{-2x}+\cdots, \tag{4}$$

where $P_{\infty\pm}$ etc. are universal numbers.

Theoretical estimates for some of the universal coefficients in Eqs. (2) and (4) have been provided by renormalization group (RG) theory (to order ϵ) [16], Monte Carlo (MC) simulations [21], and an interpolation scheme [12]; the different methods of calculation only provide qualitative agreement with each other and with experiments [13]. In addition the manner in which the asymptotic form at small x crosses over to the asymptotic form at large x is not well understood and the various estimates for the form of this crossover, in the region where it occurs near $x\sim 1$, differ considerably (Fig. 1). Liu and Fisher [8] have suggested various *Ansätze* which correctly possess the leading order terms for small and large x. The most consistent form that they suggest is perhaps the ''exponential-Pade'' (EP) profile which we discuss in more detail below.

Smith and Law [11] have shown how to determine the universal numbers $\int P_\pm=\int_0^\infty[P_\pm(x)-P_\pm(\infty)]dx$ from ellipsometric data $[\overline{\rho(t)}]$ collected at sufficiently large reduced temperatures t. They deduced the universal numbers [22]

$$\int P_+\equiv\int_0^\infty P_+(x)dx=1.97\pm 0.08, \tag{5}$$

$$\int P_-\equiv\int_0^\infty[P_-(x)-1]dx=1.65\pm 0.13 \tag{6}$$

from a number of different critical liquid mixtures. At small t, the ellipticity $\bar{\rho}$ must be determined by integrating Maxwell's equations using a particular model for the interfacial dielectric profile $\varepsilon(z,t)$, which is related to the volume fraction $\varphi_L(z,t)$ through the Clausius-Mossotti equation. In a later paper [13] Smith *et al.* also demonstrated that the normalized value of $\bar{\rho}_+ - \bar{\rho}_{\mathrm{bg}+}$, where $\bar{\rho}_{\mathrm{bg}+}$ is a weakly temperature-dependent background term, falls on an approximate universal curve when plotted as a function of ξ_+ (rather than t); in this plot the value of ξ_+, where $\bar{\rho}_+$ exhibits a maximum, allows one to estimate the universal ratio [23]

$$c_+/P_{\infty+} = 0.75 \pm 0.17. \tag{7}$$

The ultimate aim of theory and experiment is to determine the universal functions $P_\pm$ so that once the system-dependent parameters [M_-, ξ_{0+}, $\varphi_L(+\infty,0)$, and refractive indices] are known then the critical contributions to $\bar{\rho}_\pm(t)$ can be determined for any given critical liquid mixture. With this objective in mind we have reanalyzed the experimental data of Smith and Law [22], using the following model for $P_\pm$, which has been carefully chosen to exhibit the correct scaling forms in the asymptotic regions [24]. At small x ($<x_{0\pm}$) we retain all terms up to and including the $x^{(1-\beta)/\nu}$ term in Eq. (2) while for large $x(\geqslant x_{0\pm})$ we retain all terms up to and including the e^{-2x} term in Eq. (4). For simplicity, we chose $x_{0+} = x_{0-} = x_0 \sim 1$ [25]. In our model we have nine unknown parameters, specifically, $c_\pm$, $c_{1\pm}$, $P_{\infty\pm}$, $P_{1\pm}$, and x_0. These nine parameters are constrained by five necessary constraints, that any physically reasonable scaling function must possess, and three experimental constraints. The five *necessary constraints* are the continuity of $P_\pm(x)$ and $dP_\pm(x)/dx$ at $x = x_0$ and the continuity of $P_\pm(x)$ at $t = 0$ [Eq. (3)]. The three *experimental constraints* are $\int P_+$, $\int P_-$, and the ratio $c_+/P_{\infty,+}$ [Eqs. (5)–(7)]. We call this model the $P1$ model [representing the fact that derivatives up to and including the first derivative of $P_\pm(x)$ are continuous]. The eight constraints leave only one free parameter, x_0. The application of these constraints, for determining $P_\pm$, is quite complicated; we plan to describe our procedure in the future [20]. For a particular value of x_0, we solve Maxwell's equations using the $P1$ model for $\varepsilon(z,t)$, to obtain the ellipticity $\bar{\rho}_{P1}(t)$ at a reduced temperature t. This procedure is carried out in both the one- and two-phase regions for the four critical binary liquid mixtures studied by Smith *et al.* The average rms deviation of $\bar{\rho}$ for these four mixtures is then calculated using the standard formula $\sigma_\rho = \{\sum_{i=1}^{N}[\bar{\rho}_i(t) - \bar{\rho}_{P1}(t)]^2/(N-n)\}^{1/2}$ where $\bar{\rho}_i(t)$ represents the experimental data, $N(=400)$ is the total number of experimental data points, and $n(=5)$ is the number of adjustable parameters [26]. The crossover distance x_0 is adjusted until the minimum value for σ_ρ, denoted $\sigma_\rho^{\min}$, is determined. Excellent agreement is found between the $P1$ model and the four critical binary liquid mixtures (Fig. 2) for the parameters given in Table I. If we assume that the $\bar{\rho}$ data collected from the four liquid mixtures represent the typical agreement that one can expect between a good model for $P_\pm$ and experiment then $\sigma_{\rho,P1}^{\min} = 1.38 \times 10^{-4}$ provides a measure of the typical errors in $\bar{\rho}$ due to measurement error, sample preparation, temperature stability, influence of small thermal gradients ($\leqslant 1$ mK/cm for our experiments), and knowledge of the system-dependent parameters M_- and ξ_{0+}.

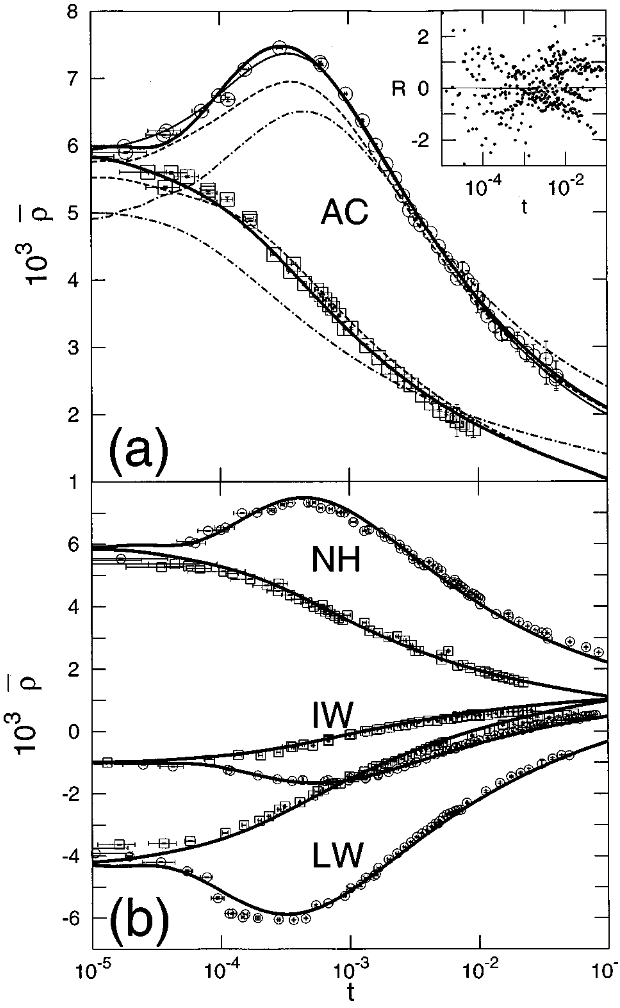

FIG. 2. Comparison of various critical adsorption models with ellipsometric data. In this figure the $P1$ model (heavy solid line) is compared with three upper critical solutions [aniline + cyclohexane (AC), nitrobenzene + hexane (NH), and isobutyric acid + water (IW)] and one lower critical solution [2,6 lutidine + water (LW)] where the experimental data are from Ref. [22]. The circles (squares) are for the one- (two-) phase region. In (a) we also show the EP (light solid line), RG (dashed-dotted line), and MC models (dashed line) for the AC mixture while the inset shows the residuals $R = (\bar{\rho}_i - \bar{\rho}_{P1})/\sigma_{\rho,P1}^{\min}$ for the $P1$ model for all four mixures in both the one- and two-phase regions. The agreement between the EP, RG, and MC models with experimental data for the mixtures in (b) is similar [13,20].

If we assume that $\sigma_{\rho,P1}^{\min}$ is a good measure of the *true experimental* standard deviation for $\bar{\rho}(t)$ then we can use the $P1$ model and the χ^2 distribution to estimate upper and lower 95% confidence levels [27]. According to this distribution for the number of degrees of freedom $v = N - n = 395$ the reduced $\chi_v^2 = 1.12$ at the 95% confidence level. Accordingly we modify the $P1$ model, with the condition that the necessary constraints must hold (but the experimental constraints do not necessarily have to hold), by adjusting c_+ until $\chi_v^2 = 1.12$ for fixed x_0 and $P_{\infty\pm}$ (Table I); similarly we adjust $P_{\infty\pm}$ until $\chi_v^2 = 1.12$ for fixed x_0 and $c_\pm$ (Table I).

TABLE I. $P1$ model paramters ($\pm 95\%$ confidence levels).

$c_+ = 0.787^{+0.009}_{-0.015}$, $c_- = 1.116^{+0.012}_{-0.022}$, $P_{\infty +} = 0.955^{+0.133}_{-0.213}$, $P_{\infty -} = 0.584^{+0.351}_{-0.160}$
$c_{1+} = -0.242$, $c_{1-} = 0.169$, $P_{1+} = 1.482$, $P_{1-} = 0.486$, $x_0 = 1.17$, $\sigma^{\mathrm{min}}_{(\mathrm{rho})} = 1.38 \times 10^{-4}$

The true surface scaling functions $P_{\pm}(x)$ most probably lie in the overlap between these two regions. The residuals for the $P1$ model [Fig. 2(a), inset] demonstrate that this model provides an excellent description of the data.

The $P1$ model fits the experimental data considerably better than either the RG or MC models, Fig. 2(a) and Ref. [13]. The P_+ function determined from a neutron reflectometry experiment [9] lies further from the $P1$ model than the MC curve [Fig. 1(a)], therefore, this neutron P_+ function will provide worse agreement with the ellipsometric data than the MC model. One disadvantage of the $P1$ model is that it is discontinuous in $d^2P_{\pm}/dx^2$ at x_0. Our model can be systematically improved by considering additional terms in the asymptotic sequences [Eqs. (2) and (4)] and requiring an appropriate number of higher derivatives to be continuous at x_0, so that x_0 remains the sole adjustable parameter [20]. In Fig. 2(a) we also show a comparison between the EP model and experimental data where we have required that only Eq. (5) hold [20]. The agreement is good, however, the larger value of $\sigma^{\mathrm{min}}_{\rho,\mathrm{EP}} = 1.55 \times 10^{-4}$ for the four liquid mixtures indicates that the $P1$ model provides a better fit to the experimental data . The function P_+, for the EP model, lies just outside the 95% confidence levels for the $P1$ model and possesses a very similar shape [Fig. 1(a)]. It appears therefore that the discontinuity in $d^2P_{\pm}/dx^2$ at x_0 for the $P1$ model is relatively unimportant.

In this publication we have determined expressions for the universal surface scaling function $P_{\pm}(x)$ (Table I) which describes critical adsorption at a semi-infinite, noncritical interface of a critical binary liquid mixture, in the strong surface field limit. This is a demonstration that the concept of surface universality, which predicts the existence of universal surface scaling functions, holds despite the presence of nonuniversal long-range surface forces. We have estimated the upper and lower 95% confidence levels for $P_{\pm}(x)$ (Table I) between which we believe the true surface scaling function must lie. Hopefully this accurate experimental determination of $P_{\pm}(x)$ will stimulate further theoretical developments in this field and assist in the study of weak surface fields (h_1), geometry-dependent effects on critical adsorption, as well as finite-size effects in critical films. We also believe that the function $P_{\pm}(x)$ may be useful in understanding local mechanical properties in the vicinity of an interface when preferential adsorption is present.

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[24] The experiments of Smith and Law are in the strong h_1 limit [22].

[25] This restriction will be removed in a later paper [20]; it does not make a significant difference to the shape of $P_{\pm}(x)$.

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