

## Probing the Universal Critical-Adsorption Profile by Neutron Reflectometry

Hong Zhao,<sup>1,2,\*</sup> Anne Penninckx-Sans,<sup>2</sup> Lay-Theng Lee,<sup>2</sup> Daniel Beysens,<sup>1,†</sup> and Gérard Jannink<sup>2</sup>

<sup>1</sup>*Service de Physique de l'Etat Condensé, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette Cedex, France*

<sup>2</sup>*Laboratoire Léon Brillouin (CEA-CNRS), Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette Cedex, France*

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We present the results of a neutron-reflectivity study of the universal critical-adsorption profile near the liquid-vapor interface of a binary-liquid mixture (methanol + deuterated cyclohexane) near criticality. As the critical temperature is approached from the one-phase region, we observed an abrupt decrease in the intensity of the specularly reflected neutron beam near the total-reflection edge. By interpreting the observation as the expected neutron-reflectivity *discontinuity* associated with a slowly decaying power-law profile, we evaluated the power-law exponent ( $\beta/\nu = 0.50 \pm 0.05$ ).

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After Fisher and de Gennes' original work on the scaling theory of critical adsorption (CA) [1], it is now generally accepted that [2], for systems belonging to the 3D Ising universality class near criticality, such as a binary-liquid mixture near its critical temperature  $T_c$ , the order parameter at a normal distance  $z$  from a planar interface deviates from its equilibrium bulk value according to the following scaling law:

$$m(z) = m_0 t^\beta P(z/\xi(t)), \quad (1)$$

for  $z$  greater than a molecular length. Here  $t$  is the reduced temperature  $(T - T_c)/T_c$ ,  $m_0$  and  $\beta$  are the amplitude and the critical exponent of the bulk two-phase coexistence curve, respectively [3],  $\xi(t)$  is the bulk correlation length defined in the exponential form of the density-density correlation function, and diverges as  $\xi(t) = \xi_0 t^{-\nu}$  near criticality. The order parameter is defined as the deviation of the volume fraction  $\phi(z)$  of the preferentially adsorbed component from its bulk value, i.e.,  $m(z) \equiv \phi(z) - \phi(\infty)$ . The scaling theory suggests that the universal scaling function  $P(x)$  should satisfy the following conditions [3,4]:

$$P(x) = \begin{cases} P_0 x^{-\beta/\nu} & \text{as } x \rightarrow 0, \\ P_\infty e^{-x} & \text{as } x \rightarrow \infty, \end{cases} \quad (2)$$

where  $P_0$  and  $P_\infty$  are amplitudes. A recent field theoretical calculation of CA suggests  $P_0 = 0.94 \pm 0.05$  [3]. The theoretically expected exponent for the 3D Ising model is  $\beta/\nu = (d - 2 + \eta)/2 \approx 0.52$ , where  $\eta$  is a critical exponent and  $d$  is the dimension of space.

Experimental studies of CA in binary-liquid mixtures have been carried out mainly by optical methods, e.g., ellipsometry [5–7], reflectometry [8], and fluorescence measurements [9]. From the analyses of the fluorescence measurements, it was estimated that  $\beta/\nu \approx 0.3$ – $0.6$  [9]. In addition, the optical reflectivity and ellipticity measurements yielded the exponents for the first moment of the concentration profile [8] and the adsorption excess amount [6]. Although the results of these studies seemed to agree with the scaling theory, to our knowledge no accurate determination of both the exponent and the

amplitudes from direct probing of the adsorption profile has been reported. Thus we set out to use neutron reflectometry [10], which in principle has nanometer resolution [11], to study CA. The purpose of this Letter is to demonstrate that, under certain conditions (see below), important profile information can be obtained from analyses of neutron-reflectivity data near the total reflection edge (TRE).

The underlying physics in the new approach adopted in this work involves exploiting resonant conditions [12–14] in the interaction between an incoming neutron beam and the reflecting sample. The resonance appears in the form of a discontinuity  $\Delta R$  in the reflectivity profile at the TRE, which was first predicted by Schack [15] and tested by Guiselin [12] on long polymer chains adsorbed at a liquid-air interface. It reveals the existence of a long algebraic region over which the concentration profile decreases singularly as a power law of the distance from the interface. The necessary condition for the existence of a discontinuity is a neutron-sample interaction potential, which increases with  $z$ . Such a potential can be seen as a half well, generating bound and quasibound states. In the case of CA in binary-liquid mixtures, the interaction potential  $V(z)$  is directly related to the volume fraction  $\phi(z)$  of the adsorbed species:

$$V(z) = \frac{2\pi\hbar^2}{m_n} \dot{b}_d \left\{ 1 + \left( \frac{\dot{b}_a}{\dot{b}_d} - 1 \right) \phi(z) \right\}, \quad (3)$$

where  $m_n$  is the mass of neutron and  $\dot{b}_a$  and  $\dot{b}_d$  are the scattering length densities of the adsorbed and the depleted species, respectively [10]. The volume fraction of the adsorbed species  $\phi(z)$  is a decreasing function of  $z$ . If  $\dot{b}_a < \dot{b}_d$  (which can be achieved, as in our experiment, by deuterating the depleted species),  $V$  increases with  $z$ , and thus the above condition is satisfied. If  $m(z)$  scales as  $z^{-\mu}$  for  $z \ll \xi$ , it is shown that [12] a true discontinuity appears in the limit  $\xi \rightarrow \infty$  for  $0 < \mu < 2$ . For CA, the decay in the algebraic region is slower, and consequently the discontinuity in the reflectivity profile is expected to be much more pronounced than the polymer problem; this was indeed shown to be true in a numerical simulation

[13]. Note that for methanol  $\dot{b}_a = -0.379 \times 10^{-6} \text{ \AA}^{-2}$ , and for deuterated cyclohexane  $\dot{b}_d = 6.68 \times 10^{-6} \text{ \AA}^{-2}$ ; the contrast is high.

In reality,  $\xi(t)$  is always finite. The scaling theory predicts a crossover from algebraic to exponential decay. For  $z \gg \xi(t)$ , the order-parameter profile decreases exponentially. For a pure exponential profile  $m(z) \sim \exp\{-z/\xi\}$  over the entire region  $z \geq 0$ , a second type of resonance occurs [14,16] at characteristic decay lengths  $\xi_n$  ( $n = 1, 2$ , etc.), which is displayed as zero reflectivities at wavelengths  $\lambda_n$  close but not equal to  $\lambda_c$ , the TRE. If the methanol-deuterated cyclohexane mixture had a pure exponential profile (which is not true in reality), we would find that  $\xi_1 = 234 \text{ \AA}$ ,  $\xi_2 = 458 \text{ \AA}$ , etc. If the decay length of the pure exponential profile is at these values, the reflectivity profile displays an abrupt decrease near  $\lambda_n$ , which is not a discontinuity but may look like one within the finite resolution. In CA, the order-parameter profile is a juxtaposition of the algebraic and exponential regions, and we expect a combination of the effects described above. Of course, the algebraic-region effect dominates when  $\xi(t)$  is large. In the limit  $\xi \rightarrow \infty$ , the order-parameter profile reduces to  $m(z) = m_0 P_0 (z/\xi_0)^{-\beta/\nu}$ . We calculated the reflectivity numerically in this limit and obtained the reflectivity discontinuity  $\Delta R$ . In Fig. 1, we show  $\Delta R$  vs  $\mu$  ( $\equiv \beta/\nu$ ) for  $P_0 = 1.0$ , which fits the data well near the TRE (see below), and  $\xi_0 = 3.6 \text{ \AA}$  and  $m_0 = 0.71$ , which were obtained from an earlier experimental study of the same liquid mixture in the bulk critical state [17]. We note that the slope of the curve is significant around  $\mu = 0.52$ , which is an ideal situation from the experimental point of view. In fact,  $\Delta R(\mu)$  is not a universal function of  $\mu$  since it also depends on other parameters (e.g.,  $P_0$ ), which determine the interaction potential. However, the existence of the reflectivity discontinuity depends solely on the power-law type of concentration profile, and is thus a universal manifestation of CA. Therefore, it is possible to determine  $\beta/\nu$  from experimental observation of the reflectivity discontinuity as long as the amplitudes are known [18].

We performed the neutron-reflectivity measurements on the DESIR reflectometer at the Orphée reactor at Saclay.

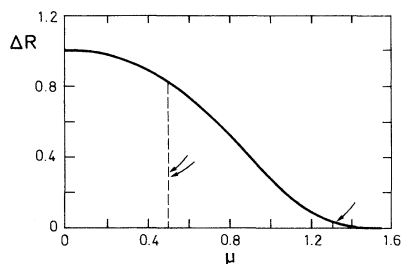


FIG. 1. Calculated  $\Delta R$  at the TRE vs  $\mu$  for  $m_0 = 0.71$ ,  $\xi_0 = 3.6 \text{ \AA}$ , and  $P_0 = 1.0$ . The single arrow corresponds to the polymer case. The double arrow corresponds to the CA problem.

Our sample is a near critical mixture of methanol and deuterated cyclohexane (25.9 wt % of methanol) partially filled in a quartz cell of inner dimensions  $10 \times 2.9 \times 0.6 \text{ cm}$ . A thermostat is used, which provides a temperature stability of better than  $\pm 0.5 \text{ mK}$  over a couple of hours and  $\pm 2 \text{ mK}$  over 48 h. The critical temperature of the sample was estimated by a simultaneous laser turbidity measurement (perpendicular to the neutron-beam plane). We found  $T_c = 42.188 \pm 0.01 \text{ }^\circ\text{C}$ , without apparent drift during the 2 week neutron-beam time. The time-of-flight method [10] was employed, which allows us to obtain the reflectivity as a function of neutron wavelength ( $\lambda$ ) at a fixed grazing angle,  $\theta = 0.81^\circ \pm 0.04^\circ$ , which was determined separately from a measurement with pure  $\text{D}_2\text{O}$ . We have measured the spectra of the specularly reflected neutron beam from the vapor-liquid interface on the vapor side at several reduced temperatures. Since methanol has a lower surface energy than deuterated cyclohexane, it is preferentially adsorbed at the interface. Figure 2 shows three measured reflectivity profiles at  $t = 5.6 \times 10^{-2}$ ,  $1.0 \times 10^{-2}$ , and  $9.8 \times 10^{-4}$ . The corresponding bulk correlation lengths are approximately 22, 66, and 287  $\text{\AA}$ , respectively. Total reflection takes place roughly at  $\lambda \geq 11.3 \text{ \AA}$ . For the higher  $t$ , the observed reflectivity profile is close to the Fresnel reflectivity for a sample with a uniform bulk concentration, while for the lower  $t$  an abrupt decrease in reflectivity near the TRE is observed. This is a clear indication of a critically adsorbed layer and a precursor of the predicted discontinuity at criticality.

Interpolation formulas for the scaling relations over the algebraic and exponential regions have been proposed [4,19]. One such formula, which was shown to be at least approximately correct in fitting the optical data, is the following model scaling function proposed by Liu and Fisher [4]:

$$P(x) = P_0 \left( \frac{1 + cx}{x} \right)^{\beta/\nu} \exp(-x), \quad (4)$$

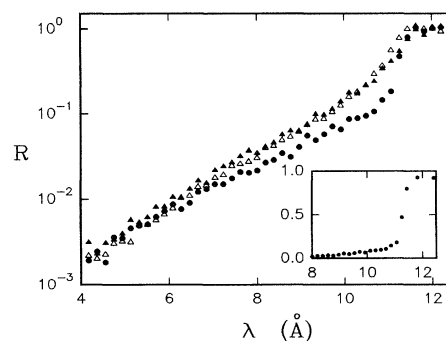


FIG. 2. The observed neutron reflectivities at a fixed grazing angle vs  $\lambda$ :  $t = 0.056$  (light triangles),  $1.0 \times 10^{-2}$  (dark triangles), and  $0.98 \times 10^{-3}$  (circles). The inset plotted in linear scale illustrates the observed "discontinuity" at  $t = 9.8 \times 10^{-4}$ .

where  $c$  is a constant which measures the crossover region and the amplitude ratio [ $c = (P_\infty/P_0)^{\nu/\beta}$ ]. We calculated the reflectivities associated with the Liu and Fisher profile and also a single exponential profile by solving the Schrödinger equation numerically. We fitted the  $t = 0.98 \times 10^{-4}$  data by Eqs. (1), (3), and (4) in the full  $\lambda$  range 4–12 Å with  $\beta/\nu = 0.52$ ,  $c = 0.1$ , and  $P_0 = 0.34$ . The solid lines in Fig. 3 are the fitted curves. We want to stress here that the values of these fitted parameters should not be overemphasized because our calculation does not include any near-interface structures which affect the reflectivity, particularly in the low- $\lambda$  region ( $\leq 8$  Å) [20], not to mention that Eq. (4) itself is a crude model. Our purpose here is to show that the Liu and Fisher model, which contains the algebraic decay of CA, fits the data better than a pure exponential profile [Fig. 3(b)] which does not have the CA ingredient. Note if we limit the  $\lambda$  range to the vicinity of the TRE (10.5–12 Å), where the near-interface structures have negligible effects, the Liu and Fisher model fits the data well with  $c = 1.1$  and  $P_0 = 1.0$  [see the inset of Fig. 3(a)], a value which is close to the theoretical one, 0.94, of the field theoretical calculation [3]. Though more refined fit-

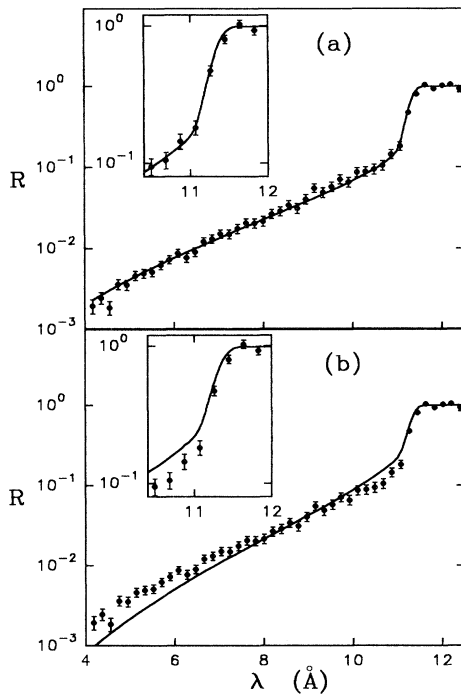


FIG. 3. Comparison of the fitted reflectivity profiles using (a) the Liu and Fisher model and (b) a single exponential model, at  $t = 0.98 \times 10^{-3}$  ( $\beta/\nu = 0.52$ ,  $c = 0.1$ ,  $P_0 = 0.34$ ). The insets are the fits in a limited  $\lambda$  range (10.5–12 Å) near the TRE ( $\beta/\nu = 0.52$ ,  $c = 1.1$ ,  $P_0 = 1.0$ ). The fitted curves shown here have been convoluted with a triangular response function to account for the finite resolution effect (see Ref. [12]).

ting procedures which test different models and contain detailed near-interface structures are currently under way, our present work demonstrates that crucial information of CA can be obtained from studying the neutron reflectivity near the TRE only. We can understand the results in the framework of Refs. [16,21,22]. The crucial point is to estimate the weight of the algebraic region versus the exponential region. To do this, we apply the Bohr-Sommerfeld quantization rule [23] to the neutron momentum at the energy corresponding to total reflection. The quantization tells us that for methanol and deuterated cyclohexane a single oscillation of the neutron wave extends over a distance of 250 Å. This limits the smallest correlation length  $\xi(t)$  which is necessary to identify the algebraic region by reflectivity discontinuity. We are thus confident that the observed  $\Delta R$  in the reflectivity profile at  $t = 10^{-3}$  ( $\xi \approx 287$  Å) accounts for the algebraic-region effect. Note that in the case of polymer adsorption the situation is less favorable. The same criterion tells us that chains with minimum radii of 3400 Å are required to produce the discontinuity effect.

Let us now focus on the determination of the exponent  $\beta/\nu$  from the observed reflectivity jump assuming  $P_0 = 1.0$ , which fits the data well near the TRE. Our numerical simulations of the reflectivity at finite  $t$  indicate that for  $t \leq 10^{-3}$  the reflectivity jump near the TRE already reaches the theoretical limit at  $t = 0$  within the experimental uncertainties. This result is supported by our observation that the reflectivity profile near the TRE for  $t = 1.9 \times 10^{-4}$  (not shown here for the sake of clarity) overlaps within the experimental error bars with the  $t = 0.98 \times 10^{-3}$  profile. This feature enables us to obtain the value of the reflectivity discontinuity from our finite  $t$  data and therefore derive a value of  $\beta/\nu$  by comparing the observed  $\Delta R$  with the predicted one (Fig. 1). But due to the finite angular resolution of the reflectometer ( $\Delta\theta/\theta = 0.05$ ), the observed reflectivity profile is a convolution of the ideal profile ( $\Delta\theta/\theta = 0$ ) and a resolution function [12]. The range of wavelength spanning  $\Delta R$  is broadened from the theoretical limit by approximately  $\Delta\lambda = \lambda_c(\Delta\theta/\theta) \approx 0.6$  Å [12]. Following the above considerations, we were able to estimate from our reflectivity data that  $\Delta R = 0.82 \pm 0.04$  (see the inset of Fig. 2). This corresponds to  $\beta/\nu = 0.50 \pm 0.05$  in Fig. 1. Note that if we had used  $P_0 = 0.34$  in the calculation of Fig. 1 we would have found that  $\beta/\nu = 0.74 \pm 0.05$ . Further experiments with improved angular resolution and neutron counting statistics over a wider spectrum, and refined data fitting procedures, should be able to provide more detailed information of the concentration profile, including the exponent and the amplitudes.

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- \*Address after Oct. 1, 1995: Argonne National Lab., APS/XFD, 9700 S. Cass Ave., Argonne, IL 60439.  
†Present address: CEA/DRFMC, CE Grenoble, F-38041 Grenoble Cedex, France.
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