

Neutron reflectivity studies of critical adsorption: The correspondence between a critical adsorption profile and specular neutron reflection

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For interfacial order parameter profiles which decay as $Az^{-\mu}$, such as the composition profile of the noncritical interface of a binary liquid mixture at a critical end point, there is a reported one-to-one correspondence between the profile and the reflectivity which can be described by an analytical theory [S. Dietrich and R. Schack, Phys. Rev. Lett. **58**, 140 (1987)]. Evidence for $\mu=0.53\pm 0.02$ for adsorption at the hydrophilic silicon/liquid surface of the mixture (2-butoxyethanol+deuterium oxide) near its lower critical end point, determined from neutron reflectivity measurements, is presented. This value is in good agreement with the theoretical prediction of $\mu=0.516\pm 0.004$. Further examination of the data permits the determination of the asymptotic surface enrichment scaling factor amplitude $P_0\approx 0.11$, which is not in agreement with the theoretical value $P_0=0.94\pm 0.05$ and values determined by other experimental methods. [S1063-651X(99)01704-3]

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At the critical end point (CEP) of a binary liquid mixture, two liquid phases merge identity to form a single phase in the presence of a spectator (noncritical) phase which does not participate directly in the phase transition. This spectator phase can be, for example, the vapor, a solid container wall, or a completely immiscible liquid phase. Consideration of the Gibbs adsorption equation along paths of either constant temperature or constant composition shows that, according to scaling arguments, as the CEP is approached the relative adsorption of component 2 with respect to component 1, Γ_{21} , diverges [1]. Such an effect is the critical adsorption predicted by Fisher and de Gennes [2]. Further than predicting a large excess of one component at the noncritical interface, Fisher and de Gennes conjectured a universal expression for the order parameter profile

$$m(z) = m_0 t^\beta P(x). \quad (1)$$

Here $m(z) = \phi(z) - \phi$ is the order parameter at a position z , where z is the coordinate normal to the interface, ϕ is the bulk mixture composition, and $\phi(z)$ is the local composition at position z . The quantity m_0 is the amplitude of the bulk solution order parameter in the two-liquid phase region, which behaves as $\Delta\phi = m_0 t^\beta$, and $x = z/\xi$, where ξ is the correlation length of the composition fluctuations in the bulk fluid which behaves as $\xi = \xi_0 t^{-\nu}$, where ξ_0 is the correlation length amplitude, $\nu = 0.63$, $\beta = 0.326$, and $t = |T - T_c|/T_c$ is the scaled reduced temperature, where T_c is the critical temperature. The quantity $P(x)$ is the surface-enrichment scaling function which scales the bulk order parameter and possesses the following asymptotic limits:

$$P(x) = P_0 x^{-\beta/\nu} \quad \text{for } x \rightarrow 0: \quad \text{power law decay,} \quad (2a)$$

$$P(x) = P_\infty \exp(-x) \quad \text{for } x \rightarrow \infty: \quad \text{exponential tail.} \quad (2b)$$

P_0 and P_∞ are universal constants whose magnitudes depend only on whether the mixture is in one or two phases. This critical adsorption profile has provoked much experimental work—mostly by ellipsometric [3] or optical reflectivity methods, but also more recently using neutron reflectometry [4,5]—and the major aims have been to confirm the universal aspects, i.e., the values of P_0 , P_∞ , and $\mu = \beta/\nu$. Although Liu and Fisher [6] provided model $P(x)$ profiles for the analysis of the optical data, Smith *et al.* [3] presented the most testing data analyses for determining these quantities using a method free from the imposition of fixed models. They evaluated universal integrals, and compared the results obtained from ellipsometric measurements with results from renormalization group calculations and Monte Carlo simulations. As Smith *et al.* pointed out, neutron reflectivity experiments offer a more stringent test of Eq. (2a) than optical experiments can offer, but only recently were the first experimental tests of critical adsorption performed using neutron reflectometry. Zhao *et al.* presented some results of a neutron reflectivity study of a critical adsorption profile for the mixture methanol plus deuterated cyclohexane, and convincingly demonstrated the existence of the power-law part of the profile [4].

The neutron scattering length density Nb of a medium is directly proportional to the potential which a neutron experiences while propagating through that medium, and is simply related to the neutron refractive index $n \approx 1 - (\Lambda^2/2\pi)Nb$. Here Λ is the neutron wavelength, N is the number density of the nuclei, and b is the averaged coherent neutron scattering length per nucleus. For the mixture chosen by Zhao *et al.*, the expected Nb increases with increasing distance z through the interface toward the bulk liquid. With such an Nb versus z behavior, if the interfacial profile corre-

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sponds to the power law part of the critical adsorption profile [Eq. (2a)], the reflectivity should exhibit a discontinuity near the total reflection edge (TRE) [7]. Indeed the data of Zhao *et al.* clearly show the expected discontinuity in the reflectivity near the TRE at a temperature very close to the critical temperature T_c . At temperatures removed from T_c no discontinuity is apparent, indicating that the order parameter profile no longer has a dominating $Az^{-\mu}$ dependence. Further analysis determined a value for $\mu = \beta/\nu = 0.55 \pm 0.05$, by assuming $P_0 = 1.0$ (theory: $P_0 = 0.94 \pm 0.05$), but it is stated that a value of $\mu = 0.74 \pm 0.05$ could also represent the reflectivity measurements if $P_0 = 0.34$ is chosen. The former choice offers excellent agreement with theory, but is reliant on a chosen value of P_0 . Apart from that work an independent determination of the value of the μ exponent was made by Zalczer [8], who analyzed the optical data of Beysens and Leibler obtained from a guided-wave experiment [9]. From this numerical study a value of μ in the range $0.3 < \mu < 0.6$ provides a satisfactory fit to the data. The drawback with these methods is that the value of μ cannot be determined unambiguously.

However, over a decade ago Dietrich and Schack (DS) [10,11] presented a theorem which allowed a determination of the exponent μ in a unique manner from reflectivity measurements. Their theory is general, and applies to any order parameter profile which decays as $Az^{-\mu}$. Such profiles include polymer adsorption at interfaces, for which $\mu = 1.3$ [12,13]. The DS theorem applies to the converse case of the Zhao *et al.* experiment, i.e., Nb decreases with increasing distance z through the interface. In this instance the reflectivity should show no discontinuity near the TRE, but if the reflectivity is represented graphically in an appropriate manner a linear dependence should be yielded for a unique value of μ . In this case both the value of the exponent μ and the amplitude A of the critical adsorption profile near a CEP, which can be directly related to P_0 , can be determined unambiguously. Zhao *et al.* pointed out that, in principle, this is a better approach to determining μ and P_0 . The aim of this paper is to provide a complementary report to that of Zhao *et al.* on the choice of exponent μ , which is directly—and uniquely—determined from neutron reflectivity measurements.

In the context of this paper it is not necessary to recount the DS theory in detail. Instead we will provide a record of the necessary stages in the analysis of the experimental data, and outline any assumptions made on our part. Consider neutrons with wavelength Λ incident from a medium i (with potential \tilde{V}_i) which are reflected at the medium i -medium b (with potential \tilde{V}_b) interface with a grazing angle of incidence α . The potential \tilde{V}_m of a medium m is $\tilde{V}_m = (\hbar^2/2\pi m_n)Nb$ where m_n is the mass of the neutron, \hbar is Planck's constant, and Nb the scattering length density of the medium m . With a knowledge of the \tilde{V}_m and the position of the critical angle of total external reflection α_c , which is measured experimentally or can be calculated using Snell's law, the incidence energy \tilde{E} is determined and the neutron wave eigenvalue E is calculated via

$$\alpha_c = \arcsin[(\tilde{V}_b - \tilde{V}_i)/(\tilde{E} - \tilde{V}_i)]^{1/2}, \quad (3a)$$

$$E = \frac{8\pi^2 m_n}{h^2} (\tilde{E} - \tilde{V}_i) (\sin^2 \alpha - \sin^2 \alpha_c). \quad (3b)$$

The eigenvalue E is a rescaled and redimensioned wave vector transfer Q ($Q = 4\pi \sin \alpha/\Lambda$) which is zero at $\alpha = \alpha_c$. According to the DS theory, the value of μ is determined by plotting a graph of $y = \ln[1 - R(E)]$ versus $x = E^{1/2 - 1/\mu}$, where $R(E)$ is the reflectivity at a given E . The value of μ is varied until a value $\mu = \mu'$ produces a straight line as $x \rightarrow \infty$, i.e., as $E \rightarrow 0$ or $Q \rightarrow Q_c$ (for $Q > Q_c$, where $Q_c = Q(\alpha_c)$). This should occur, according to theory, for $\mu' = 0.516 \pm 0.004$.

The Dietrich and Schack theorem is strictly limited to a region of E space close to the TRE. The useful data are thus limited to a window $E_- < E < E_+$, where the values of E_+ and E_- depend on several factors. The upper-bound value E_+ is governed by two factors. The first is the point at which the experimental situation deviates considerably from the asymptotic behavior predicted by the theory. The second consideration is the true power law behavior of the order parameter profile, since the $Az^{-\mu}$ term is the leading term of a series expansion, and higher orders may become prominent at larger E . The limiting lower-bound value E_- is determined by the finite temperature resolution, and the exponential contribution to the critical adsorption profile. In reality, this effect is likely to be masked by the real instrumental resolution near the TRE, although the experimental temperature resolution will also contribute.

Reflectivity measurements were performed on the V6 reflectometer at the BERII reactor at the Hahn-Meitner-Institut, Berlin, Germany. A horizontal beam of monochromatic neutrons with wavelength $\Lambda = 4.66 \text{ \AA}$ ($\pm 3\%$) are incident at the hydrophilic silicon/liquid-mixture interface. The polished surface of the silicon block (Holm Siliciumbearbeitung) was rendered hydrophilic by the RCA cleaning method [14]. The silicon block was then sealed using a Viton O-ring to a clean polytetrafluoroethylene trough furnished with filling holes and tubes. This unit was then sandwiched between two aluminium blocks thermostated by circulating water from a HAAKE Thermostat F6-C25 circulating bath. A bubble-free liquid sample was introduced into the sample cavity through the filling holes. The aluminium sections were designed so that the thermal mass and area of thermal contact were maximized while maintaining a cell suitable for reflectometry. The cell is similar to that described by Russell [15].

Alignment of the cell was achieved by performing a series of rocking scans and table height scans. The neutrons are transmitted through the silicon block and reflected from the silicon/liquid interface. The sample temperature was monitored using a platinum resistance thermometer inserted in the underside of the polytetrafluoroethylene trough section of the cell. The temperature control and homogeneity were better than ± 0.1 K. After each temperature change a short equilibration time was allowed before checking the alignment of the cell. In all cases there was no drift in alignment beyond the realms of the accepted experimental error. The 2-butoxyethanol (C_4E_1) was purchased from Aldrich, and the D_2O from Eurisotop isotopes. The liquid mixture was prepared by mass, and was introduced as a single phase into the sample chamber. The mass fraction composition of the sample was $w(C_4E_1) = 0.27$ [16], and the measured critical temperature was $T_c = 41.95^\circ\text{C}$. The phase volumes after

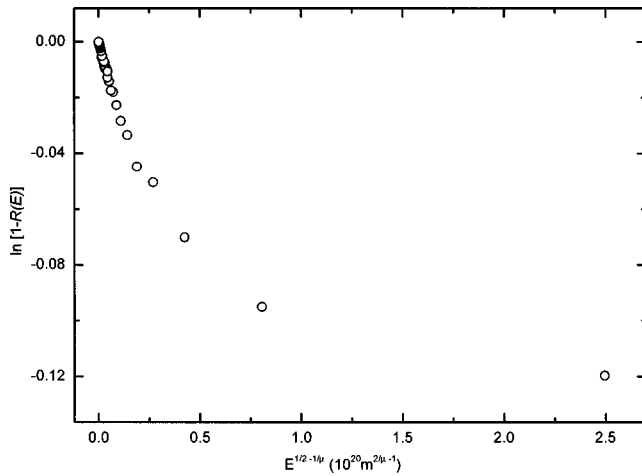


FIG. 1. Dietrich-Schack (DS) plot for the Si/air interface with $\mu=0.52$. This shows that there is no power law decay with $\mu=0.52$ in our control experiment.

separation were almost identical, and the sample was very turbid prior to separation. Reflectivity spectra were measured from the silicon/D₂O interface at 20 °C, and from the silicon/liquid mixture interface at several temperatures in the one-phase region ($T < T_c = 41.95$ °C)—24.90, 39.18, 39.90, 40.11, 40.86, 41.36, 41.70, 41.82, and 43.99 °C (two-phase region). Finally, the silicon surface was rinsed with distilled water and the reflectivity of the silicon/air interface was measured at 20 °C. Before applying the DS analysis, only data with $R < 0.1$ were chosen. This is partly to remove the effect of instrumental resolution—which rounds off the critical edge—and partly to introduce the E_- cutoff. Instrumental resolution alone would suggest that the cutoff be made at $R = 0.3$; however, the empirical choice of $R = 0.1$ appears also to remove the effects arising from temperature resolution.

In Figs. 1 and 2 we show the DS fitting for the silicon/air and silicon/D₂O (control runs) interfaces, assuming a slowly decaying profile with $\mu = 0.52$. Clearly, this is not the case, since there is no linear relationship as $x \rightarrow \infty$. Furthermore,

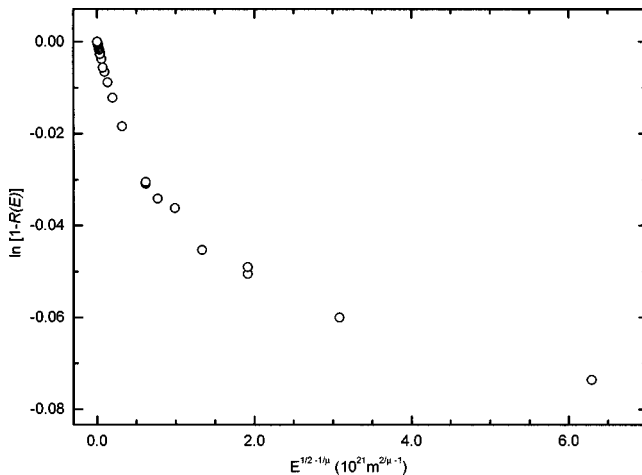


FIG. 2. DS plot for the Si/D₂O interface with $\mu=0.52$. This shows that there is no power law decay with $\mu=0.52$ in our control experiment.

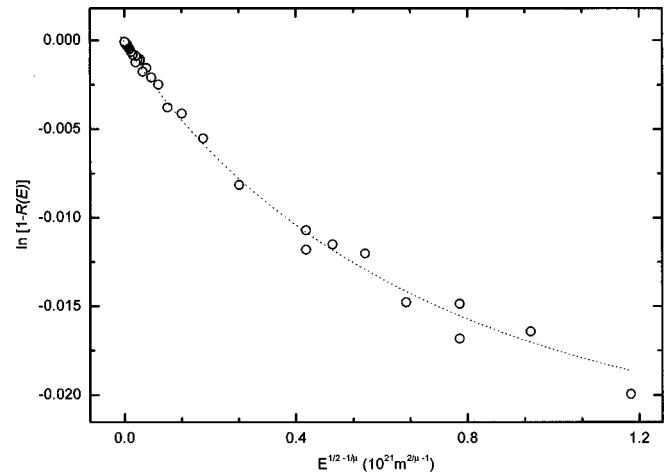


FIG. 3. DS plot for the Si/liquid mixture interface at 24.90 °C with $\mu=0.52$, showing that there is no pronounced power law decay. (The dotted curve is a guide to the eye.)

the data for the liquid mixture at 24.90 °C also do not produce a straight line for $\mu=0.52$, as shown in Fig. 3. However, at temperatures closer to T_c (Fig. 4) a linear relationship is obeyed with the exponent $\mu=0.52$ being satisfactory. In Fig. 5 we examine how well the exponents $\mu=0.34, 0.52$, and 0.70 represent the data at $T=41.82$ °C. In Fig. 6 we show how the “goodness of fit” (product moment correlation coefficient) of the straight line varies as a function of μ for these data and for the data at $T=24.90$ °C by plotting the correlation coefficients versus μ . The available data indicate an optimum value $\mu=0.53 \pm 0.02$.

If the data over the experimental temperature range are fitted with a value of $\mu=0.52$ and the correlation coefficient plotted as a function of the reduced temperature, as shown in Fig. 7, then it is interesting to note how dominant the power law part of the critical adsorption profile is even 2–3 K away from T_c .

In principle, a further straightforward stage in the analysis is the evaluation of the universal constant P_0 . Dietrich and Schack considered potentials with the asymptotic limit $V(z$

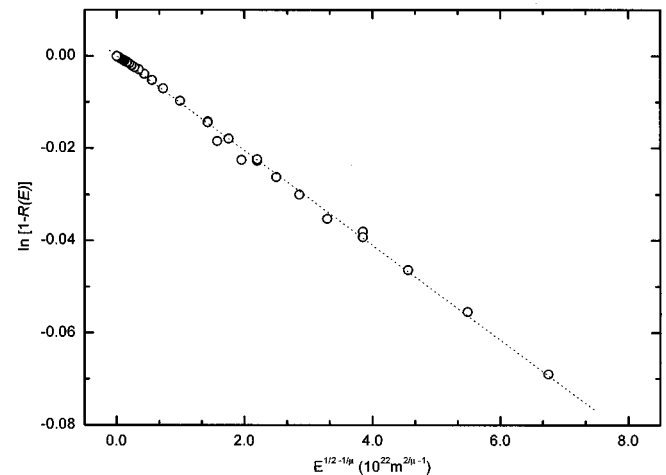


FIG. 4. DS plot for the Si/liquid mixture interface at $T=41.82$ °C, clearly indicating the adherence of the data to a straight line for $\mu=0.52$, in agreement with theory. The dotted line is a linear fit to the data.

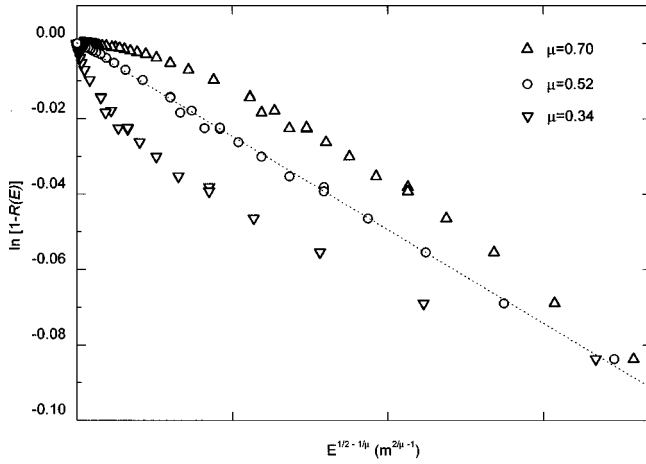


FIG. 5. DS plot showing the evolution of the straight line shown in Fig. 4 for a selection of μ values. The horizontal scales for $\mu = 0.34, 0.52,$ and 0.70 are $0 \rightarrow 8 \times 10^{-37}, 0 \rightarrow 3.15 \times 10^{-21},$ and $0 \rightarrow 1.85 \times 10^{-14},$ respectively. The dotted line is a linear fit to the data $\mu = 0.52.$

$\rightarrow \infty) = \lambda z^{-\mu},$ where $V(z) = (8\pi m_n/h^2)[\tilde{V}_m(z) - \tilde{V}_b].$ The parameter λ can be derived from the gradient dy/dx of the straight line plotted earlier through $\lambda = |(dy/dx)/[2I(\mu)]|^\mu.$ $I(\mu)$ is a universal function given for the case of interest here by

$$I(\mu) = \sum_{n=0}^{\infty} c_n \{ [1 + \mu(n-1/2)] n! \}^{-1}, \quad (4)$$

where $c_n = -\Gamma(n-1/2)(2\pi^{1/2}),$ and Γ is the gamma function. P_0 is then calculated from the relationship

$$P_0 = \frac{\lambda}{(4\pi\xi_0^\mu m'_0)}. \quad (5)$$

In Eq. (5) m'_0 is related to the m_0 defined earlier, and is the amplitude of the bulk solution order parameter written in terms of the scattering length densities of the two coexisting phases. Although it is preferable to measure the amplitudes

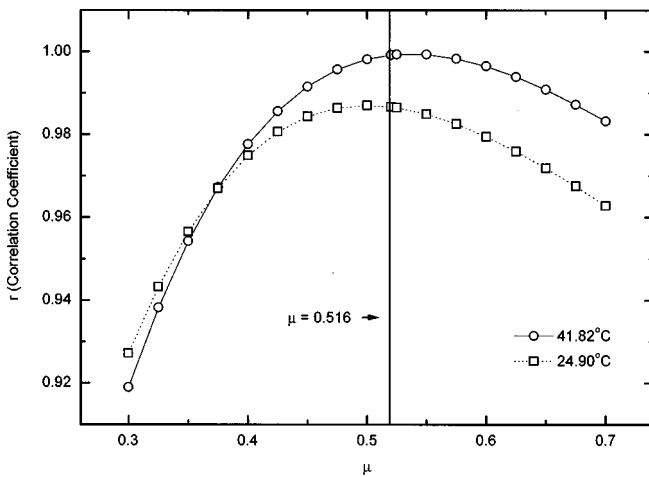


FIG. 6. r (correlation coefficient) as a function of μ for $T = 24.90$ and $41.82^\circ\text{C}.$

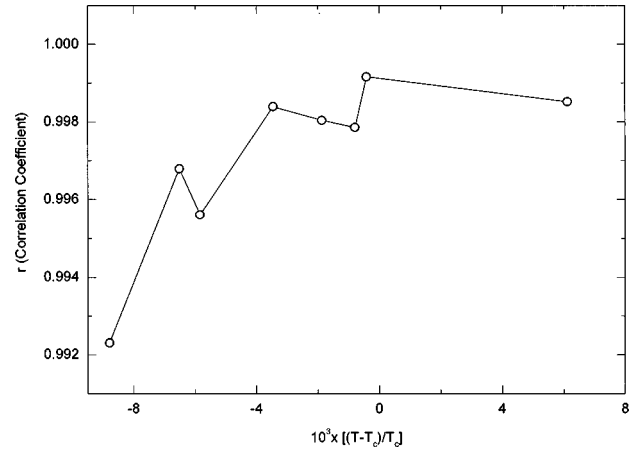


FIG. 7. r (correlation coefficient) as a function of scaled reduced temperature. Note that for $T = 24.9^\circ\text{C}$ [$t = (T - T_c)/T_c = -0.0541$], $r = +0.98161$ (see Fig. 6).

ξ_0 and m'_0 independently, for the mixture studied here the values of $\xi_0 = 3.90 \text{ \AA}$ [16] and $m'_0 = 1.10 \times 10^{15} \text{ m}^{-2}$ [17] are available from the literature, and we use these values to estimate $P_0.$ Putting these values into Eq. (5) and taking the optimized value of $\mu = 0.53,$ we calculate a value of $P_0 \approx 0.11,$ which is considerably smaller than the theoretical value of $P_0 = 0.94 \pm 0.05.$ However, despite the determination of λ being extremely sensitive to the value of μ chosen, the calculated value of P_0 is reasonably insensitive to $\mu.$ Accordingly, we need to seek an explanation for the discrepancy between the value of P_0 determined here and the values determined by other experimentalists and theorists. Flöter and Dietrich [18] summarized the values of P_0 (also written as c_+) reported in the literature. It was pointed out by Flöter and Dietrich that the definition of the correlation length needs to be fully taken into account when calculating the amplitude $P_0.$ However, it is unlikely that this is the source of the discrepancy.

A possible source of error may be assuming that the mixture is a true binary mixture. In fact, this is not strictly true, since the system, through ionic dissociation of the water, contains at least four components. However, the critical signatures remain unchanged but the coexistence curve is skewed, and T_c is not the minimum coexistence temperature [17]. The uncertainty in the choice, or indeed definition, of m'_0 may therefore affect the outcome of the calculation, although, we believe, to a minor extent. In future experiments it would be worthwhile to investigate simpler binary liquid mixtures such as the alkane + perfluoroalkane type.

Before closing this paper, we should mention the remaining findings of this study. Principally, we find that the total reflection edge advances toward higher angles, and the reflectivity spectrum in its proximity changes shape as $T \rightarrow T_c;$ this advancement is a signature of the critical adsorption. On the whole, despite the small measurable changes in reflectivity near the TRE, the spectra do not change significantly in the region $39.90 < T/^\circ\text{C} < 41.82.$ However, there is a measurable change in reflectivity at higher Q between the spectra at 24.9 and $39.9^\circ\text{C}.$ There are insufficient spectra to determine whether this is an abrupt transition or whether there is a smooth change in structure with increasing tem-

perature. The spectra can be analyzed in terms of layer models using the traditional optical matrix method. What is clear from this analysis is that the D₂O is preferentially adsorbed, as is borne out by the success of the DS analysis. What is unclear, unfortunately, is the nature of the short-range profile. Either a single-layer model (with a D₂O-rich composition) or oscillatory multilayer models with an unquantifiable number of layers can be used. However, toward phase separation the single layer model becomes increasingly unfavorable [19]. Further work has been proposed which concentrates on determining the details of this interesting short-range structure.

In summary, we have been able to provide experimental evidence for the theoretically predicted one-to-one correspondence between the power-law part of the critical adsorption profile and the neutron reflectivity for the interface between a near-critical mixture of 2-butoxyethanol+D₂O and silicon. The profile decays as $Az^{-\mu}$ and the experimentally determined value of $\mu = 0.53 \pm 0.02$ is in excellent agreement

with the theoretical value $\mu = 0.516 \pm 0.005$. The parameter A can also be determined for a given μ , and, in turn, the universal constant P_0 can be evaluated. The so-determined value of $P_0 \approx 0.11$ is not in agreement with the theoretically predicted ($P_0 = 0.94 \pm 0.05$) or other experimentally determined values. Further work is necessary to reconcile the discrepancy in the value of P_0 .

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