

Evidence for dipole surface orientational order at critical interfaces

A. Mukhopadhyay,¹ C. L. Caylor,² and B. M. Law¹

¹Condensed Matter Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506-2601

²Physics Department, Cornell University, Ithaca, New York 14853

(Received 13 October 1999)

At the critical interface of dipolar systems theory predicts that the amplitude of the surface orientational order $\alpha_2(z) \sim m^* d^2 v(z)/d^2 z^2$, where m^* is a reduced dipole moment and $v(z)$ is the local composition at position z within the interface. We find quantitative agreement with these predictions for two different critical binary liquid mixtures composed of a highly polar and a nonpolar component.

PACS number(s): 68.10.-m, 68.35.Rh, 68.35.Bs, 78.20.-e

Orientalional order at the interfaces between two phases is of importance in determining the physical, rheological, and mechanical properties of many different systems. For example, the orientational alignment of a rubbed polymer film on a solid substrate induces orientational order in an adjacent thick liquid crystal film [1]; such effects are important in flat panel liquid crystal displays. Similarly, the orientational alignment of amphiphilic molecules at the interface between an oil-rich phase and a water-rich phase in surfactant solutions produces micellar, hexatic, or lamellar phases under differing conditions of composition and temperature [2]. Frequently the orientational order at an interface occurs within a single monolayer, and therefore it is sufficient to determine the average orientation θ of the molecules relative to the surface normal (z direction) within this layer. If, however, the thickness of the interface ξ is much larger than a molecular size, for example, near a phase transition point, then the average orientation through the interface may be a gross misrepresentation of the orientational order within the interface and, in general, this orientational order denoted by α_2 will be a function of z through the interface. The positional dependence of $\alpha_2(z)$ has largely been ignored in the interpretation of most experiments where surface orientational order is present, however, it has been the subject of considerable theoretical interest for many years [3].

A particularly appropriate example where the z dependence of $\alpha_2(z)$ cannot be ignored is at the interfaces of highly polar solutions. In these solutions, within a distance $\sim \xi$ of the interface, dipoles in the phase of higher (lower) static dielectric constant preferentially orient parallel (perpendicular) to the interface (Fig. 1). The physical origins for this surface orientational order can be qualitatively understood by considering the electrostatic interaction between a dipole and its image dipole near an interface. The interaction energy is given by

$$E = -\frac{m^2}{16} \frac{\epsilon_{bs} - \epsilon_{as}}{\epsilon_{as}(\epsilon_{as} + \epsilon_{bs})} \frac{1 + \cos^2 \theta}{z^3}, \quad (1)$$

where m is the dipole moment and ϵ_{is} is the bulk static dielectric constant in phase i . The dipole is assumed to be situated in phase a . For fixed z if $\epsilon_{as} < \epsilon_{bs}$ E is a minimum for $\theta = 0$ or π and the dipole is preferentially oriented per-

pendicular to the interface while if $\epsilon_{as} > \epsilon_{bs}$ E is a minimum for $\theta = \pi/2$ or $3\pi/2$ and the dipole is preferentially oriented parallel to the interface.

These electrostatic considerations only provide a *qualitative* understanding of how dipolar orientational order arises at interfaces. In reality, the situation is far more complicated because the local volume fraction $v(z)$ depends upon the distance z in the vicinity of an interface and, in fact, there is a coupling between the orientational order $\alpha_2(z)$ and $v(z)$. If $\hat{v}(z, \theta)$ denotes the local volume fraction of polar molecules at z with orientation θ , then this function can be deconvoluted into $v(z)$ (the local volume fraction averaged over all angles θ) and a normalized angular distribution $\alpha(z, \theta)$ via the equation $\hat{v}(z, \theta) = v(z)\alpha(z, \theta)/2\pi$ where $\int_0^\pi \alpha(z, \theta) \sin \theta d\theta = 1$ [4]. The function $\alpha(z, \theta)$ is conveniently expanded in Legendre polynomials

$$\alpha(z, \theta) = \frac{1}{2} + \alpha_2(z) \frac{3 \cos^2 \theta - 1}{2}, \quad (2)$$

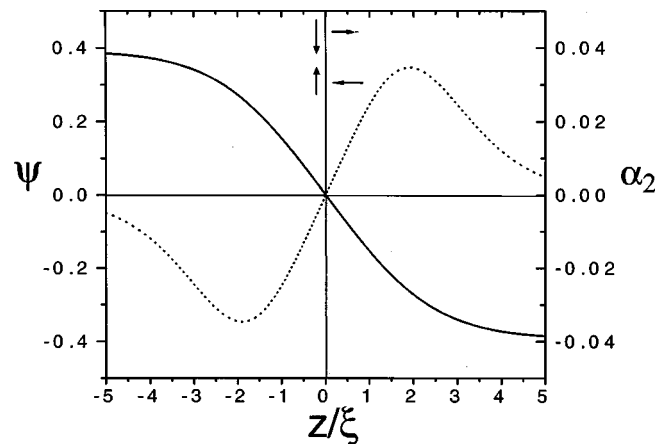


FIG. 1. The solid line represents the dipolar order parameter $\psi(z)$ [Eq. (4)], while the dotted line represents the orientational order $\alpha_2(z)$ [Eq. (3)] as a function of z/ξ for the critical mixture cyclohexane+2-nitroanisole at a reduced temperature of $t=0.1$. The interface is situated at $z=0$. In regions of higher (lower) dipole density corresponding to negative (positive) values of $\alpha_2(z)$ the dipoles are preferentially oriented parallel (perpendicular) to the interface. For $|z/\xi| \gg 1$ orientational order is absent [$\alpha_2(z)=0$].

where we have neglected higher order terms and also assumed that external fields are absent so that odd terms in Eq. (2) are zero. In this equation $\alpha_2(z)$ provides a measure of the amplitude of the orientational order at position z . If $\alpha_2(z) = 0$ then orientational order is absent. A number of theoretical calculations [5,6] indicate that $\alpha_2(z)$ couples to $d^2 v(z)/dz^2$ and $[dv(z)/dz]^2$ although the predominant contribution seems to be provided by the former [7].

These surface dipolar effects are particularly interesting to study at the critical liquid/liquid interface of a critical binary liquid mixture because the thickness of the interface, measured by the correlation length $\xi = \xi_0 t^{-\nu}$, can conveniently be controlled by varying the reduced temperature $t = |T - T_c|/T_c$ relative to the mixture's critical temperature T_c where the universal critical exponent $\nu = 0.632$ [8] and ξ_0 is a system dependent amplitude. A comparison of the density functional calculations of Frodl and Dietrich [4] with the theoretical analysis of Sluckin [5] indicates that $\alpha_2(z)$ is described by the equation [9]

$$\alpha_2(z) \approx \frac{D \xi_0^2 m^*}{\psi_0} \frac{d^2 \psi(z)}{dz^2} \sim t^{\beta+2\nu}, \quad (3)$$

where the dimensionless dipole moment $m^* = m/\sqrt{\sigma^3 u_0}$, σ is the average hard sphere diameter, u_0 is the Lennard-Jones interaction well depth between two dipoles, $D = 0.2402$, and for a critical interface the local order parameter $\psi(z)$ is described by the Fisk-Widom interfacial profile [10]

$$\psi(z) = v(z) - v_c = \psi_0 t^\beta f(z/2\xi), \quad (4)$$

where the universal function

$$f(x) = \tanh(x) \sqrt{\frac{2}{3 - \tanh^2(x)}}. \quad (5)$$

Here $\psi_0 t^\beta$ describes the shape of the coexistence curve for the liquid mixture with critical exponent $\beta = 0.328$ [8] and v_c is the dipolar critical volume fraction. The functions $\psi(z)$ [Eq. (4)] and $\alpha_2(z)$ [Eq. (3)] are shown in Fig. 1 for the critical liquid mixture cyclohexane + 2-nitroanisole at a reduced temperature of $t = 0.1$. This figure illustrates that the orientational order is present only in the vicinity of the interface [i.e., $\alpha_2(z) = 0$ for $|z| \gg \xi$] and negative (positive) values of $\alpha_2(z)$ indicate a preferential orientation parallel (perpendicular) to the interface [4] in agreement with our previous simple electrostatic considerations. The form of $\alpha_2(z)$ in Eq. (3) implies that surface orientational order vanishes proportional to $t^{\beta+2\nu}$; according to the simplistic electrostatic considerations [Eq. (1)] this is because the dipole/image dipole interaction weakens as T_c is approached ($\epsilon_{bs} - \epsilon_{as} \sim t^\beta \rightarrow 0$ as $t \rightarrow 0$). In earlier work [9] Eq. (3) was used to qualitatively account for the ellipsometric data acquired from the critical interface of a critical ionic solution where it is believed that oppositely charged ion pairs form pseudodipoles. The purpose of this Rapid Communication is to quantitatively test Eq. (3) using a more ideal model composed of a critical binary liquid mixture formed from a highly polar and a non-polar component where the dipole moment and optical anisotropy of the polar component are known.

Each dipole moment m has an optical dielectric ellipsoid with principal dielectric constants ($\epsilon_1, \epsilon_2, \epsilon_3$) associated with it where, for the dipoles we consider, ϵ_1 lies to a reasonable approximation along the m direction. These dipoles are assumed to be situated within a structureless nonpolar solvent with optical dielectric constant ϵ_s . Our surface sensitive optical technique of ellipsometry couples to these optical dielectric constants. This technique measures the ellipticity [11]

$$\bar{\rho} = \text{Im}(r_p/r_s)|_{\theta_B} = \bar{\rho}_{int} + \bar{\rho}_{cap} \quad (6)$$

at the Brewster angle θ_B , where r_i is the complex reflection amplitude for polarization i , which for a liquid interface has contributions from the intrinsic composition variation (int) through the interface and from capillary wave fluctuations (cap). The surface orientational order [Eq. (3)] gives rise to a local optical anisotropy $\epsilon_{\parallel}(z) \neq \epsilon_{\perp}(z)$ where these terms represent the *angle* and *composition* averaged dielectric constants parallel (\parallel) and perpendicular (\perp) to the interface. The connection between the dipole dielectric ellipsoid ($\epsilon_1, \epsilon_2, \epsilon_3$), the angular distribution $\alpha(z, \theta)$, and $\epsilon_{\parallel(\perp)}(z)$ is somewhat complicated and is explained in [12,13]. The intrinsic ellipticity contribution is described by the anisotropic Drude equation [11,14]

$$\bar{\rho}_{int} = \frac{\pi}{\lambda} \frac{\sqrt{\epsilon_a + \epsilon_b}}{\epsilon_a - \epsilon_b} \int \left[\epsilon_{\parallel}(z) + \frac{\epsilon_a \epsilon_b}{\epsilon_{\perp}(z)} - (\epsilon_a + \epsilon_b) \right] dz, \quad (7)$$

where $\epsilon_i = n_i^2$ ($i = a, b$) are the optical dielectric constants of the two bulk phases at wavelength λ with $i = a$ representing the incident medium while the capillary wave contribution takes the form [9]

$$\bar{\rho}_{cap} = \frac{\pi}{\lambda} (n_a - n_b) \xi A \int \frac{dK}{2\pi} [|\phi_{\parallel}(K)|^2 + 2|\phi_{\perp}(K)|^2] \times \ln[1 + (B/K)^2], \quad (8)$$

which is a generalization of an earlier result [15] in the presence of surface anisotropy, where $\phi_i(K)$ is proportional to the inverse Fourier transform of $d\epsilon_i(z)/dz$ [9], $A = 0.11$, $B = 1.5$, and K is a surface wave vector.

In the absence of any surface anisotropy $\epsilon_{\parallel}(z) = \epsilon_{\perp}(z) = \epsilon(z)$ in Eqs. (7) and (8) and the ellipticity [15]

$$\bar{\rho} = C [I_{int} + I_{cap}] t^{\beta-\nu} \quad (9)$$

where the *shape* of the interfacial dielectric profile $\epsilon(z)$ only enters through the *universal* numbers I_{int} and I_{cap} which represent, respectively, integrals over the universal function $f(z)$ [Eq. (5)] or over the inverse Fourier transform of $df(z)/dz$, and all system dependent parameters are contained within the factor C . Excellent quantitative agreement [15] is found between Eq. (9) and the experiments of Schmidt and coworkers at the critical interfaces of binary liquid mixtures [16], polymer solutions [17], and pure fluids [18] with no adjustable parameters. In Fig. 2 we show a comparison between Eq. (9) (solid line) and the critical binary liquid mixture methanol plus carbon disulphide (triangles) where methanol has a small reduced dipole moment $m^* \approx 1.0$ (Table I) and carbon disulphide is nonpolar. The small m^*

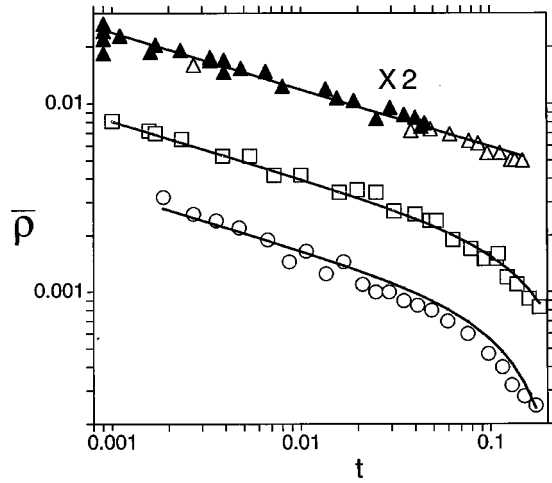


FIG. 2. Plot of the ellipticity $\bar{\rho}$ as a function of reduced temperature t for carbon disulphide + methanol (CM, triangles), which has been multiplied by a factor of 2 for clarity, carbon disulphide + acetonitrile (CA, squares), and cyclohexane + 2-nitroanisole (CN, circles). The solid (open) triangles for CM are from [16] (our measurements). In this mixture methanol possesses only a small reduced dipole moment $m^* \approx 1.0$ and the interface is to a good approximation isotropic where the ellipticity $\bar{\rho} \sim t^{\beta-\nu}$ [Eq. (9)]; the solid line is from the theory in [15] in the absence of orientational order. For CA and CN the solid lines represent a fit to Eqs. (2)–(8) as described in the text. At small t the surface anisotropy vanishes as expected according to Eq. (3) and the ellipticity returns to the isotropic case with $\bar{\rho} \sim t^{\beta-\nu}$. In this figure our $\bar{\rho}$ data (open symbols) possess an error of $\sim 5 \times 10^{-5}$.

value for methanol only leads to deviations less than $\sim 0.6\%$ from the isotropic theory represented by Eq. (9) for all $t \leq 0.15$ because of the m^{*4} dependence in Eq. (3).

It is important to note that the shape of the interfacial profile only enters $\bar{\rho}$ through the universal numbers I_{int} and I_{cap} in Eq. (9), hence, the ellipticity $\bar{\rho}$ will always exhibit a $t^{\beta-\nu}$ temperature dependence provided the interfacial profile is locally isotropic; any deviations from a $t^{\beta-\nu}$ dependence can only be produced by the presence of surface anisotropy with $\varepsilon_{\parallel}(z) \neq \varepsilon_{\perp}(z)$. Additionally according to Eq. (3) surface orientational order will only be apparent for sufficiently large t where $\alpha_2(z)$ is nonzero; in the limit $t \rightarrow 0$, $\alpha_2(z) \rightarrow 0$ and

therefore $\varepsilon_{\parallel}(z) \approx \varepsilon_{\perp}(z)$ and we return to the locally isotropic case [Eq. (9)]. This is precisely the behavior that we observe for two different nonpolar + polar critical mixtures, carbon disulphide + acetonitrile (CA) and cyclohexane + 2-nitroanisole (CN) (Fig. 2), where the parameters for the dipolar components are provided in Table I. These experiments were performed using a thermostat possessing a temperature stability of 1 mK over 4 h and thermal gradients less than 1 mK/cm where the liquid mixture was contained inside a horizontal 20 cc annealed pyrex cylinder of length 8 cm. The ellipticity $\bar{\rho}$ deviates from $t^{\beta-\nu}$ behavior only at large $t \sim 0.1$. The solid lines in Fig. 2 are a comparison between experiment and Eqs. (3)–(8) with only the reduced dipole moment $m^* = m^*(\text{expt})$ treated as an adjustable parameter. In Table I we compare $m^*(\text{expt})$ with estimates of this parameter from other sources $m^*(\text{est})$ [20–27]. Good agreement is found between $m^*(\text{expt})$ and $m^*(\text{est})$ to within $\sim 10\%$. Precise agreement with Eq. (3) should not be expected because the theoretical calculations [4] on which this equation is based assume *spherical* dipoles with a hard sphere diameter of σ . Of course, most highly polar molecules will be non-spherical in shape and therefore Eq. (3) can only provide an estimate of the actual behavior. Recently the influence of the nonspherical shape of dipolar molecules on the bulk phase diagram has been studied using density functional theory [19]; these methods have not yet been applied to the interfacial properties of such systems. Finally we note that the behavior observed for the highly polar mixtures in Fig. 2 cannot be explained by, for example, a cross-over to mean field behavior (far from T_c); under such circumstances $\beta = \nu = 0.5$ and $\bar{\rho} \sim t^{\beta-\nu}$ would level off at very large t .

In conclusion, we have found strong evidence for the existence of dipolar surface orientational order at the critical liquid/liquid interface of highly polar + nonpolar critical binary liquid mixtures where the amplitude of the surface anisotropy at position z is described by Eq. (3). As predicted the effects of surface anisotropy are only evident for sufficiently large reduced temperatures t ; at sufficiently small t the dipole/image dipole interaction weakens and we return to a locally isotropic interface where the ellipticity $\bar{\rho} \sim t^{\beta-\nu}$ [Eq. (9)]. This phenomenon of dipole/image dipole orientational order is expected to be generally applicable at any

TABLE I. Dipolar parameters.

	2-nitroanisole	acetonitrile	methanol
$\sigma(nm)^a$	0.65	0.45–0.50	0.38–0.46
$u_0 \times 10^{21}(J)^b$	2.68–2.83	3.33–3.71	3.94–4.44
$m(D)^c$	4.51	3.52	1.61
$m^*(\text{est}) = m / \sqrt{\sigma^3 u_0}$	1.59–1.64	1.65–2.00	0.75–1.08
$m^*(\text{expt})$	1.81	2.23	
Principal dielectric constants ^d			
ε_1	3.17	2.45	1.99
ε_2	2.64	1.55	1.73
ε_3	1.73	1.55	1.57

^aReference [20].

^bReference [23].

^cReference [25].

^dReference [27].

liquid/liquid interface even far from a critical point. The surface orientational order $\alpha_2(z)$ is expected to couple to $d^2 v(z)/dz^2$ for molecules of large dipole moment and the orientational order should *not* be represented by an average value through the interface. The interpretation of the orien-

tational order may become very complicated if both components of the liquid mixture are polar.

This research was supported by the National Science Foundation through Grant No. DMR-9631133.

- [1] X. Wei *et al.*, Phys. Rev. Lett. **82**, 4256 (1999).
- [2] S. Hyde *et al.*, *The Language of Shape* (Elsevier, Amsterdam, 1997).
- [3] See, for example, K. E. Gubbins, in *Fluid Interfacial Phenomena*, edited by C. A. Croxton (Wiley, Chichester, 1986), p. 469.
- [4] P. Frodl and S. Dietrich, Phys. Rev. E **48**, 3741 (1993).
- [5] T. J. Sluckin, Mol. Phys. **47**, 267 (1982); **43**, 817 (1981).
- [6] I. Szeifer and B. Widom, J. Chem. Phys. **90**, 7524 (1989); J.-P. Carton and L. Leibler, J. Phys. (Paris) **51**, 1683 (1990); B. Widom, J. Phys. Chem. **100**, 13 190 (1996).
- [7] A. Mukhopadhyay and B. M. Law (unpublished).
- [8] M. E. Fisher and J.-H. Chen, J. Phys. (Paris) **46**, 1645 (1985).
- [9] C. L. Caylor *et al.*, Phys. Rev. E **56**, 4441 (1997).
- [10] S. Fisk and B. Widom, J. Chem. Phys. **50**, 3219 (1969).
- [11] D. Beaglehole, Physica B & C **100**, 163 (1980).
- [12] For a dielectric ellipsoid oriented at angle θ relative to the z axis the *dipole* dielectric constants (signified by superscript d) perpendicular and parallel to the interface averaged over the azimuthal angle are, respectively, $\varepsilon_{\perp}^d(\theta) = [(\cos^2\theta/\varepsilon_1 + \sin^2\theta/\varepsilon_2)(\cos^2\theta/\varepsilon_1 + \sin^2\theta/\varepsilon_3)]^{-1/2}$ and $\varepsilon_{\parallel}^d(\theta) = {}_2F_1[\varepsilon_2\varepsilon_3/(\sin^2\theta/\varepsilon_1 + \cos^2\theta/\varepsilon_2)(\sin^2\theta/\varepsilon_1 + \cos^2\theta/\varepsilon_3)]^{1/4}$, where the hypergeometric function ${}_2F_1 = {}_2F_1\{\frac{1}{2}, \frac{1}{2}, 1; [-(\varepsilon_2 - \varepsilon_3)^2/4\sqrt{\varepsilon_2\varepsilon_3}]\}$. For each z we can now calculate the *dipole* dielectric constant averaged over the angular distribution $\alpha(z, \theta)$, namely, $\varepsilon_{\parallel(\perp)}^d(z) = \int_0^\pi \varepsilon_{\parallel(\perp)}^d(\theta) \alpha(z, \theta) \sin\theta d\theta$. Ellipsometry is sensitive to the *composition* averaged dielectric constant at each z [$\varepsilon_{\parallel(\perp)}(z)$], which can be calculated from the two-component Clausius-Mossotti relationship $F[\varepsilon_{\parallel(\perp)}(z)] = v(z)F[\varepsilon_{\parallel(\perp)}^d(z)] + [1 - v(z)]F(\varepsilon_s)$, where $F(x) = (x-1)/(x+2)$ [13] and $v(z)$ is the local volume fraction of dipoles Eq. (4).
- [13] R. F. Kayser, Phys. Rev. B **34**, 3254 (1986).
- [14] J. Lekner, *Theory of Reflection* (Martinus Nijhoff, Dordrecht, 1987).
- [15] V. L. Kuzmin and V. P. Romanov, Phys. Rev. E **49**, 2949 (1994).
- [16] J. W. Schmidt, Phys. Rev. A **38**, 567 (1988).
- [17] D. G. Miles, Jr. and J. W. Schmidt, J. Chem. Phys. **92**, 3881 (1990).
- [18] J. W. Schmidt and M. R. Moldover, J. Chem. Phys. **99**, 582 (1993).
- [19] B. Groh and S. Dietrich, Phys. Rev. E **55**, 2892 (1997).
- [20] Estimated from Eqs. (7.1) and (7.2) in [21] using data from [22].
- [21] J. N. Israelachvili, *Intermolecular and Surface Forces*, 2nd ed. (Academic, London, 1991).
- [22] *CRC Handbook of Chemistry and Physics*, 66th ed., edited by R. C. Weast, M. J. Astle, and W. H. Beyer (CRC Press, Boca Raton, 1985).
- [23] Estimated using Eq. (6.35) in [21] where the uv absorption frequency was determined from a Cauchy plot [13] using the refractive index data in [24] and assuming a typical error in this calculation of 10%.
- [24] J. Timmermans, *Physico-chemical Constants of Pure Organic Compounds* (Elsevier, New York, 1950).
- [25] Dipole moment in a non-polar solvent estimated using Eq. (8) in [26] using the gas phase dipole moment data in [22].
- [26] I. G. Ross and R. A. Sack, Proc. Phys. Soc. London, Sect. B **63B**, 893 (1950).
- [27] Estimated using J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), Sec. 13.2.