Dipole Orientational Order at Liquid/Vapor Surfaces

Jae-Hie J. Cho and Bruce M. Law

Condensed Matter Laboratory, Department of Physics, Kansas State University, Manhattan, Kansas 66506-2601
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We present ellipsometric observations of the orientational order α_2 of highly polar molecules at the noncritical liquid/vapor surface of critical polar + nonpolar mixtures. The dipoles, which are repelled from the interface via interactions with their image dipoles, are preferentially oriented with their axes parallel to the surface and possess an orientational order which is well described by $\alpha_2 \sim -t^{2\beta}D_+(z/\xi)$, where $t = |T - T_c|/T_c$ is the reduced temperature, $\beta = 0.328$ is a critical exponent, and D_+ is a universal function of the dimensionless depth z/ξ with *surface* correlation length ξ.

In recent years, there has been a lot of interest in trying to understand and ultimately trying to control the orientational order at surfaces. Molecules may become orientationally ordered because of steric, dipolar, or local interactions (e.g., hydrogen bonding) with the interface. This is a difficult problem because *both* the local orientational order $\alpha_2(z)$ (defined later) and local volume fraction $v(z)$ vary over similar length scales measured by the correlation length ξ, in the vicinity of the interface. There have been numerous theoretical studies and computer simulations of surface mediated orientational order [1]; however, experiments have never been as definitive or as detailed as one would desire. Essentially, without exception, the experiments have measured an average surface quantity which is invariably an integral over these local quantities, such as the relative adsorption $\Gamma \sim \int v(z)dz$ [2,3], the average orientational order within a surface layer [4], or the surface tension as a function of the dipolar mole fraction [3]. These average quantities are poor representations of how the local volume fraction and local orientational order vary as a function of distance z away from the surface. In general, $v(z)$ and $\alpha_2(z)$ are coupled [5]; therefore, $\alpha_2(z)$ can be definitively studied only after $v(z)$ is well understood.

The local volume fraction $v(z)$ has recently been determined in critical binary mixtures [6]; this now allows a study of $\alpha_2(z)$ in these systems. An important type of orientational order is dipole-induced orientational order, where a highly polar molecule becomes orientationally ordered due to its interaction with its image dipole in the vicinity of a surface. The purpose of this paper is to investigate this dipole/image dipole interaction at the liquid/vapor surface of critical binary liquid mixtures. The results determined from this investigation are applicable to pure fluids and uniaxial ferromagnets, as well as systems far from any critical point. Hence, the results should be of interest to a wide audience.

In binary mixtures, the orientational order can become extremely complex, especially if *both* components are polar. One component may become orientationally ordered in the vicinity of the other component; this asso-

ciated dipolar structure may then orient in the vicinity of an interface [7]. These intermolecular complications can be avoided by studying critical binary liquid mixtures composed of a nonpolar (N) + highly polar (P) component. Even for this simplest of choices, *four* distinct classes of interfacial behavior are expected where each class is determined by the relative magnitudes and signs of the short- and long-ranged forces that are present. For a dipole of dipole moment p, situated in phase α but near the surface of substrate phase s (vapor in our case), the energy of interaction between this dipole at depth z and angle θ (with respect to the $\hat{z}$ axis) and its image is given by [8]

$$U = +\frac{p^2(\epsilon_\alpha - \epsilon_s)(\cos^2\theta + 1)}{16\epsilon_\alpha(\epsilon_\alpha + \epsilon_s)z^3}, \qquad (1)$$

where ϵ_α and ϵ_s are the static dielectric constants. Equation (1) determines the long-range dipolar behavior. (A) If $\epsilon_\alpha < \epsilon_s$, the energy is a minimum for $\theta = 0$ or π, and the dipole preferentially has its axis oriented perpendicular to the surface where the dipoles tend to be *attracted* towards the interface because U is negative. Conversely, (B) if $\epsilon_\alpha > \epsilon_s$, the energy is a minimum for $\theta = \pi/2$ or $3\pi/2$, and the dipole preferentially has its axis parallel to the surface where, because U is positive, the dipoles tend to be *repelled* from the interface. The short-ranged behavior is governed by the relative magnitudes of the surface tension of the polar (σ_P) and nonpolar (σ_N) components. If (a) $\sigma_P < \sigma_N$, then the dipolar component is adsorbed at the surface and $v(z)$ represent the dipolar volume fraction; conversely (b) for $\sigma_P > \sigma_N$, the dipolar component is desorbed from the surface where $v(z)$ now represents the nonpolar volume fraction. The various combinations of conditions A or B with either conditions a or b lead to the four distinct classes of orientational adsorption behavior. Theory predicts that this dipole-induced orientational order will become important at interfaces when the reduced dipole moment $p^* = p/\sqrt{\sigma^3 u_o} \gg 1$ [9], where σ is the average

hard-sphere diameter and u_o is the Lennard-Jones potential well depth.

For the nonpolar + highly polar mixtures that we study, where the polar component is desorbed from the liquid/vapor surface, these mixtures fall into class Bb, where the dipoles are repelled from the interface by both short- and long-ranged forces with the dipolar axis oriented preferentially parallel to the surface. Equation (1) provides only a qualitative description of the orientational structure at an interface. In practice, the local volume fraction $\hat{v}(z, \theta)$, which is a function of both z and θ, must be minimized in order to determine the interfacial structure which possesses the lowest total free energy. It is convenient to separate $\hat{v}(z, \theta)$ into a local volume fraction $v(z)$, integrated over all orientations, and an orientational order parameter $\alpha(z, \theta)$ which determines the angular distribution where $\hat{v}(z, \theta) = v(z)\alpha(z, \theta)/2\pi$ with $\int_0^\pi \alpha(z, \theta)\sin\theta d\theta = 1$. The angular dependence of $\alpha(z, \theta)$ can be expressed in terms of Legendre polynomials [9,10],

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

where we have neglected higher order terms and also assumed that external fields are absent, so that odd terms in Eq. (2) are zero. For isotropic interfaces, $\alpha_2(z) = 0$ and orientational order is absent. The primary advantage of working near a second order phase transition, which simplifies this problem and makes it tractable, is that both $v(z)$ and $\alpha_2(z)$ are described by *universal* functions of the dimensionless distance z/ξ. The local volume fraction $v(z)$ is well understood [6], and will be described shortly. The local orientational order $\alpha_2(z)$, as far as we are aware, has never been measured previously at a liquid/vapor interface.

In our mixtures, component N completely saturates the liquid/vapor surface; in this "strong critical adsorption limit," the local volume fraction order parameter $m(z)$ is described by [11,12]

$$m(z) \equiv v(z) - v_c = M_- t^\beta P_\pm(z/\xi_\pm), \qquad (3)$$

where v_c is the critical volume fraction of component N, $M_- t^\beta$ describes the coexistence curve which separates the one-phase from the two-phase regime, $\xi_\pm = \xi_{0\pm} t^{-\nu}$ is the correlation length, $t = |T_c - T|/T_c$ is the reduced temperature relative to the critical temperature T_c, $\beta(= 0.328)$ and $\nu(= 0.632)$ are standard bulk critical exponents, $P_\pm \equiv P_\pm(x)$ is a universal surface scaling function (SSF), and throughout the remainder of this paper a subscript $+(-)$ refers to a quantity in the one- (two-) phase region. For the strong critical adsorption SSF, $P_\pm(x) \sim x^{-\beta/\nu}$, $x \ll 1$ [11] and $P_\pm(x) \sim e^{-x}$, $x \gg 1$ [12]. A single universal function with these properties has been shown to describe the adsorption behavior for five different non-

polar [13] or weakly polar [6] critical binary liquid mixtures.

The orientational order parameter will exhibit a similar scaling form to $m(z)$; specifically, it will take the scaling form

$$\alpha_2(z) = M_D t^\phi D_\pm(z/\xi_\pm), \qquad (4)$$

where M_D is a system dependent parameter, ϕ is a new critical exponent, while $D_\pm$ is another universal SSF. The universal function $D_\pm$ will possess the following features: $D_\pm(\infty) = 0$, $D_\pm(x) \sim e^{-x}$ for $x \gg 1$ [12], and $D_\pm(x) \sim x^Y$, where $Y = -\phi/\nu$ for $x \ll 1$, to ensure that the orientational order $\alpha_2(z)$ is finite and nonzero at T_c.

In order to test these scaling predictions, we study the dipole orientational order which occurs at the liquid/vapor interface of two PN critical liquid mixtures, 2-nitroanisole + cyclohexane (2NC) and 4-nitroanisole + cyclohexane (4NC), using the experimental technique of Brewster angle ellipsometry. The two differing forms of nitroanisole possess similar physical and optical properties, but rather different molecular structures which produce large ($p^* \simeq 2$) but differing dipole moments. For both mixtures $\sigma_N \ll \sigma_P$ and component N strongly adsorbs at the liquid/vapor surface. Ellipsometry measures the ellipticity $\bar{\rho} = \text{Im}(r_p/r_s)|_{\theta_B}$ at the Brewster angle θ_B, where r_i is the complex reflection amplitude for polarization i. The presence of dipole orientational order $\alpha_2(z)$ generates differing optical dielectric constants parallel $[\varepsilon_\parallel(z)]$ and perpendicular $[\varepsilon_\perp(z)]$ to the interface; the ellipticity $\bar{\rho}$ is sensitive to $v(z)$, $\varepsilon_\parallel(z)$, and $\varepsilon_\perp(z)$ as described in [14].

Only the one-phase orientational order behavior will be considered in this publication. The two-phase behavior, which is slightly more complicated, will be described in a future publication [15]. The P_+ function provides an excellent description of the behavior of the local volume fraction $v(z)$ for weakly polar or nonpolar mixtures. The ellipticity $\bar{\rho}_P$ (light solid line), calculated using P_+, is compared with the nonpolar critical binary liquid mixture 1,1,2,2-tetrabromoethane + n-dodecane (TD, circles) [13] in Fig. 1(a). For highly polar mixtures, such as 2NC, the experimental data [Fig. 1(b), squares] deviates significantly from $\bar{\rho}_P$ (light solid line) because of the presence of dipole-induced orientational order, where $\bar{\rho}_P$ has been calculated using the *bulk* correlation length amplitude $\xi_{0+} = 0.27$ nm. Two key physical differences between the experimental data and $\bar{\rho}_P$ should be noted: (i) the peak experimental ellipticity $\bar{\rho}_{peak}$ occurs at a *higher* reduced temperature t_{peak} than for the corresponding $\bar{\rho}_P$ curve, and (ii) the experimental amplitude for the ellipticity $\Delta\bar{\rho} \equiv \bar{\rho}_{peak} - \bar{\rho}_{BG}$, where $\bar{\rho}_{BG}$ is the background ellipticity at large t (~ 0.1), is *smaller* than for the $\bar{\rho}_P$ curve.

In earlier work on weakly polar or nonpolar mixtures, the position of the peak ellipticity was found to be well

described by [6]

$$(\xi_+/\lambda)_{\text{peak}} = \xi_{0+} t_{\text{peak}}^{-\nu}/\lambda = 0.064 \pm 0.006, \qquad (5)$$

provided that the surface tension difference between the two components $\Delta\sigma > 0.2$ erg/cm^2 [16]. Here, λ is the wavelength of the light used in the measurement of the ellipticity. Can Eq. (5) provide a good estimate of the correlation length amplitude *at the surface* ξ_{0+}^s (indicated by a superscript s) even for highly polar mixtures, or, does the orientational order parameter $\alpha_2(z)$ strongly influence the peak position? In order to make progress on these questions, following [12], we consider the following algebraic ansatz:

$$D_+(x) = \left(\frac{1 + dx}{x}\right)^{\phi/\nu} e^{-x}. \qquad (6)$$

This ansatz provides a simple description of the crossover behavior between the two asymptotic forms at small and large x. Hence, for the orientational order parameter $\alpha_2(z)$, with Eq. (6) in Eq. (4), there are three adjustable parameters, M_D, d, and ϕ, with which to improve the agreement between theory and experiment. Variation of these three parameters was found to change the shape of the $\overline{\rho}$ curve, but the reduced temperature t_{peak} at which $\overline{\rho}_{\text{peak}}$ occurs was only marginally influenced by these three parameters [15]. Thus, introduction of orientational order $\alpha_2(z)$ with the correlation length *fixed* at its bulk value ξ_{0+}, cannot explain the 2NC experimental results. The only other parameter which is available for shifting the peak position is the correlation length amplitude at the surface ξ_{0+}^s due to the dipolar interaction, which may differ from its bulk value ξ_{0+}. Larger values of ξ_{0+}^s ($> \xi_{0+}$) shift $\overline{\rho}_{\text{peak}}$ to larger reduced temperatures; these larger values for ξ_{0+}^s, corresponding to a *stretched* adsorption profile, are indicative that the dipoles are *repelled* from the surface by their image dipoles. The dashed line in Fig. 1(b) shows the influence of increasing $\xi_{0+}^s = 0.42$ nm on the ellipticity $\overline{\rho}_P$, in the absence of orientational order [$\alpha_2(z) = 0$]; this value for ξ_{0+}^s is approximately what one would calculate using Eq. (5). It can be seen in this figure that larger ξ_{0+}^s not only shifts the peak to larger reduced temperatures but also increases the amplitude $\Delta\overline{\rho}$.

Extensive modeling with $\xi_{0+}^s = 0.42$ nm and $\alpha_2(z)$, given by Eqs. (4) and (6), indicates that the experimental data is best described by a surface critical exponent $\phi \simeq 2\beta$ [15]. This new surface critical exponent is rather provocative. Previous theoretical [5,10,17] and experimental work [14] at the *critical liquid/liquid interface* indicates that $\alpha_2(z)$ is coupled to $d^2m(z)/dz^2 \sim t^{\beta+2\nu}$ and/or $[dm(z)/dz]^2 \sim t^{2(\beta+\nu)}$; neither of these forms work here, for the *noncritical liquid/vapor interface*. However, if we continue to believe that $\alpha_2(z)$ is coupled to some function of $m(z)$, then $\phi \simeq 2\beta$ suggests that perhaps
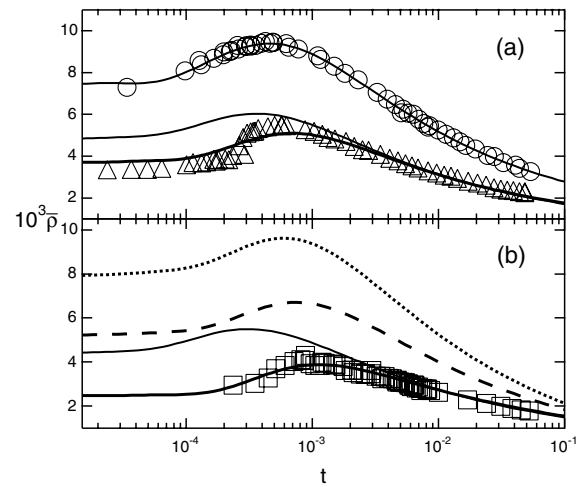

FIG. 1. (a) Comparison of the nonpolar mixture TD (circles) and highly polar mixture 4NC (triangles) with either the strong adsorption $\overline{\rho}_P$ (light solid line) or orientational order model $\overline{\rho}_\alpha$ (heavy solid line). (b) Comparison of various adsorption/orientational order models with the highly polar critical mixture 2NC (squares): $\overline{\rho}_P$ model with $\xi_{0+} = 0.27$ nm (light solid line) or $\xi_{0+}^s = 0.42$ nm (dashed line), $\overline{\rho}_\alpha$ model with $\xi_{0+}^s = 0.42$ nm and $M_D = -15.1$ (heavy solid line) or $M_D = +15.1$ (dotted line).

$$\alpha_2(z) = M_D[m(z)/M_-]^2. \qquad (7)$$

Equation (7) is an acceptable ansatz in accordance with Eq. (4) and the expected scaling properties. Thus, in this new model, there are only two adjustable parameters: ξ_{0+}^s and M_D. The ellipticity, denoted in this case by $\overline{\rho}_\alpha$, is compared with the 2NC data for $M_D = -15.1$ (heavy solid line) and $M_D = +15.1$ (dotted line) with $\xi_{0+}^s = 0.42$ nm in Fig. 1(b). The former curve provides a quantitative description of the experimental data. Negative (positive) values for M_D indicate that the dipolar molecules are oriented with their axes parallel (perpendicular) to the interface [9,10]. These results therefore demonstrate that dipolar molecules are *repelled* from the interface ($\xi_{0+}^s > \xi_{0+}$) with their axes oriented primarily *parallel* to the interface ($M_D < 0$) in agreement with the simple electrostatic considerations from Eq. (1).

The ellipticities $\overline{\rho}_P$ (light solid line, for the bulk correlation length ξ_{0+}) and $\overline{\rho}_\alpha$ (heavy solid line) are also compared with the 4NC mixture in Fig. 1(a) (triangles) where the parameters for both mixtures are listed in Table I. The experimental deviation from the $\overline{\rho}_P$ curve

TABLE I. Dipolar parameters.

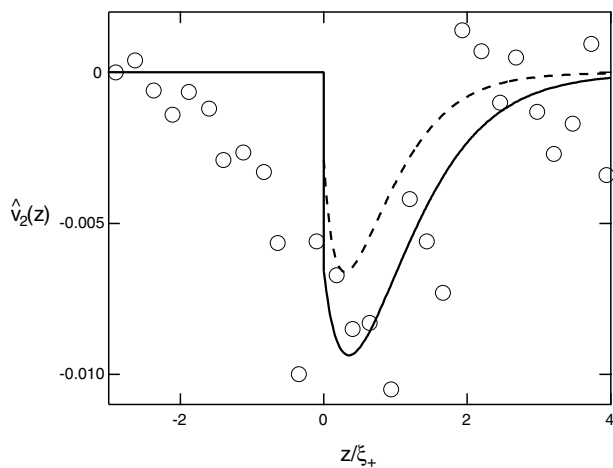| Mixture	ξ_{0+} (nm)	ξ_{0+}^s (nm)	M_D	$p(D)$[a]	p^*
2NC	0.27	0.42	-15.1	4.81	1.77
4NC	0.26	0.35	-6.2	4.75	1.74

[a]Ref. [18].

FIG. 2. Comparison of the local density $\hat{v}_2(z)$, derived from the $\alpha_2(z)$ model [Eq. (7)] at $t = 0.05$, for 2NC (solid line) and 4NC (dashed line) with computer simulations (circles) [9].

is less for 4NC than for 2NC implying that the dipole moment $p(4NC)$ is significantly less than $p(2NC)$ in deference to the vapor values listed in Table I. The 4NC mixture is described well by $\overline{\rho}_\alpha$ with $\xi_{0+}^s > \xi_{0+}$ and $M_D < 0$ (Table I).

Is there any theoretical evidence which supports the form for $\alpha_2(z)$ exhibited in Eq. (7)? Many years ago Eggebrecht, Thompson, and Gubbins [9] studied the orientational order that occurs at the liquid/vapor surface of a highly polar *pure* fluid far from its critical point, using computer simulations. There is a one-to-one correspondence between the local number density $\rho(z)$ of a pure fluid and $v(z)$; hence, these computer simulations can be directly compared with our experimental results. In our notation, the localized density $\hat{v}_2(z) \equiv [1 - v(z)]\alpha_2(z)/4\pi$ is calculated as a function of z/ξ_+, where ξ_+ is the bulk correlation length. There is remarkable agreement between the computer simulation results (circles, Fig. 2) and our model function deduced for 2NC (solid line) and 4NC (dashed line), at least on the liquid side of the interface ($z > 0$). Our experiments provide no information about the behavior of molecules on the vapor side of the interface ($z < 0$).

In summary, we have studied the desorption and orientational order of dipolar molecules at the liquid/vapor surface of two nonpolar + highly polar critical mixtures. The long-ranged dipole-image dipole repulsion stretches the adsorption profile causing the surface correlation length amplitude $\xi_{0+}^s > \xi_{0+}$ (its bulk value), where, in addition, the dipolar axis is preferentially oriented parallel to the surface ($M_D < 0$). These observations are in agreement with simple considerations arrived at via the dipole interaction [Eq. (1)]. Furthermore, we have shown

that the experimental results are consistent with an orientational order critical exponent $\phi \equiv 2\beta$ where, in particular, the orientational order parameter $\alpha_2(z)$ couples to the *square* of the local volume fraction order parameter $m(z)$ via Eq. (7) (Fig. 1). These surprising results are in excellent agreement with simulation data on the liquid side of the interface (Fig. 2, $z > 0$).

Finally, we hope that this work will stimulate additional theoretical and experimental research into this interesting area of surface physics. Measurements using other techniques would be particularly welcome, as they would provide an alternative test of the model proposed in this publication.

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