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An X-ray diffuse scattering study of domains in $F(CF_2)_{10}(CH_2)_2OH$ monolayers at the hexane-water interface

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Abstract. – X-ray off-specular diffuse scattering is used to directly probe the statistical distribution of domains in monolayers of $F(CF_2)_{10}(CH_2)_2OH$ adsorbed at the hexane-water interface. These domains appear very near a transition from a monolayer solid to gas phase. The domains have a nearly constant radius of $\approx 1.5\,\mu$m and a nearest-neighbor separation that varies from 2 to $8\,\mu$m with temperature. Evidence that the domains are of equilibrium size suggests that the domain line tension, $\lambda_t \approx 3 \times 10^{-11}$ N, can be determined.

Gibbs monolayers of soluble surfactants at liquid-liquid interfaces have a potentially very rich phase behavior, similar to Langmuir monolayers of insoluble surfactants supported at the liquid-vapor interface [1]. Recently, Brewster angle microscopy (BAM) was used to demonstrate the formation of domains in a monolayer of soluble surfactants, $F(CF_2)_{10}(CH_2)_2OH$, adsorbed at the water-hexane interface [2]. It is reasonable to expect that these domains are stabilized by a balance between the domain line tension and repulsive dipole interactions from the oriented surfactants, similar to domain formation in Langmuir monolayers [3, 4]. This balance would determine the size of a domain in equilibrium. However, equilibrium domain sizes are commonly not observed in Langmuir monolayers. For example, compression of a Langmuir monolayer increases the interfacial density and, in equilibrium, should result in the creation of more domains of equilibrium size. Instead, McConnell has shown that the energy barrier to create a new domain in a Langmuir monolayer is very large and the monolayer is more likely to develop larger metastable domains, as is commonly observed [3, 4]. It is also observed that domains can be altered in shape and size by heating the monolayer through a melting transition, then re-cooling, again indicating that the original domains were not in equilibrium [5].

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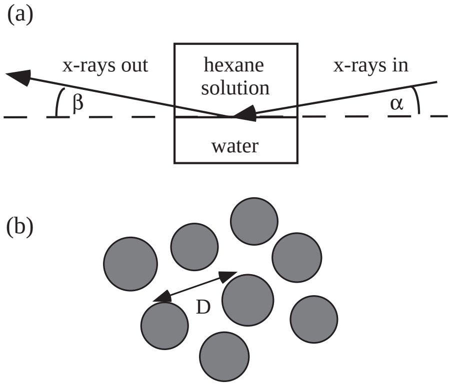

Fig. 1

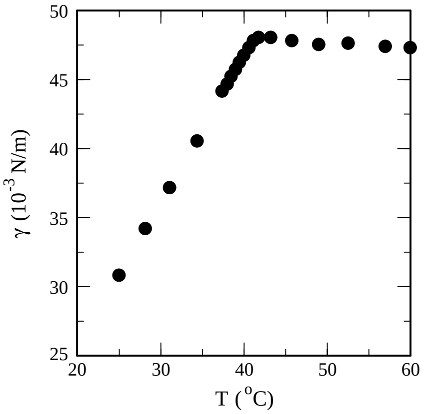

Fig. 2

Fig. 1 – (a) Experimental geometry. (b) Cartoon of interface domain model.

Fig. 2 – Interfacial tension γ measured with a Wilhelmy plate.

Here, we introduce the use of off-specular diffuse scattering to probe the domain structure of monolayers at liquid-liquid interfaces in the same system earlier studied by BAM [2]. These measurements allow us to probe domain sizes below the resolution of the earlier BAM measurements. They reveal the presence of small domains at temperatures near the solid-to-gas monolayer transition. Within this small temperature range the interfacial surfactant density changes by a factor of ten and the domain radius is nearly constant. This indicates that domains are created or annihilated as a function of temperature. In addition, heating and cooling through the solid-gas transition does not change the domain size in the lower temperature phase. These observations suggest that the domains are of equilibrium size.

When a small amount of $F(CF_2)_{10}(CH_2)_2OH$ (denoted $FC_{12}OH$) is dissolved in hexane a monolayer of $FC_{12}OH$ molecules spontaneously assembles at the interface between this solution and bulk water [6]. The liquids were contained in a vapor-tight, temperature-controlled, stainless-steel sample cell with Mylar X-ray windows [7]. Samples were prepared by placing 50 ml of a 2 mmol/kg solution of $FC_{12}OH$ in hexane on top of 100 ml of water (fig. 1a). Prior to X-ray measurements, the sample was stirred to ensure thermal equilibration.

Measurements of the interfacial tension γ of this system as a function of temperature demonstrated that the change in $\mathrm{d}\gamma/\mathrm{d}T$ is stepwise at the phase transition temperature [8], as illustrated in fig. 2. The difference in slope on either side of the transition yields the entropy change per area associated with this transition ($\Delta S \approx 1.1\times10^{-3}\ \mathrm{J/m^2K}$). This value is similar to that measured in studies of the surface freezing transition of the top molecular layer at the liquid-vapor interface and in studies of Langmuir monolayers at the water surface [9].

These interfacial tension measurements are consistent with our earlier X-ray reflectivity measurements that showed that a) the $FC_{12}OH$ monolayer far below the transition temperature is in a close-packed, solid phase with the $FC_{12}OH$ molecules oriented nearly perpendicular to the interface, and b) far above the transition temperature the surfactants have desorbed from the interface and the monolayer is in a low-density gas phase [10]. The low-temperature (32 °C) solid phase was modeled simply as a thin slab of higher electron density sandwiched between the two bulk liquids (slab thickness $L = 12.4 \pm 0.3$ Å and slab electron density $\rho_{\mathrm{e,layer}}/\rho_{\mathrm{e,water}} = 1.90 \pm 0.04$). The high-temperature (48 °C) reflectivity data were fit by a

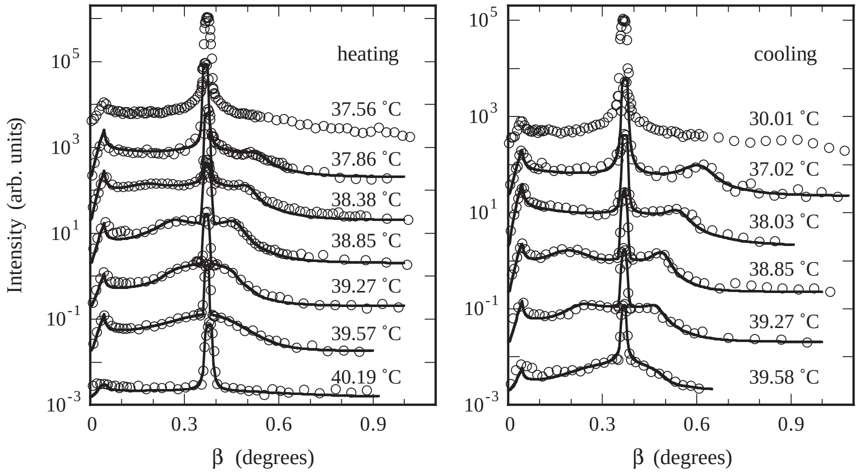

Fig. 3 – Transverse diffuse scattering (β scans) for a heating-cooling cycle (heated first, then cooled); lines are fits described in the text. Curves are shifted for clarity.

model of a single interface between the hexane solution and the water, indicating that less than 3% of the interface is covered by $FC_{12}OH$ molecules. At intermediate temperatures near the phase transition, the earlier reflectivity data are consistent with an interface partially covered by the low-temperature solid phase. However, the reflectivity does not provide detailed information about the domain structure of this inhomogeneous monolayer.

To probe the domain structure, X-ray off-specular diffuse scattering measurements were performed at beamline X19C at the National Synchrotron Light Source (Brookhaven National Laboratory, USA) with a liquid surface spectrometer and measurement techniques described elsewhere [11]. The X-rays ($\lambda = 0.825 \pm 0.002\,\text{Å}$) penetrate through the upper bulk hexane solution (fig. 1a). After changing the temperature by a small amount ($\approx 0.1\,\text{K}$), we monitored the scattering until it reached a steady-state value (in ≈ 1 hour).

X-ray scattering obtained by scanning the scattered angle β at fixed incident angle $\alpha = 0.37\,\text{deg}$ for a heating-cooling cycle is illustrated in fig. 3. The tall peaks at $\beta = 0.37\,\text{deg}$ in fig. 3 are the specular reflections, the small peaks near $\beta = 0.045\,\text{deg}$ are the surface field enhancement peaks that indicate the presence of interfacial inhomogeneities [12]. Here we are interested in the excess diffuse scattering in the "shoulders" immediately adjacent to the specular peaks. The shape of this off-specular diffuse scattering reveals quantitative statistical information about the domain structure in the monolayer.

The scattering intensity can be described by the distorted wave Born approximation as [12]

$$I(Q) \propto |T(\alpha)|^2 |T(\beta)|^2 \langle |A(Q)|^2 \rangle, \tag{1}$$

where $T(\alpha)$ or $T(\beta)$ are the Fresnel transmission coefficients and $|A(Q)|^2$ is the scattering intensity in the first Born approximation (the brackets indicate an average taken over the domain distribution). To describe $|A(Q)|^2$, let the Fourier transform of the electron density gradient be given by $f(x,y) = \int_{-\infty}^{+\infty} (\mathrm{d}\rho_\mathrm{e}(x,y,z)/\mathrm{d}z) \exp[iQ_z z]\,\mathrm{d}z$, where the z-axis is perpendicular to the interface, x and y are in the plane of the interface, ρ_e is the electron density, and $Q_z = (4\pi/\lambda)\sin\alpha$ is the wave vector transfer perpendicular to the interface. The interface is modeled as having solid monolayer domains separated by regions of the gas monolayer phase (fig. 1b), therefore $f(x,y)$ has only two values, *i.e.*, f_1 when the point (x,y) is occupied by the solid phase and f_2 when it is occupied by the gas phase. The scattering intensity per unit area can be written as [13, 14]

$$\langle |A(Q)|^2 \rangle = \left|\theta f_1 + (1-\theta) f_2\right|^2 \delta(Q_{xy}) + \theta(1-\theta)\left|f_1 - f_2\right|^2 \mathcal{F}\phi(r), \tag{2}$$

where Q_{xy} is the wave vector transfer in the plane of the interface, θ is the coverage of the solid phase (the fraction of interface covered by the solid phase), and $\mathcal{F}\phi(\boldsymbol{r})$ is the Fourier transform of the spatial correlation function $\phi(r)$ of domains of the phases separated by a vector $\boldsymbol{r}$ ($\phi(r)$ ranges from 1 at $r = 0$ to 0 at $r = \infty$). The scattering consists of two parts, the δ-function specular peak and the diffuse scattering.

Equation (2) expresses the diffuse scattering in terms of scattering from a set of objects (see fig. 1b). $\mathcal{F}\phi(r)$ is written in terms of a form factor describing the shape of the objects and a structure factor describing the distribution of the centers of the objects, $\mathcal{F}\phi(r) = \langle b^2(Q_{xy})\rangle |s(Q_{xy})|^2$. For simplicity, we assume that the domains are circular in shape. The squared form factor of the disks is written as [15, 16]

$$\langle b^2(Q_{xy}) \rangle = \int_0^\infty \mathrm{d}R\, p(R) \left[\frac{2J_1(Q_{xy}R)}{Q_{xy}R}\right]^2, \tag{3}$$

where $p(R)$ is the distribution of radii with mean value $\overline{R}$, and J_1 is the Bessel function of order one. The 2d structure factor can be approximated by [17]

$$\left|s(Q_{xy})\right|^2 = \frac{1 - \left|\mathcal{F}p(D)\right|^2}{1 - 2\left|\mathcal{F}p(D)\right| \cos Q_{xy}\overline{D} + \left|\mathcal{F}p(D)\right|^2}, \tag{4}$$

where $\mathcal{F}p(D)$ is the Fourier transform of the distribution, $p(D)$, of the nearest-neighbor separation distance with a mean value $\overline{D}$. Log-normal distributions were used for both radii and nearest-neighbor separation distances. Namely, $p(X) = \exp[-\ln^2(X/X_0)/2\delta^2_{R,D}]/\sqrt{2\pi}\delta_{R,D}X$, where $X = R$ or D [18]. The mean value $\overline{X} = X_0 \exp[\delta^2_{R,D}/2]$ and the standard deviation $\sigma_{R,D} = \overline{X}\sqrt{\exp[\delta^2_{R,D}] - 1}$, where σ_R is the standard deviation for the domain radii and σ_D is the standard deviation for the mean distance between domain centers. In the approximations used in eqs. (3) and (4), the R-dependence appears only in the form factor.

Equation (1), when convoluted with an instrumental resolution function [19], was used to simulate the diffuse scattering data in fig. 3. The coverage θ in eq. (2) was written in terms of $\overline{R}$ and $\overline{D}$ assuming a nearest-neighbor hexagonal ordering. Four parameters were used to fit the data: R_0, D_0, δ_R, and δ_D which determine $\overline{R}$, σ_R, $\overline{D}$, and σ_D. The good agreement between measurement and simulation confirms our assumption that the domains are in the solid state with the same electron density and thickness as those measured by reflectivity at 32 °C. The lack of higher-order peaks originating from either the structure or form factors indicates the presence of polydispersity in both the domain radii and separation as illustrated in fig. 4.

Above the transition temperature the diffuse scattering is featureless (at $T = 40.19\,^\circ\mathrm{C}$), as expected for a monolayer in the gaseous phase (see fig. 3). In the absence of domains, the small amount of diffuse scattering is due to capillary waves (used for the fit at $T = 40.19\,^\circ\mathrm{C}$) [12]. Immediately below the transition temperature, diffuse scattering from capillary waves becomes negligible compared to the scattering from domains. The small peaks in the shoulders of the specular peak indicate that the nearest-neighbor distance is well defined. The small peaks

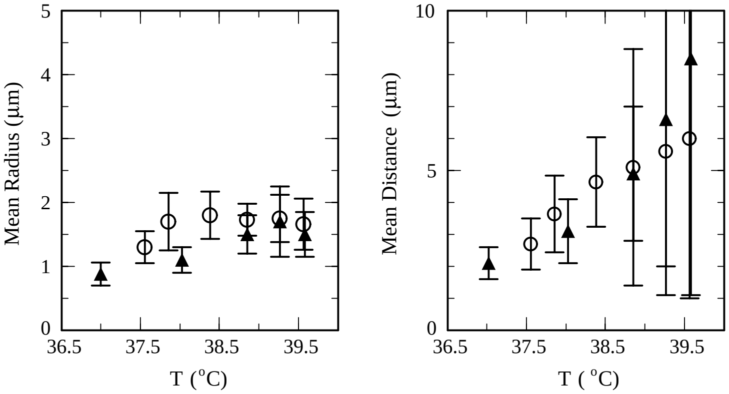

Fig. 4 – Mean radius $\overline{R}$ *vs.* temperature (left) and mean separation distance ($\overline{D}$) *vs.* temperature (right). Circles: heating curve; filled triangles: cooling curve. The error bars indicate $\pm\sigma_{R,D}$, a measure of the polydispersity in $\overline{R}$ and $\overline{D}$.

appear as the system is heated from 37.86 °C to 38.85 °C or cooled from 39.27 °C to 37.02 °C. The movement of these small peaks with temperature shows that the domains are spaced progressively further apart as the monolayer undergoes a transition from a solid to gas phase. The domain radii are ≈ 1 to 2 μm and nearly constant with temperature (fig. 4) [20]. Further below the transition temperature (as illustrated by the curves at 37.56 °C or 30.01 °C), the diffuse scattering again becomes featureless. Reflectivity measurements indicate that the coverage is nearly one in this region [10,21]. However, there is more scattering than accounted for by capillary waves alone. The additional scattering is most likely due to grain boundaries between domains that remain in a monolayer of coverage nearly equal to one. It is likely that domains merge at high coverage and our model of circular domains is not appropriate in this region.

Figure 5 shows that the coverage of the solid phase changes over a narrow temperature range near the transition temperature. The coverage values near the phase transition

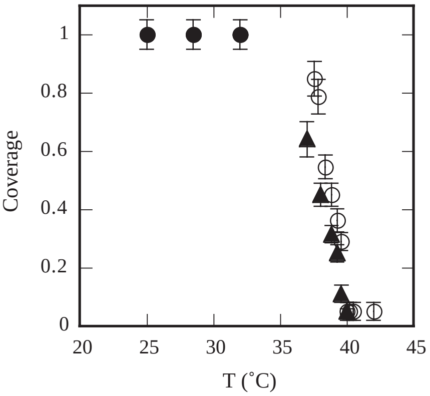

Fig. 5 – Interfacial coverage (fraction of interface covered by the low-temperature solid phase) as a function of temperature. Open circles: heating curve; filled triangles: cooling curve; dots: from earlier reflectivity measurements.

are consistent with those deduced from the earlier reflectivity measurements (values at the three lowest temperatures are taken from the earlier reflectivity data for reasons discussed above) [10, 21]. The sharp change in coverage at the transition temperature corresponds to the location of the discontinuity in the slope $\mathrm{d}\gamma/\mathrm{d}T$ in fig. 2. The slight difference in transition temperature between fig. 2 and fig. 5 is due to variations in the concentration of the hexane solutions that result in variations of ±1 °C in transition temperature for these samples. There are also small differences in the transition temperature and domain distributions upon cooling or heating the sample, however, $\overline{R}$ and $\overline{D}$ follow similar trends with temperature (fig. 4).

Our measurements reveal a nearly constant domain size over a range of temperatures for which the interfacial density changes by a factor of ten. This shows that new domains are created or annihilated as the temperature is changed. Also, the domain sizes are unchanged by heating and cooling through the solid-gas transition. Earlier BAM observations indicated uniform domain sizes (resolution limited), in contrast to observations on many Langmuir monolayers that show a large variation in domain sizes [2]. These three observations suggest that the domains may be of equilibrium size. Equilibrium can be established by exchange of $\mathrm{FC_{12}OH}$ molecules between the monolayer and the bulk hexane solution.

If the domains are in equilibrium, the measured mean domain radius $\overline{R}$ can be used to determine the mean line tension of domains. Balancing the effect of line tension and electrostatic dipole forces leads to an expression for the domain radius, $\overline{R} \approx (e^3 a/8)\exp[4\pi\epsilon_0\lambda_t/P^2]$, where $e \approx 2.718$, $a \approx 5\,\text{Å}$ is an intermolecular distance within the solid domain, and λ_t is the domain line tension [3, 22]. The difference in the interfacial polarization densities of the two interfacial phases, $P = |P_1 - P_2|$, can be estimated by assuming that the contribution from the water is similar for both surface phases, then using the surfactant dipole moment and measured structure of the monolayer phases to find $P \approx 2 \times 10^{-11}\,\mathrm{C/m}$. This is similar to measured values of P for monolayer phases at the water-vapor interface [23]. Combining these values leads to the domain line tension $\lambda_\mathrm{t} \approx 3 \times 10^{-11}\,\mathrm{N}$ near the phase transition. This is comparable to values ($3 \times 10^{-11}\,\mathrm{N}$ to $5 \times 10^{-12}\,\mathrm{N}$) previously measured by other techniques on monolayer domains at the liquid-vapor interface [24].

In summary, we used X-ray off-specular diffuse scattering to characterize domains within monolayers at the liquid-liquid interface. Domains of nearly constant radius appear over a range of temperature for which the interfacial coverage changes by a factor of ten, indicating that domains can be created or annihilated. Although earlier theories of Langmuir monolayer formation indicated that the creation (nucleation) of small domains is energetically unfavorable [3], the additional degree of freedom of surfactant exchange between the interface and the bulk hexane solution may allow for this process in Gibbs monolayers at the liquid-liquid interface. The domain radii were $\approx 1.5\,\mu\mathrm{m}$, at the resolution limit for Brewster angle microscopy. We anticipate that this X-ray technique will be useful for measuring domains at least a factor of ten smaller, though the ultimate limit will be determined by issues of signal-to-noise dependent upon characteristics of individual systems.

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