Demixing Transition in a Quasi-Two-Dimensional Surface-Frozen Layer

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A thin/thick transition was observed by x-ray reflectivity in a surface-frozen crystalline bilayer on the surface of a molten binary mixture of long alcohols. This rare example of a solid-solid phase transition in a quasi-2D system is shown to result from an abrupt temperature-driven change in the layer's composition, kinetically enabled by the layer's ability to exchange molecules with the underlying 3D liquid bulk. Mean-field thermodynamics yields a Gibbs-adsorption-like expression which accounts very well for the transition.

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The free surface of molten alcohols [$CH_3(CH_2)_{n-1}OH$, $16 \leq n \leq 28$, denoted C_nOH] was found [1] to solidify at a temperature, $T = T_s$, several degrees *above* bulk freezing, $T = T_f$. This effect, known as surface freezing (SF), was first discovered in alkanes [2], and observed since in a variety of chain molecules [1,3]. It was suggested to originate in the reduced dimensionality of the surface, which allows larger surface-normal motion, and hence larger entropy [4], for the molecules at the quasi-2D surface than for those of the 3D bulk, and lowers the interfacial tension [5]. In the two well-studied model systems for 2D matter, water-supported Langmuir films (LFs) [6] and self-assembled monolayers (SAMs) on solid and liquid substrates [7], two-dimensionality is achieved by confining a monolayer to the surface of an impenetrable or immiscible subphase. Like SAMs, the molecules of the SF layer self-assemble on, albeit without chemically binding to the subphase, as in SAMs. The inplane structure of SF layers is dominated by the chain-chain interactions, as LFs, not by the headgroup-sub phase ones, as SAMs. However, unlike both LFs and SAMs, the molecules in the SF layer and the bulk are identical and can interchange freely. Thus, SF layers occupy a unique position, intermediate between 3D bulk and artificially confined quasi-2D matter. The 2D character is achieved here by spontaneous self-assembly, not confinement, yet the interaction with the 3D bulk by exchange of molecules is retained. This interaction can be tuned by using a binary mixture of different-n alcohols and varying the bulk concentration ϕ. For a *liquid* surface, this will also vary the liquid surface concentration ϕ_s (generally $\neq \phi$) through the well-known Gibbs surface enrichment rule [8]. If a similar behavior prevails also in the *solid SF* layer, regions of phase space could be reached, which are unexplorable in monocomponent C_nOH due to their limited SF existence ranges, $\Delta T = T_s - T_f \lesssim 2$–3°C and $16 \leq n \leq 28$. This should allow observation of new 2D phases and phase transitions.

We demonstrate here that this is indeed possible, and present x-ray measurements of a temperature-driven thin/thick transition in a SF crystalline surface layer of a molten binary mixture of alcohols. Using simple thermodynamical arguments, we derive a Gibbs-like relation between the solid bilayer's composition x and that of the bulk ϕ, which agrees very well with the experimental x values at all T. This relation shows the thin/thick transition to result from an abrupt change between two fixed compositions x in the SF layer.

A $C_{18}OH + C_{28}OH$ mixture was employed, with a nominal bulk molar concentration $\phi = 0.2$ of $C_{28}OH$ under a saturated water vapor atmosphere. As with all alcohols [1] the SF layer is a bilayer, with the alcohols' OH groups residing at the center. Water molecules intercalate the OH slab of the bilayer at a water/alcohol molecular ratio of 1:2 [1], as shown schematically in Fig. 1 (inset). In the 3D bulk, the large chain-length mismatch, $28 - 18 = 10$, causes phase separation upon solidification. The lower steric constraints on the 2D SF layer should, however, facilitate cocrystallization of different chain lengths, and a mixed layer may ensue. We demonstrate below that this indeed occurs.

Materials, purchased from Aldrich and marked as $\gtrsim$99% pure, were comelted, vigorously stirred, and poured onto a preheated copper substrate, placed inside a sealed cell, the temperature of which was regulated to $\lesssim$0.01°C. A water container placed inside the cell yielded a water-saturated atmosphere. The mixtures' surfaces were studied by x-ray reflectivity (XR), which probes the surface-normal electron density profile [9]. Measurements, at $\lambda = 1.54$ Å wavelength, were carried out at beam line X22B, NSLS. For details of the cell, experiment, and data analysis, see [1,3,10,11].

Figure 1 shows three of the ten XR curves, $R(q_z)$, measured for a mixture of $\phi = 0.2$ of $C_{28}OH$. $q_z = (4\pi/\lambda)\sin\alpha$, is the surface-normal momentum transfer, and α is the grazing angle of incidence of the x rays. Curve a at $T > T_s$ decreases monotonically, as typical of a liquid surface. For $T_f < T < T_s$, curves b and c, the appearance of Kiessig-like fringes indicate the existence

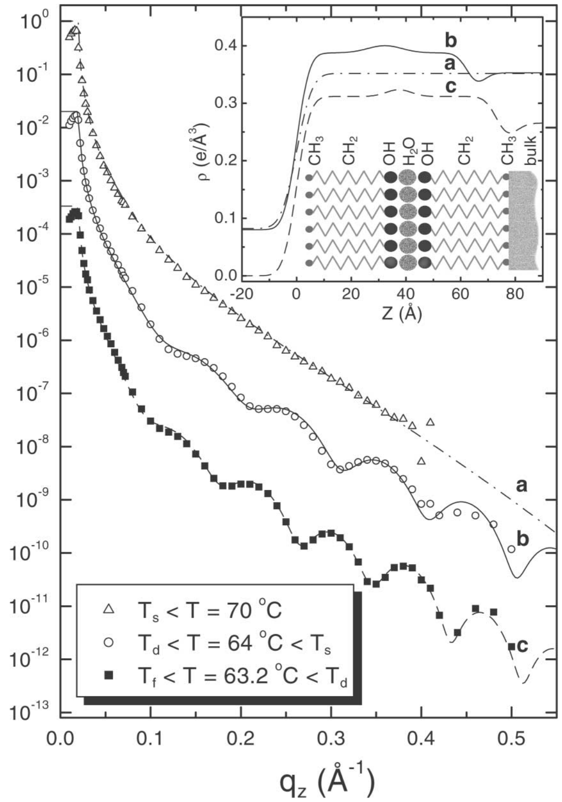

FIG. 1. The measured (points) and slab-model fitted (lines) x-ray reflectivity curves for the free surface of a 20%$C_{28}OH$:80%$C_{18}OH$ hydrated alcohol mixture melt. *a* is typical of a liquid surface. *b* and *c* show Kiessig-like fringes due to the solid surface-frozen bilayer. The thin/thick transition causes the period difference between *b* and *c*. The inset shows the surface-normal density profiles obtained from the fits and the molecular structure of the bilayer. Curves are shifted vertically for clarity.

of a surface layer denser than the bulk, i.e., surface freezing [2]. Unlike all previous alcohols studied, two different fringe periods, Δq, are observed over the $\Delta T \approx 1.2$°C existence range of the SF layer. This, in turn, indicates a structural change in the SF layer upon cooling, from a thin, $D = 2\pi/\Delta q \approx 67$ Å, to a thick, $D \approx 77$ Å, layer. As these values are bracketed by twice the *effective* molecular lengths, $d_{18} = 25.5$ Å and $d_{28} = 39.5$ Å, of hydrated $C_{18}OH$ and $C_{28}OH$ [1], we conclude that the SF layer is a bilayer, the same as for pure alcohols. A T scan, i.e., $R(q_z)$ measured at a fixed $q_z = 0.21$ Å^{-1} as T is varied, is shown in Fig. 2. The onsets of SF at $T_s \approx 64.1$°C and of bulk freezing at $T_f \approx 63$°C are clearly marked by sharp jumps in R. A similarly sharp jump at $T_d \approx 63.4$°C marks the thin/thick transition. Although continuous transitions are predicted by some well-known 2D models, e.g., the Ising model [12], first-order 2D transitions are also possible theoretically, e.g., the *XY* model for He films and planar magnets and the grain-boundary-mediated melting model [13]. The abruptness of the present thin/thick transition seems to indicate a first-order transition, the same as that of the SF effect [2,14]. Note that T_f and T_s above are closer to $T_f \approx 60$°C of pure hydrated $C_{18}OH$ than to $T_f \approx 84$°C of pure hydrated $C_{28}OH$ [1], in line with the low bulk concentration of $C_{28}OH$, $\phi = 0.2$.

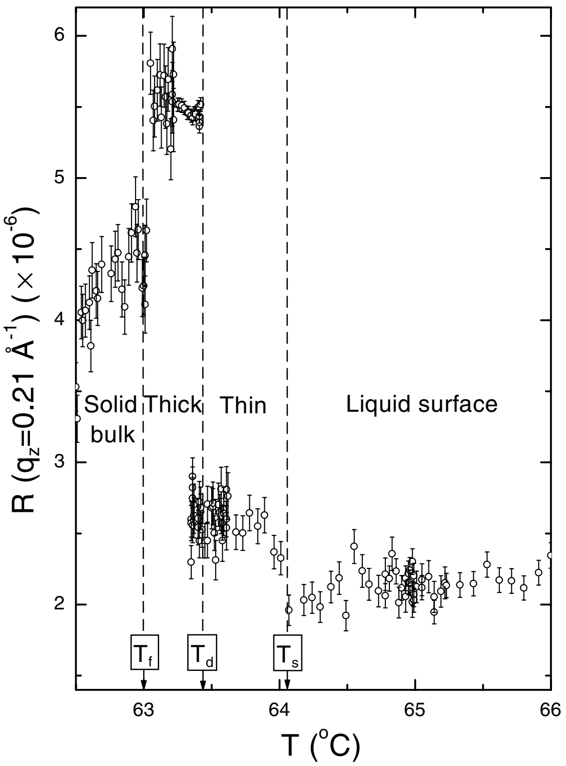

FIG. 2. XR at a fixed $q_z = 0.21$ Å^{-1}, measured upon cooling. The onsets of surface (T_s) and bulk (T_f) freezing and the thick/thin transition (T_d) are clearly observed.

To quantify the thin/thick transition a slab-model of the bilayer, shown schematically in the inset to Fig. 1 and successfully used previously [1], was employed to fit the XR data. The model consists of four slabs representing (i) the upper layer of $(CH_2)_{n-1}$ alkyl chains, (ii) the OH head groups and H_2O molecules, (iii) the lower-layer of $(CH_2)_{n-1}$ alkyl chains [same as slab (i)], and (iv) the lower-layer CH_3 terminal groups at the layer subphase interface. Good fits of the model are obtained as shown in Fig. 1 (lines). The corresponding density profiles are plotted in the inset. In principle, the layer thickness values obtained from the fits, d, should allow a determination of the SF layer's composition, since these values must be weighted averages of d_{18} and d_{28}. The weighting should depend on the relative abundance of each species in the SF layer. The surface composition is different, in general, from that of the bulk, even when the surface is liquid, due to the well-known Gibbs enrichment of the surface region by the lower-energy species in a binary mixture [8]. For our *solid* SF bilayer, a similar enrichment can be expected. To determine the surface concentration $x(\neq \phi)$ from the fitted d a weighting scheme needs to be adopted. We adopt first, as a zeroth-order approximation, a linear interpolation of the molecular lengths, $d = d_{28}x + d_{18}(1 - x)$, which is analogous to Vegard's law for the bulk spacing of layered binary mixed crystals [15]. The resultant open triangles in Fig. 3, show the ”thin” SF phase to be a 50%C_{28}OH:50%C_{18}OH mixture, while the ”thick” phase is an almost pure C_{28}OH: a 90%C_{28}OH:10%C_{18}OH mixture. The thin/thick transition is, therefore, a demixing transition in the surface-frozen layer.

Linear weighting, however, is too simplistic, since x-ray studies demonstrate that in alkane mixtures the thickness of SF monolayers [16] and the bulk's layer spacing [17] are only little influenced by the shorter component at small concentrations. The linear weighting results also disagree with simple theory, as we show below. In addition, the bulk spacing of many layered crystals deviate considerably from the linear Vegard's law [18], e.g., two-component intercalation compounds [19,20], Langmuir-Blodgett films of mixed molecules [21], and crystals of binary mixtures of alkane [17,18,22] and alcohol [23]. In these cases a power law, $d = d_A(1-x)^P + d_B[1-(1-x)^P]$, with $2 \lesssim P \lesssim 7$, is found to interpolate the effective bulk layer thickness, d, between those of the pure components, dA and d_B. This behavior was rationalized within molecular-level packing models [23,24]. In particular, for low-rigidity layers (e.g., Langmuir-Blodgett films [21] and class-I intercalation compounds [20]) $P \approx 2$–3 was reported. In analogy with these bulk mixtures, we adopt as a next-order approximation a quadratic weighting, $d = d_{18}(1-x)^2 + d_{28}[1-(1-x)^2]$. This yields the closed circles in Fig. 3. For this weighting the thin/thick transition is also a compositional one, but from 30%C_{28}OH:70%C_{18}OH to 70%C_{28}OH:30%C_{18}OH. The quadratic interpolation, while admittedly somewhat *ad hoc*, is in line with the non-Vegard-law behavior of the bulk systems above, and agrees very well with the simple thermodynamical theory discussed below and shown by the solid line in Fig. 3. Regardless of the weighting scheme, the fact that this compositional change *in a solid layer* is not inhibited by very slow kinetics, is due to the layer's ability to exchange molecules with the underlying bulk melt. This is not possible in the highly compressed solid phases of a Langmuir film, where the molecules are confined to, and have to diffuse along, the surface of the water subphase [3]. For this reason, analogies with demixing transitions in other quasi-2D systems [25] must be drawn with caution.

Classical thermodynamics was used to account for the transition. The bulk is assumed to be an ideal mixture [26], while the solid surface is treated as a “strictly regular” mixture [26] with a nonzero chain-length mismatch energy between the extended C_{18}OH and C_{28}OH molecules. This approach was previously employed successfully for similar mixtures [10].

The coexistence line between two solid surface phases having different molar concentrations, x_1 and x_2, is determined by equating the corresponding chemical potentials [16]. For C_{28}OH this yields

$$k_B T \ln x_1 + \omega(1-x_1)^2 = k_B T \ln x_2 + \omega(1-x_2)^2. \quad (1)$$

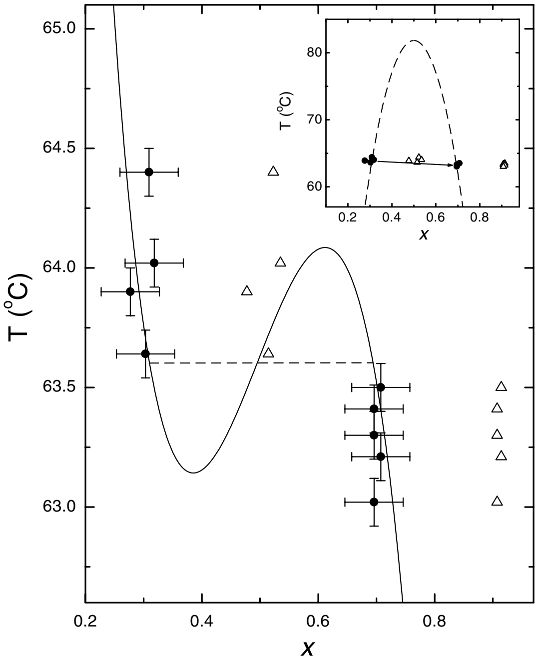

FIG. 3. The C_{28}OH concentrations, x, in the surface-frozen layer as derived from the XR measurements using linear (triangles) and quadratic (solid circles) averaging of the molecular lengths. The Gibbs relation $T(x)$ (line) agrees remarkably well with the experiment for quadratic weighting. The system's thermodynamically stable trajectory (dashed line) shows the thin/thick transition to be a compositional transition in the SF layer from 30%C_{28}OH:70%C_{18}OH to 70%C_{28}OH:30%C_{18}OH. The phase coexistence curve (dashed line) between the two compositions and the measured points are shown in the inset.

Here $\omega = 5.9$ kJ/mol is the interchange energy of the two molecules [10,26], determined from the measured $T_s(\phi)$ of the mixture [10,16]. This, and the corresponding equation for C_{18}OH, where $x_{1,2}$ is replaced by $(1 - x_{1,2})$, yield $x_1 = x_2$ and, upon being substituted into Eq. (1), the coexistence curve shown in the inset of Fig. 3. In this mean-field approach the calculated coexistence curve is strictly symmetric around $x = 0.5$. The agreement of the points (circles) with the calculated curve supports both the quadratic weighting scheme, and the identification of the thin/thick transition as an abrupt compositional transition between two points on the coexistence curve.

This conclusion is further enhanced when the surface/bulk interaction is taken into account in a way similar to the well-known Gibbs relation [8,11], with changes dictated by the SF layer being a solid rather than a liquid. Noting that the surface tension γ is the excess free energy of the surface over the bulk, the chemical potential of C_{28}OH in the (liquid) bulk is related to that at the (solid) surface as

$$f_{28,lb} + k_B T \ln\phi = f_{28,cs} + k_B T \ln x + \omega(1-x)^2 - \gamma. \quad (2)$$

$f_{28,lb}$ and $f_{28,cs}$ are the chemical potentials of the *pure* hydrated C_{28}OH in the liquid bulk (lb) and at the crystalline surface (cs), respectively. Since at $T_{28,s}$, the onset of SF in pure hydrated $C_{28}OH$, the chemical potentials of the solid and the liquid *surface* phases are equal, we get [10,16]:

$$f_{28,cs} - f_{28,lb} = (T - T_{28,s})\Delta S_{28} + \gamma_{28}, \qquad (3)$$

where γ_{28} is the surface tension of pure hydrated $C_{28}OH$ and ΔS_{28} is the surface entropy loss upon surface freezing. Using now Eqs. (2) and (3) and the corresponding expressions for $C_{18}OH$, we obtain a Gibbs-like relation between T and the concentrations of the SF layer, x, and the bulk, ϕ:

$$T = \frac{T_{28,s}\Delta S_{28} - T_{18,s}\Delta S_{18} + (\gamma_{18} - \gamma_{28}) - \omega(1 - 2x)}{(\Delta S_{28} - \Delta S_{18}) + k_B \ln[(1-\phi)x/(1-x)\phi]}. \qquad (4)$$

Here the subscripts 18 and 28 indicate values for the pure hydrated species. $T_{18,s} = 335$ K and $T_{28,s} = 359$ K were measured directly. In the absence of measured surface entropies values for hydrated alcohols, dry bulk $\Delta S_{18} = 113.2$ J/mol K and $\Delta S_{28} = 197.5$ J/mol K were used [27]. Equation (4) is plotted (line) in Fig. 3, with the only adjustable parameter being a shift of the bulk concentration ϕ from the *nominal* $\phi = 0.2$ to an *effective* $\phi = 0.18$. The shift may result from a small supercooling of the actual demixing transition relative to the calculated one, due to a kinetic barrier to the demixing set up by the need of the molecules to slide in and out of the solid bilayer at the transition. Alternatively, the shift may ensue from our too-simplified classical approach and/or the approximate values employed for several of the parameter. Finally, the thermodynamically stable behavior in the region $0.3 < x < 0.7$ is shown by the dashed line at $T = T_d$ [28], representing a discontinuous transition from $x \approx 0.3$ to $x \approx 0.7$.

In conclusion, a solid-solid demixing transition was observed in a quasi-2D SF bilayer on the surface of a nominal $80\%C_{18}OH{:}20\%C_{28}OH$ molten bulk mixture. The composition of the SF layer changes abruptly from $x \approx 0.3$ at $T > T_d$ to $x \approx 0.7$ at $T < T_d$. Simple thermodynamical arguments yield a Gibbs-like expression for $x(T)$ which agrees well with the x values derived from the x-ray measurements. Future studies on similar transitions in other alkane and alcohol mixtures may elucidate some of the less-clear aspects of this phenomenon, e.g., the order of the transition, its reversibility, and its generality.

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