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Solid-liquid interface of a 2-propanol–perfluoromethylcyclohexane mixture: From adsorption to wetting

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The liquid-solid interface between a silicon substrate and the binary mixture perfluoromethylcyclohexane (PFMC) and 2-propanol (IP) is examined by x-ray specular reflectivity and diffuse scattering under grazing angles. The wetting films between the PFMC-rich phase and the substrate are characterized with respect to the density profile and lateral fluctuations. We find that the liquid-liquid interface of the film is anomalously broadened as compared to capillary wave theory. This broadening is caused by a locally slow variation of the density between the liquid phases and marks an adsorption profile that does not reflect the bulk properties of the film phase. Essentially the same behavior is present for a fused silica substrate.

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I. INTRODUCTION

The understanding of the structure of liquids has reached a high degree of perfection. It has become possible to calculate detailed features of equilibrium liquid interfaces on a true atomic scale and as well to experimentally detect these properties [1–4]. The concept of capillary waves has proven to be a powerful concept to describe the transition region between fluid phases. Additional broadening of the interface can occur due to the finite molecular dimension of the constituents or in the vicinity of the critical points of the adjacent phases. In the vicinity of wetting transitions an additional component of instability can occur, when, near the transition, a thin confined film of the phase that intrudes in between the second fluid phase and an inert phase tends to be thickened due to a delicate balance of interactions. One main contribution to interfacial broadening comes from capillary waves. These waves are expressed in the lateral fluctuation of the interface and result in an effective broadening of the interface. The presence of a rigid wall nevertheless leads to an effective damping of the fluctuations [5]. The normally logarithmic thickness dependence can also be altered to a power law decay if short range forces govern the interfacial interactions. A frequent case is nevertheless an overestimation of broadening compared to experimental results [6,2].

A recent study of a thin film of a binary liquid mixture points out the importance of local density gradients due to an increased bulk correlation length near a critical point [2] when observing the liquid-liquid interface. The essential assumption of the above descriptions is that a liquid wetting film can be described by a bulklike thin region with a well-defined interface to the second fluid phase. In binary liquids this assumption is questionable for ultrathin films and a more general approach of excess adsorption has to be used.

In the present paper we describe the structure at the liquid-solid interface of a binary liquid mixture, which tends to form a thin layer of the thermodynamically instable phase at the interface of the stable phase to the solid. The discontinuous wetting transition with pronounced pretransitional effects has been reported elsewhere [7]. The present case deals with the characterization of the liquid-liquid interface near the solid wall. The films are observed far from the critical point of the mixture, so that both capillary waves and intrinsic broadening do not diverge. Nevertheless we found an anomalously broad liquid-liquid interface that cannot be understood with the concept of capillary waves alone. By characterizing the interface in equilibrium along the wetting transition and off coexistence, we shed light on the origin of the broadening. The distinction between lateral fluctuations and local broadening of the interface can be made by the measurement of both specular reflectivity and diffuse scattering near the specular condition. The first represents information of the density change uniquely perpendicular to the surface, whereas the latter is also sensitive to density variations along the interface, e.g., capillary fluctuations.

II. TECHNIQUES AND MATERIALS

A. X-ray reflectivity and diffuse scattering

In the past years diffraction methods at interfaces (particularly liquid and soft matter interfaces) have allowed new insight into the structural and energetical aspects involved (for a recent overview see [8]). Here we employ specular reflectivity and diffuse scattering under grazing incidence to quantify the wetting films, both perpendicular to the surface and for lateral properties.

Grazing angle x-ray reflectivity can be described in terms of classical optics if the appropriate index of refraction n of the given material is used in Fresnel's equations [9]. For x rays, $n=1-\delta-i\beta$ with

$$\delta=\frac{r_0}{2\pi}\lambda^2\rho_e,$$

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*Present address: ESRF, BP 220, F-38043 Grenoble, France; email address: plech@esrf.fr with $r_0 = 2.818\times 10^{-15}$ m, λ, and ρ_e representing the classical electron radius, x-ray wavelength, and electron density of the material (dispersion and absorption corrections can be included [9,10]). Except for the vicinity of absorption edges, the reflectivity can be expressed as a function of the scattering vector $Q = (4\pi/\lambda)\sin\alpha$. This is an excellent approximation for organic materials with low Z components when using hard x rays.

The important structural information accessible by reflectivity corresponds to the laterally averaged electron density profile along the surface normal, denoted in the following as the z direction. Within a kinematic approach, the measured reflectivity is related to the Fresnel reflectivity R_F of an ideal surface by the Fourier transform of the derivative of the averaged electron density profile $\rho(z)$ [11,12]:

$$\frac{R}{R_F} = \left| \frac{1}{\rho_{z\rightarrow -\infty}} \int \frac{d\langle \rho(z)\rangle}{dz} e^{iQz} dz \right|^2 . \tag{1}$$

Therefore reflectivity experiments are very sensitive to electron gradients. Furthermore, Eq. (1) indicates that a finite jump in the electron density, e.g., caused by a layer with contrasting scattering density, leads to reflectivity oscillations, the frequency of which allows to determine the layer thickness. As the x-ray wavelength is typically in the angstrom range, structural details can be derived on an atomic scale. The strong decay of R_F ($\propto Q^{-4}$) and additional nonspecular scattering contributions limit the accessible momentum transfer and, therefore, the spatial resolution of the experiment.

To include data close to the total reflection regime, where the kinematical approach breaks down, a generalized Parratt algorithm [13] can be used for simulations, taking into account properly multiple reflections, dispersion, and absorption corrections by calculating the appropriate reflection coefficients at assumed interfaces and multiplying them in a matrix formalism. Here the approach in the interpretation of the measured data consists in an assumption of density steps perpendicular to the surface. These stepped interfaces (modeled by boxes of constant density for a given z range) approximate the real density distribution of the wetting layers, by including a broadening of the step edge by, e.g., an error function with defined width. This root-mean-square roughness σ of the interfaces was included in our simulations according to Névot and Croce [14]. The advantage of the Parratt approach together with density boxes over the computation of Eq. (1) is a robust fitting of the reflectivity even at reduced statistical definition.

Interfaces of fluid phases are always corrugated by lateral thermal fluctuations, the so-called capillary waves. These fluctuations lead to a broadening of the interfacial width due to the fact that the measured density profile is always an average over a certain distance within the interface. Expressions based on thermodynamic calculations have been derived, which connect the measured width with experimental resolution $[Q_{min}; Q_{max}]$ and interface tension γ [15,16]:

$$\sigma_{eff}^2 = \sigma_{int}^2 + \frac{1}{2} B \ln\left[\frac{Q_{max}^2}{Q_{min}^2 + A_{eff}/2\pi\gamma d^4} \right], \tag{2}$$

B representing the amplitude $B = k_B T/\pi\gamma$ of the capillary contribution with an important relation to the interface tension γ In a more rigorous approach, additional cutoffs have to be introduced into the logarithm, whereas we focus only on the leading terms with an instrument cutoff Q_{min}. In proximity to a hard wall, these fluctuations are effectively damped out leading to a contribution in the low cutoff that varies with the film thickness d and the Hamaker constant A_{eff} of the layer system. The major feature of the capillary wave approach on confined liquid interfaces is the slow, logarithmic growth of σ_{eff} with increasing film thickness [5,8], assuming that van der Waals forces govern the interfacial interactions.

As specular reflectivity is only sensitive to the vertical structure factor, one needs to include nonspecular (diffuse) scattering to obtain information about in-plane structural properties such as fluctuations of the mean surface height. The diffusely scattered intensity can be described within the distorted-wave Born approximation as:

$$I \propto |T_i(Q)|^2 |T_f(Q)|^2 S(C(R),Q),$$

where $T_i(Q), T_f(Q)$ represent the Fresnel transmission functions and $S(C(R),Q)$ is the structure factor of a rough surface including the height-height correlation function $C(R) = \langle z(0) z(R)\rangle$ [16]. R denotes an in-plane position vector $R = (X,Y)$ and Q should be taken as the lateral scattering vector in the medium. In the case of a free liquid surface, $C(R)$ is fully determined by capillary waves. In this case

$$C(R) = \frac{k_B T}{2\pi\gamma} K_0(R\sqrt{\delta\rho g \gamma^{-1}}),$$

with the asymptotic behavior of a logarithmic correlation function. k_B and $\delta\rho$, respectively, denote the Boltzmann constant and density difference between the two phases separated by the interface. K_0 is the modified Bessel function of the second kind of order 0 with $\lim_{x\rightarrow 0} K_0(x) \simeq -\ln x$. Solid surfaces are often modeled with the assumption of self-affine roughness distributions with a height-height correlation function depending on the preparation mechanism [16].

For a liquid wetting layer on a solid silicon substrate, Tidswell *et al.* give an expression for the observable diffuse scattering along Q_z that also comprises cross-correlation terms. The formula has been shown to fit the measured diffuse scattering distribution [17]

$$I_{diff}(Q) = \frac{I_0}{\alpha_i \Delta\alpha_i} \left(\frac{r_e}{k} \right)^2 \int d^3Q \left\{ \frac{T_i T_f}{Q_z} e^{-\sigma^2 Q_z^2} \right. \tag{3}$$

$$\times [S_D(Q) |(\rho_{\mathrm{Si}} - \rho_{film}) + \rho_{film} \chi(Q) e^{iQ_z l}|^2 \tag{4}$$

$$\left. + S_{cap}(Q)] \right\} \tag{5}$$

with the parameters being the incident angle α_i, the angular divergence, $\Delta\alpha_i$, the (fitted) scattering function of the silicon substrate $S_D(Q)$, and the scattering distribution of the liquid surface $S_{cap}(Q)$. The latter as well as the interfacial roughness are quantitatively described within the capillary wave model [16,15]. Here the cross correlation is expressed by a factor that depends on thickness, describing the van der Waals interaction between the surface and fluctuating interface [18]:

$$\chi(Q)=\frac{a^2}{|Q_\parallel|^2 l^4+a^2}.$$

In the present study the densities ρ_{Si}, ρ_{film} were expressed according to the effective density steps of the subsequent layers, being the density difference of the liquid perfluoromethylcyclohexane (PFMC) bulk and the IP layer, and the substrate, respectively. Although the effective interaction of the interfaces in the present case is not necessarily dominated by van der Waals interactions and thus the description of the cross-correlation factor is not precise, we found that owing to the low amount of scattering from the silicon interface and relatively thick films, small variations of $\chi(Q)$ did not affect the level of diffuse scattering considerably. In addition, bulk liquid scattering could not be separated within the experiment and is included in the phenomenological Si scattering.

B. Scattering setup

In order to access the liquid-solid interface with interface sensitive x-ray techniques, we employed an x-ray beam of sufficiently high energy to enhance the transmission through 20 mm of bulk liquid [19]. The experiments were performed at beamlines E2 and D4 (Hasylab), using a Si(111) double monochromator and single monochromator, respectively, selecting an energy between 18.5 and 20 keV. Even at this energy the transmission through the solid amounts only to 7–10 % of the primary intensity. Diffuse scattering and reflectivity have been separated by a detector slit at a large distance (0.8–1 m) from the sample. The resolution in $Q_{||}$ was, therefore, given as 3×10^{-5} $(\text{Å})^{-1}$. Measurements off coexistence have also been performed at a sealed anode laboratory reflectometer and Mo K_α radiation at 17.44 keV [20], where the limited Q_z range allows a quantification of the film density but not details of the liquid-liquid interface profile.

C. Sample environment and materials

The sample chamber consists of a polished massive stainless steel body with clamped polyimide windows, which serve as container walls and x-ray windows. When assembled, these parts form a rectangular cavity with a horizontal base plane of 20 mm×20 mm, which is occupied by the wafer substrate. The plane of reflection is, therefore, vertical, but as the grazing angles usually are below 1.5°, the aperture for the x-ray beam can be kept very small (5 mm). Above the substrate the liquids are prepared such as to form a phase separated binary liquid, assuring that the phase coexistence is always reached from the undersaturated side. The chamber was ultrasonically cleaned in pure methanol and MilliQ water and dried afterwards in a nitrogen stream. The sealed chamber is positioned in a symmetrically surrounding resistive heater box. The temperature can be controlled by means of a Lakeshore temperature controller model 420 and could be kept stable to several millikelvin over hours. The same should hold for the temperature homogeneity considering the symmetrical shielding and large mass of the arrangement. Distortive effects on the film structure were observed as soon as the temperature change near the probed surface exceeded 30 mK/min. More experimental details are given in [7,21].

The liquids perfluoromethylcyclohexane (PFMC, Alfa, 97% fully fluorinated) and 2-propanol (IP, Sigma-Aldrich, 99.5%) were used without further purification. The reproducibility of the critical mixing point of the mixture and the wetting transition [22] reported in [23] give us confidence about the defined state of the liquids.

The substrates consisted of Si(111) wafers (Wacker Siltronic) with a native oxide layer of at least 14 Å and a surface roughness of 2.3 Å as derived by x-ray reflectivity. The comparison was done with polished fused silica wafers (Schott) with a surface roughness of 2.9 Å. Both were cut into pieces to fit into the sample chamber.

The preparation included the steps of cleaning the silicon wafer in pure methanol and MilliQ water and drying it in a dry nitrogen stream. The assembled chamber was allowed to equilibrate at the desired temperature before filling it with PFMC to form an 8-mm column of liquid above the silicon surface. The surface was characterized with x-ray scattering before carefully adding 2-propanol on top. At this stage the solid-liquid interface still is formed only by pure PFMC. In a slow diffusional step ($\propto$800 min) 2-propanol is enriched at the interface to form the gravity separated two phase mixture. By this procedure it is ensured that the liquid is always slightly below coexistence and the wetting film thickness of 2-propanol does not overshoot.

III. RESULTS AND DISCUSSION

A. Interfacial structure at two phase coexistence

It is known for the present system that the alcohol-rich *liquid-gas* interface undergoes a first order wetting transition at 38 °C with an intruding film of the PFMC-rich phase [23,22]. The film interfaces on the partial wet phase can be sufficiently well described by the existing theory. In addition we found a wetting transition between the PFMC-rich phase and *an inert solid wall* formed by a silicon wafer [7]. Here a film of the alcohol-rich phase appears, which diverges at 50 °C. It is recognized as a first order transition but with a remarkable pretransitional film growth. We attribute this to the dominance of short range interactions [24]. The Hamaker constant can be modeled by using the optical properties of silica [25] and is found to be very small ($<3\times10^{-22}J$) compared to the Hamaker constant at the liquid-vapor wetting transition ($9\times10^{-21}J$). This assumption is related to the fact that the silicon surface is covered by a native oxide layer. Indeed we found that by replacing the silicon wafer by a polished surface of fused silica, the main features of the wetting transition are not altered [24,21]. As an example we show the specular reflectivity of the wetting film at the silicon interface at 48 °C and at the fused silica interface at 48.8 °C in Fig. 1.

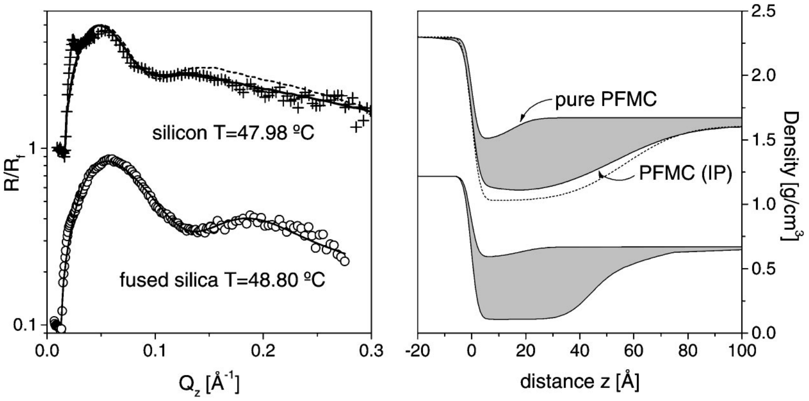

FIG. 1. Normalized reflectivities at the interface of silicon to the PFMC-rich phase with an intruding IP wetting layer and the same for fused silica (lowered by a factor of 10 for clarity). The density profiles corresponding to the simulations are displayed in the right image. The dashed line marks the best fit for a single box model. The profile for fused silica has been lowered by 1 g cm^{-3}.

As already reported, the reflectivity at the silicon interface can be fitted to a certain extent with a single layer model (dotted line in Fig. 1 left), but a better agreement is achieved with a two layer model with a slightly modified slope of the density profile within the first 15 Å next to the solid boundary. This can be related to the observation of a density anomaly already present for pure PFMC (see upper curves of each density profile in the right image). Such a behavior has been reported following high resolution studies of a pure liquid to solid interface [3]. A more detailed discussion is not possible due to the restricted spatial resolution. The resulting excess adsorption profile is marked by the shaded area. In addition to the comparable thickness of the films on silicon and fused silica, the same broad transition from the wetting film to the bulk PFMC-rich phase is observed. For the above curves we derived 17 Å at the silicon wall and 20.8 Å at the silica wall. The similar interface between the IP-rich bulk phase and the PFMC-rich thin film at the gas-liquid wetting transition displays widths of only 11 Å for comparable film thicknesses [21]. The details of the phase transition for different substrates will be discussed elsewhere. In summary the nonuniveral first order phase transition is observed far from the critical point and the film thickness in the completely wet phase exceed 2000 Å.

A second unexpected feature was observed for the density profile at the solid interface when collecting reflectivities during equilibration of the mixture at constant temperature. The film growth is characterized by a separated change in the density of the film followed by a growth in thickness to reach the equilibrium wetting film. We attribute this behavior to a close correspondence of the nonequilibrium growth of the wetting film to the structure of the adsorption films in the single phase region of the PFMC-rich phase when approaching the coexistence concentration of IP. This will be discussed below. We will first estimate the interfacial width of the liquid-solid interface from theory and compare it with the roughness derived from x-ray reflectivity measurements on our system.

In principle, the thermodynamics and structure of noncritical fluid interfaces is well understood. As far as no critical point is involved, the local profile should be sharp with respect to concentration or density down to the order of the bulk correlation length. Additionally this interface can display lateral fluctuations that are limited by interfacial tension. In the case of a boundary close to a flat substrate, these fluctuations are damped out through the effective interaction with the rigid plane. Thus one can normally observe sharp interfaces, which, by laterally averaging the position of the fluctuating interface, show a broadening of only several Å for typical (organic) liquid interfaces. As the interface model is quantitative with no adjustable parameters, our results can be compared to theory. We use Eq. (2) for the free liquid-liquid interface width and the damping in the vicinity of a rigid wall, irrespective of the nature of the interactions. An extension to short range interactions will only affect the damping for small film thicknesses but cannot alter the limiting width ($z \rightarrow \infty$). The logarithmic z dependence is a robust assumption. Using materials constants of $B = 9.88$ Å^2, which contains the interface tension between IP and PFMC [26] and a cutoff Q_{max} of 2 Å^{-1}, we can calculate the theoretical dependence of the interfacial width from the film thickness. In Fig. 2 we have plotted the derived roughness for equilibrium films as well as for growing films for the silicon and fused silica boundary (no difference in both substrates can be found).

The width in true equilibrium is compared to the interfacial broadening during the growth of the wetting films. One

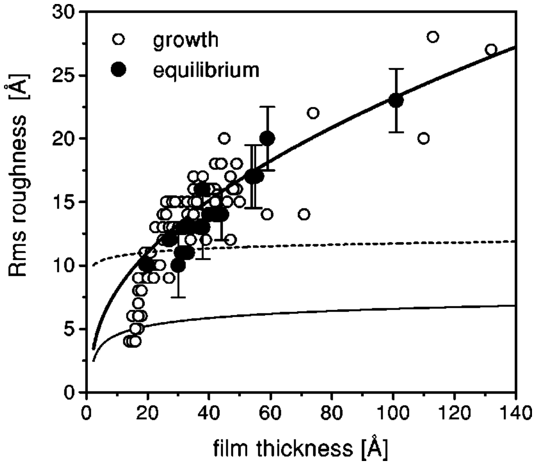

FIG. 2. Interfacial width between the IP wetting film and the PFMC bulk phase obtained from fits to reflectivity measurements. The solid dots represent the width of equilibrium films at a set of temperatures, whereas the open circles are derived from growing films at a fixed temperature. The lines represent models explained in the text.

can see that both data agree well in their dependence on the film thickness. The interfacial broadening is surprisingly high and exceeds models for capillary wave fluctuations. The thin solid line represents the logarithmic growth of the width assuming that long range van der Waals forces from the substrate pin the liquid-liquid interface for thin films [according to Eq. (2)]. The interfacial tension is taken from Ref. [26] and it is found that this value can sufficiently explain the corresponding interfacial width from a PFMC wetting film at the liquid-vapor interface [22]. The intrinsic interfacial width is attributed to a molecular dimension of the respective species (strictly speaking the radius of gyration) [4]. By including an increased intrinsic length of 10 Å instead of 3 Å the simulation displays an increased width but still cannot explain the large increase especially for thick films. The thick solid line is given under the assumption of a power law increase exponent 1/2 and can sufficiently describe the observation. Such an exponent can indeed occur in systems governed by short range forces, but it would still require a much larger free liquid-liquid width.

It could be argued that we do not at all observe a continuous film in nonequilibrium, but somehow nanoscaled structures (nanodroplets) accumulating at the interface. In this case, specular reflectivity would invariably give lateral averages, which are indistinguishable from a truly homogeneous film, so that the smoothly changing density could be most naturally interpreted as an accumulation of these objects. This would equally well explain the large roughness observed for these films, without the need for introducing variable densities. On the other hand, there is no significant difference between the roughness for equilibrium films and growing wetting layers. Moreover, at the very beginning of the growth procedure, the roughness should be maximal and should probably decrease for thick films if such objects fuse, if droplets were present. Neither is the broadening explainable by a standard capillary wave approach, which disagrees in magnitude and functional behavior. On the contrary, we postulate an interface broadened locally due to a slowly varying concentration across the interface, as we will show in the next part the close correspondence to the equilibrium structure in the single phase region of the phase diagram.

B. Density profiles in the single phase region

Although it is known that wetting phenomena can only be properly treated if the excess adsorption is used as an order parameter [27,28], experiments normally focus solely on the thickness of the film and assume the density (concentration) of the wetting phase to be constant. This is a good approximation for nonsoluble liquids, but as far as binary liquids with critical mixing point are concerned, the concentration in the film becomes a variable too.

In our earlier studies we concentrated on the wetting films of IP between a (oxidized) silicon surface and the conjugated PFMC phase. By starting from a zero concentration of IP and letting the system equilibrate to binary phase coexistence, the wetting film appeared with a smooth density change from PFMC density to IP density right at the surface. We interpreted this nonequilibrium structural feature as corresponding to an equilibrium situation with a concentration below the coexistence concentration of IP. One could argue that the observed density change is a purely transient phenomenon, realizing the symmetry breaking event at the interface from no film to a wetting film. This would imply that such a structure cannot be observed in true equilibrium.

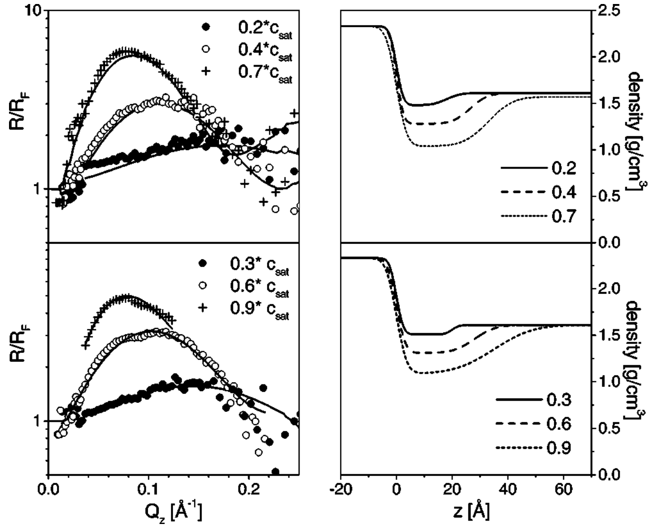

FIG. 3. Normalized reflectivities from an interface between the silicon substrate and the PFMC phase in thermodynamical equilibrium. The concentration of IP has been increased subsequently for each measurement to approach the two phase equilibrium with the numbers given in the diagram. The lower curve represents a temperature above T_w, whereas the curves in the upper diagram are performed below T_w. The right-hand side sketches the corresponding density profiles at the interface.

For that reason, an experiment was performed where a silicon surface was immersed in pure PFMC and IP was added with a microliter syringe so that the concentration remained below the saturation concentration at a certain temperature. This allows to study the equilibrium structure at the interface in the single phase region. Because of the strong demand in experimental time it could only be performed on the laboratory x-ray source. Figure 3 displays the reflectivity yield normalized to the Fresnel reflectivity of a steplike interface. Several points in the phase diagram were examined, particularly one series below the wetting transition (42 °C) and one above the wetting transition (55 °C). The right-hand side displays the density profiles at the interface that fit the reflectivity best. Although the Q range is restricted and the statistics of the data is not comparable to the data that were taken at synchrotron beamlines, it was not possible to fit the data with models that keep a constant density of films for different concentrations. The fits show a clear density change and thickness growth as the two phase coexistence concentration is approached. That proves that the film density is a variable in the adsorption regime in the homogeneous phase. The kinetic wetting experiments thus realize a situation where the film is in equilibrium with its local liquid PFMC bulk, while the concentration of IP steadily increases within the PFMC-rich phase. The structure, therefore, corresponds to a well-defined path in the phase diagram from 100% PFMC to the two phase coexistence at $c_{IP}=c_{sat}$ [29]. Strikingly we found the same behavior for this binary liquid as well in the complementary case at the liquid-gas interface, where a continuous adsorption of PFMC can be observed [22]. We conclude that a general property of binary liquids is described. Approaching the phase coexistence of a class of binary systems from the single phase region requires the adsorption at a boundary to form filmlike structures that increase smoothly in density and in thickness. Looking at calculations and simulations of simple model systems, e.g., by molecular dynamics or gradient theory reveals that such features are easily produced when approaching the phase coexistence. Gradient theory is known to miss the fine structure at a molecular level of adsorbed films, but nevertheless such calculations find a structure that is amazingly similar to our results [27]. It might be worth interpreting this in the light of phase stability in confined geometry [30].

C. Diffuse scattering

In contrast to other probes for wetting thin films, x-ray scattering can address the structure of the interface, where reflectivity contains information about the laterally averaged interface profile, whereas diffuse scattering with a wave vector transfer within the interface is sensitive to the spectrum of fluctuations.

To distinguish between lateral fluctuations of the interface plane and an intrinsic broadening, we evaluated the longitudinal diffuse scattering that was collected together with the reflectivity in thermal equilibrium for a series of film thicknesses. The offset angle from specular reflectivity corresponds to a lateral momentum transfer of 7×10^{-5} Å^{-1}, and comprises the integration over a range of momentum transfer perpendicular to the reflection plane due to lateral wide slits included within the analysis. The diffuse intensity was modeled according to the proposed expression of Tidswell *et al.* [17], where the diffuse scattering from the substrate, bulk scattering, and the (small) contribution from correlated scattering [31] to the liquid-liquid interface were modeled from the data of the pure PFMC-Si interface. The important part here is the contribution from capillary wave fluctuations of the liquid-liquid interface. Here a model of scattering distribution exists that gives a quantitative expression without adjustable parameters [32]. We used the formulation of Tidswell *et al.* to compute the capillary wave scattering from films with increasing thickness and thus increasing fluctuation due to depinning from the substrate [33]. Figure 4 presents a set of diffuse scattering results for the pure PFMC-Si interface and interfaces with wetting films of IP at different thicknesses (40.5 Å at 42.70 °C and 61 Å at 47.98 °C), together with calculations of diffuse scattering assuming an interfacial tension of 13 mJ/m^2 [26]. The capillary wave contributions are consistent with the normal interface fluctuation behavior as expressed by both lines for the logarithmic expression in Fig. 2. These simulations show a good agreement with the increase of diffuse scattering with film thickness, and sustain the capillary wave contribution as only a minor part of the total interface broadening. To explain the increase of broadening as seen in the vertical direction above that level from capillary wave contributions, one would have to accept a much larger diffuse scattering. Such an expectation is indicated by the dashed line in Fig. 4 by decreasing the interfacial energy by a factor of 4 to reach the level of interfacial width as measured in reflectivity. This is clearly above the experimental results and again implies that the broadening is not due to lateral fluctuations, but of local nature.

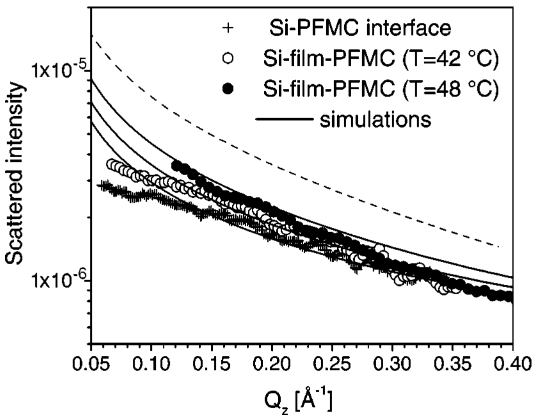

FIG. 4. Longitudinal diffuse scattering at the silicon-PFMC interface (+), and the interface with intruding IP wetting film with two different thicknesses (○, 42 Å; ●, 62 Å). The lines represent simulations for capillary wave theory explained in the text in the same order as the measured data. The dotted line is a calculation with a strongly decreased interfacial tension that leads to a strong interfacial broadening corresponding to the interfacial width measured in reflectivity (at 48 °C).

We conclude that the observed diffuse scattering is in agreement with the capillary wave model. No additional corrugations of the lateral interface position can be present on the length scale of the lateral momentum transfer, as would certainly occur in a disordered system. The specular reflectivity, therefore, reveals an excess smearing of the liquid-liquid interface compared to the broadening that stems from lateral fluctuation. The origin of this broadening can only be of a local character, i.e., a smooth density variation from the IP wetting film to the PFMC bulk phase.

IV. CONCLUSION

Unlike the findings at the liquid-vapor interface, the liquid-liquid interface displays a considerable broadening as a function of the film thickness. This broadening cannot be understood in terms of increasing fluctuations of capillary wave nature, but consists of the local broadening of the density transition between the two liquid phases. We come to this conclusion by analyzing the specular reflectivity concerning the interfacial width as a function of the film thickness that is sensitive to both lateral fluctuations and local broadening. This broadening is compared to diffuse scattering under grazing angles, which is most sensitive to lateral fluctuations. The strong broadening is observed in the density profile perpendicular to the interface but is not confirmed by the increase in diffuse scattering as is should be for increased fluctuation amplitudes. A number of theoretical investigations of model Lennard-Jones liquids using the gradient theory or Monte Carlo simulations naturally give effects of comparable structure far off from the two phase coexistence. Indeed the observation of a film profile varying smoothly in density when approaching the phase coexistence is in agreement with this scenario. The wetting film in the partial wet phase can no longer be regarded as a slablike profile with bulklike properties. Moreover, we observe a diffuse excess adsorption of the IP species at the interface, which increases smoothly in density and range. It ends at coexistence with a density that almost reaches the IP bulk density.

It is still an open question as to how the transition is made to films in the complete wet phase, as we were not able to quantify film structures with thicknesses exceeding our resolution limit of 2000 Å. The free liquid-liquid interface is certainly also accessible with x-ray scattering techniques. For the present system we found an interfacial width of 18 Å in a preliminary study. This means that if the limit of thick wetting films is described by a free liquid-liquid interface, the system has to cross a point where the interface roughness decreases again.

We gain additional confidence in our results by comparing them with the complementary liquid-vapor interface. There the anomalous broadening is absent and the width is sufficiently described by the capillary wave approach with the given parameters. Further work is required to decide whether the broadening is a generic feature of wetting films at liquid-solid interfaces, or has to be explained by specific interactions with the substrate that distort the profile of adsorption, as found recently in a variety of liquid-solid interfaces [5,34], where depletion or even lamellar ordering can be induced.

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