Observation of Capillary Waves on Liquid Thin Films from Mesoscopic to Atomic Length Scales

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The surfaces of liquid thin perfluorohexane, cyclohexane, decane, and ethanol films adsorbed on silicon wafers have been investigated by means of x-ray reflectivity, diffuse scattering, and grazing incidence diffraction. The measurements prove that the surface structure of the wetting films can be described by a universal height-height correlation function derived from a capillary wave model with the surface tension and particular cutoffs as parameters. The data favor a reduced capillary wave surface tension as predicted by exact theories, over an enhanced capillary wave surface tension, as suggested by simple mode-coupling models.

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While liquid thin films have been in the center of theoretical work (see, e.g., [1–7] and references therein) for several years, there is a considerable lack of experimental studies of their surface structure [8,9]. This is largely caused by experimental demands. One major challenge in the investigation of liquid films is to control their thickness with high accuracy. A stability of about one angstrom during many hours is required. Furthermore, liquid surfaces possess long-range correlations (capillary waves, see below). Hence, high resolution in reciprocal space is required making x-ray experiments at synchrotron sources mandatory. In fact, to our knowledge, the study of Tidswell *et al.* [10] is the only quantitative x-ray scattering experiment centering on the structure of the interfaces of liquid thin films on solid substrates. In this Letter, we show for the first time (i) that distinct capillary wave features—they will be specified below—are common for a large variety of liquids and film thicknesses; and (ii) that the surface tension which has to be used within the capillary wave model for thin films may be considerably lower than the macroscopic value.

The usual approach to describe a liquid/vapor interface is based on the presence of an “intrinsic interface” of width σ_0 and a surface tension γ_0 . The surface structure of semi-infinite liquids possessing thermally excited capillary waves superimposed on the intrinsic profile was calculated by Buff *et al.* [11,12]. It turns out that the wave spectrum depends solely on γ_0 and a short-wavelength cutoff $q_{\max}$ which is commonly assumed to be $q_{\max} \sim 2\pi/\kappa$, where κ is on the order of the molecular diameter of the liquid. In the past, this simple capillary wave model has been successfully tested for various bulk liquids [13–15]. However, the precise magnitude and physical origin of the short-wavelength cutoff are still discussed controversially [16]. Meunier’s mode-coupling approach [17,18] leads to a wave number dependent

surface tension $\gamma(q)$. To simplify the further discussion only the respective average $\gamma_{\text{cw}} = \langle \gamma(q) \rangle$ over all modes is considered with the result

$$\gamma_{\text{cw}} = \gamma_0 + 3k_B T / (32\pi) q_{\max}^2, \quad (1)$$

for the surface tension which has to be used in the capillary wave model. More recently, another approach based on the exact form of the van der Waals interactions was published by Napiórkowski, Dietrich, and Mecke [4,19,20]. They obtain rather complicated expressions for the wave number dependent surface tension $\gamma(q)$. Here, the average over all modes yields

$$\gamma_{\text{cw}} = \gamma_0 - \beta q_{\max}^2, \quad (2)$$

where $\beta \approx (0.3-0.5)\gamma_0 \text{ \AA}^2$ for many liquids [21]. Thus, Meunier proposes that the surface tension γ_{cw} of a capillary wave interface is effectively enhanced with respect to γ_0 , while Eq. (2) suggests the opposite. As we shall see later, only Eq. (2) can explain our data.

While, for bulk liquids, only the tiny gravitational background potential has to be included into the capillary wave model [13], in liquid thin films the much stronger van der Waals interaction with the substrate described with an effective Hamaker constant A_{eff} has to be considered [10]. This leads to a specific film thickness dependent additional low-wave-number cutoff $q_l = q_{\text{vdW}} = a/d^2$ in the capillary wave spectrum, where the film thickness is denoted by d , and the length $a = (A_{\text{eff}}/2\pi\gamma_{\text{cw}})^{1/2}$.

We have studied the surfaces of the highly volatile liquids cyclohexane, perfluorohexane, decane, and ethanol adsorbed on polished silicon wafers with native oxide layers (thickness $d_{\text{ox}} \approx 15 \text{ \AA}$) by means of x-ray reflectivity, diffuse scattering, and grazing incidence diffraction (GID) measurements. The wafers were cleaned by heating in sulfuric acid solution and a subsequent rinsing with

toluene. This procedure leads to very smooth substrates with surface roughnesses of about $\sigma \sim 2 \text{ \AA}$ (measured by specular reflectivity and atomic force microscopy; the diffuse scattering from the substrates is negligible).

The wetting films have been prepared inside two temperature-controlled, evacuated cells. By cooling a reservoir and stabilizing the temperature (always $\sim 300 \text{ K}$) inside the sample cell, the pressure above the wetting film, and, hence, the film thickness d , was varied. To obtain films within the thickness range $20 < d < 250 \text{ \AA}$, the temperature stability in the inner cell was better than 5 mK (for details, see Ref. [22]).

The x-ray experiments have been carried out at beam lines W1.1 and BW2 at HASYLAB (DESY, Hamburg) and at beam line ID10B (TROIKA II) at the European Synchrotron Radiation Facility (Grenoble). For the reflectivity and diffuse scattering experiments, the resolutions defined by the slit widths are $\delta_{q_z} \approx 1 \times 10^{-3} \text{ \AA}^{-1}$ and $\delta_{q_x} \sim q_z \times 10^{-4}$, where q_x and q_z are the components of the scattering vector $\vec{q} = \vec{k}_f - \vec{k}_i$ parallel and perpendicular to the sample surface in the scattering plane. In the out-of-plane direction, y , all slits were wide open leading to an effective integration over the wave vector component q_y [13]. For the GID measurements, the slits in the y direction were narrowed leading to an out-of-plane resolution $\delta_{q_y} \approx 1 \times 10^{-2} \text{ \AA}^{-1}$.

The theory of capillary waves leads to the mean quadratic height difference,

$$g(\vec{r}) = \langle [z(\vec{r}) - z(\vec{0})]^2 \rangle = 2\sigma^2 - BK_0(q_l r), \quad (3)$$

where $z(\vec{r})$ describes the vertical displacement of the liquid surface at the lateral position $\vec{r} = (x, y)$ relative to some origin $\vec{0}$, σ is the total roughness (see below), B is given by $B = k_B T / \pi \gamma_{cw}$, q_l is the low-wave-number cutoff, and $K_0(x)$ denotes the modified Bessel function. The scattered x-ray intensity, $I(\vec{q})$, in Born approximation is given by the 2D Fourier transform in (q_x, q_y) of $\exp\{-(q_z^2/2)g(\vec{r})\}$ [23]. Assuming Eq. (3) and integrating over q_y leads to characteristic power-law tails in the diffuse scattering. The rms roughness σ may be calculated by integration over the power spectrum. One obtains (for details, see Refs. [13,23])

$$I(q_x, q_z) \sim q_x^{\eta(q_z)-1}, \quad \text{for } q_x > q_l, \quad (4)$$

where the exponent $\eta(q_z)$ is given by $\eta(q_z) = Bq_z^2/2$, and [16]

$$\sigma^2 = \sigma_0^2 + (B/2) \ln(q_{\max}/q_l). \quad (5)$$

While for bulk liquids the low-wave-number gravitational cutoff q_l is so small ($q_l \sim 10^{-8} \text{ \AA}^{-1}$) that it is invisible in scattering experiments [13], the cutoff is considerably larger for thin films, namely, $q_l = q_{vdW} \sim 10^{-4} - 10^{-2} \text{ \AA}^{-1}$ in the present study. Thus, the power laws with specific q_z -dependent exponents of the diffuse scattering [Eq. (4)], the film thickness dependent lower cutoff q_l , and a logarithmic increase of the rms roughness σ with

the film thickness [Eq. (5)] are the “fingerprints” of capillary waves on surfaces of liquid thin films.

Figure 1 shows a log-log plot of the diffuse x-ray scattering data (transverse q_x scan) for a cyclohexane film of thickness $d = 225 \text{ \AA}$. Power laws can be easily identified. However, for this thickness no cutoff is visible in the data: The estimated number is $q_{vdW} \sim 10^{-4} \text{ \AA}^{-1}$ with $a \sim 5 \text{ \AA}$, a value typical for most organic liquids. Therefore, for thicker films the low-wave-number cutoff is still “hidden” under the Gaussian shaped resolution function of the instrument (see left region in Fig. 1). The inset shows a plot of the η values, as obtained from the data by Eq. (4), vs q_z^2 . It demonstrates that the prediction for capillary waves $\eta \sim q_z^2$ is well satisfied. From the slope of this line a value $\gamma_{cw} = 14 \text{ mJ/m}^2$ is obtained for the capillary wave surface tension. Using Eq. (2), this corresponds to $\gamma_0 = (26 \pm 4) \text{ mJ/m}^2$. The error bar was estimated by taking the two extreme values for β in Eq. (2). The published value $\gamma_0 = 24.8 \text{ mJ/m}^2$ is well inside the error bar region. Instead, Eq. (1) would yield $\gamma_0 \sim 10 \text{ mJ/m}^2$ and, hence, can be ruled out.

The second feature of capillary waves on thin film surfaces, namely, the direct observation of the van der Waals cutoff, can be seen in Fig. 2. Here, transverse q_x scans for fixed q_z are shown for all films. The vertical lines indicate the locations of the van der Waals cutoffs. The “kinks” in the curves coincide almost perfectly with this location. Also the power-law behavior for $q_x > q_{vdW}$, as predicted by Eq. (4) and discussed above, is evident. Hence, one has to conclude that thermally activated waves with

FIG. 1. Diffuse scattering for a cyclohexane film of thickness $d = 225 \text{ \AA}$. The transverse q_x scans (symbols) were taken at fixed $q_z = 0.14, 0.19, 0.23$, and $0.28 \text{ \AA}^{-1}$ (bottom to top). The solid straight lines highlight the power-law regions. The measured Gaussian beam profile is given by a solid line, too. In the inset, η vs q_z^2 is plotted as obtained from the slopes of the power-law regions.

FIG. 2. Transverse scans for a $d = 92$ Å thick cyclohexane film (triangles, upper two curves) at fixed $q_z = 0.21$ and 0.13 Å $^{-1}$, and for decane ($d = 60$ Å, crosses), ethanol ($d = 78$ Å, plusses), and perfluorohexane films ($d = 150$ Å, circles). The vertical lines indicate the locations of the respective van der Waals cutoffs $q_{vdW} = a/d^2$. The solid line for the upper curve is a fit of the data using the full expression given by Eq. (3) including dynamical scattering effects (see Ref. [13]).

wavelengths $\Lambda < 2\pi/q_{vdW} \sim 6000$ Å can propagate almost unhindered on the liquid surfaces while waves possessing large wavelengths $\Lambda > 2\pi/q_{vdW}$ are suppressed by the strong van der Waals background potential.

Figure 3 shows the rms roughnesses $\sigma(d)$ as obtained from the fits of the specular reflectivity data for all investigated films. It is important to note that, in contrast to previous studies of ultrathin liquid cyclohexane films [10], even for the thinnest films ($d \sim 30$ Å) no conformal roughness was detected from longitudinal diffuse scattering measurements. However, since we have used very smooth silicon wafers as substrates, this is not a contradiction to previous work. As a very small value for the width σ_0 of the intrinsic profile is found ($\sigma_0 < 0.5$ Å), the roughnesses given in Fig. 3 may be directly compared with those calculated from Eq. (5). The solid lines in the figure display calculations where the same parameters γ_{cw} and a as used for the explanation of the diffuse scattering are taken. The slight increase of σ as suggested by Eq. (5) in connection with the introduction of

FIG. 3. Surface roughness σ for the investigated liquid thin films as obtained from specular x-ray reflectivity data (open circles). The solid lines are capillary wave calculations without any adjustable parameter.

the low-wave-number van der Waals cutoff $q_l = a/d^2$ [$\Rightarrow \sigma(d) \sim \ln(d)$] can be seen. Although the error bars are relatively large, Fig. 3 shows the predicted roughness increase by capillary waves on thin film surfaces. For a polymer/polymer interface a similar effect, but with larger error bars, has recently been found in neutron reflectivity measurements [24]. In Fig. 3 departures of the measurements from the calculated $\sigma(d)$ curves for large film thicknesses are obvious. This trend may be explained by retardation effects which have to be considered for thick films and lower the value of the effective Hamaker constant yielding an increased surface roughness.

To obtain depth sensitive information about lateral distances on the order of atomic dimensions we have performed GID measurements for perfluorohexane and cyclohexane films. As an example, Fig. 4 shows the data for a cyclohexane film. The first liquid structure factor maximum corresponding to a mean lateral distance of the liquid molecules of $\kappa \sim 5.2$ Å is clearly visible [25]. This distance was used as upper cutoff $q_{max} = 2\pi/\kappa$ for the explanation of the data obtained for the cyclohexane and perfluorohexane films in Figs. 1–3. For the other liquids the published van der Waals diameters were inserted. The open circles in Fig. 4 are the x-ray data obtained for an incidence angle α_i below the critical angle. Thus, the penetration depth is limited to approximately 50 Å. The solid line is the bulk structure factor of cyclohexane as obtained by Farman *et al.* [26]. Since the two curves almost coincide, one may conclude that the lateral structure of the topmost 50 Å is little affected in a thin film. This supports the assumption of free capillary waves on top of the thin film surfaces which was used to explain the data of Figs. 1–3. If the penetration depth is increased, the region next to the substrate also contributes to the

FIG. 4. GID measurement of the liquid structure factor peak a cyclohexane film with $d = 225 \text{ \AA}$. The dashed vertical line indicates the bulk value of q_r corresponding to a pair distance of $2\pi/q_{r,\text{bulk}} = 5.2 \text{ \AA}$. The solid line is the bulk liquid structure factor as obtained by neutron scattering [26].

scattering, and departures from the lateral bulk structure become visible. This will be discussed elsewhere. Preliminary results for hexane films where this effect is most pronounced may be found in Ref. [27].

In summary, x-ray reflectivity, diffuse scattering, and GID measurements show the presence of capillary waves at the surfaces of all films. A consistent picture of the surface morphology is obtained. Furthermore, the measurements show strong evidence for a lowered surface tension of a capillary wave interface as favored by modern theories [19,20].

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- [1] D. Andelmann, J.-F. Joanny, and M.O. Robbins, *Europhys. Lett.* **7**, 731 (1988).
- [2] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J.L. Lebowitz (Academic, New York, 1988), Vol. 12.
- [3] S. Dietrich, *Phys. Scr.* **49**, 519 (1993).
- [4] S. Dietrich, *J. Phys. Condens. Matter* **8**, 9127 (1996).

- [5] M. Schick, *Introduction of Wetting Phenomena*, in *Proceedings of the Les Houches Summer School, Session XLVIII*, edited by J. Charvolin, J.-F. Joanny, and J. Zinn-Justin (Elsevier, New York, 1989).
- [6] D. Beaglehole, *Physica (Amsterdam)* **200A**, 696 (1993).
- [7] J. Jäckle, *J. Phys. Condens. Matter* **10**, 7121 (1998).
- [8] S. Garoff, E.B. Sirota, S.K. Sinha, and H.B. Stanley, *J. Chem. Phys.* **90**, 7505 (1989).
- [9] J. Daillant, L. Bosio, B. Harzallah, and J.J. Benattar, *J. Phys. II (France)* **1**, 149 (1991).
- [10] I.M. Tidswell, T.A. Rabedeau, P.S. Pershan, and S.D. Kosowsky, *Phys. Rev. Lett.* **66**, 2108 (1991).
- [11] F.P. Buff, R.A. Lovett, and F.H. Stillinger, *Phys. Rev. Lett.* **15**, 621 (1965).
- [12] J.V. Sengers and J.M.J. van Leeuwen, *Phys. Rev. A* **39**, 6346 (1989).
- [13] M.K. Sanyal, S.K. Sinha, K.G. Huang, and B.M. Ocko, *Phys. Rev. Lett.* **66**, 628 (1991).
- [14] A. Braslau, P.S. Pershan, G. Swislow, B.M. Ocko, and J. Als-Nielsen, *Phys. Rev. A* **38**, 2457 (1988).
- [15] H. Tostmann, E. DiMasi, P.S. Pershan, B.M. Ocko, O.G. Shpyrko, and M. Deutsch, *Phys. Rev. B* **59**, 783 (1999).
- [16] B.M. Ocko, X.Z. Wu, E.B. Sirota, S.K. Sinha, and M. Deutsch, *Phys. Rev. Lett.* **72**, 242 (1994).
- [17] J. Meunier, *J. Phys. (Paris)* **48**, 1819 (1987).
- [18] J. Als-Nielsen and K. Kjær, *Phase Transitions in Soft Condensed Matter*, edited by T. Riste and D. Sherrington, NATO Advanced Study Institute (Plenum, New York, 1989).
- [19] M. Napiórkowski and S. Dietrich, *Phys. Rev. E* **47**, 1836 (1993).
- [20] K.R. Mecke and S. Dietrich, *Phys. Rev. E* **59**, 6766 (1999).
- [21] Equation (2) is a crude approximation of the exact expressions for $\gamma(q)$ which are given in Ref. [19]. However, we are interested only in the general picture that the surface tension is effectively lowered with respect to γ_0 .
- [22] A.K. Doerr, Ph.D. thesis, Kiel University, 1999.
- [23] S.K. Sinha, E.B. Sirota, S. Garoff, and H.B. Stanley, *Phys. Rev. B* **38**, 2297 (1988).
- [24] M. Sferrazza, C. Xiao, R.A.L. Jones, D.G. Bucknall, J. Webster, and J. Penfold, *Phys. Rev. Lett.* **78**, 3693 (1997).
- [25] Recently, the structure factor for liquid metals next to a solid interface has been measured up to several inverse angstroms with high energy x-rays. See H. Reichert and H. Dosch (to be published).
- [26] H. Farman, F. Coveney, J.C. Dore, and M.C. Bellissent-Funel, *Mol. Phys.* **87**, 1217 (1995).
- [27] A.K. Doerr, M. Tolan, T. Seydel, and W. Press, *Physica (Amsterdam)* **248B**, 263 (1998).