Thermal diffuse x-ray-scattering studies of the water-vapor interface

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Agreement between the theoretical and measured resolution dependence of x-ray specular reflection from the H_2O-vapor interface shows that the macroscopic capillary model for surface roughness can be extended to length scales as small as 400 Å. Agreement between measured thermal diffuse scattering data and the theoretical form, with *no significant adjustable parameters,* independently leads to similar conclusions.

INTRODUCTION

The statistical physics of liquid surfaces has been the subject of extensive theoretical studies, however, experiments capable of providing relevant data have only recently become available.[1-8] One interesting development has been the interpretation of x-ray reflectivity measurements in terms of a finite microscopic width, of the liquid-vapor interface, that is dominated by roughness due to thermally excited capillary waves.[4-6] According to this interpretation, the specular reflectivity can be represented by $R(Q_z)=R_F(Q_z)\exp(-Q_z^2\sigma^2)$ where, $R_F(Q_z)$ is the Fresnel reflectivity for a smooth, sharp interface. For an incident angle α and wavelength λ, the wave-vector transfer $Q_z=(4\pi/\lambda)\sin(\alpha)$. The interfacial width σ has been represented as a combination of a local microscopic electron-density width σ_0 and the capillary-wave contribution,

$$\sigma^2=\sigma_0^2+\frac{k_BT}{4\pi^2\gamma}\int_{A_s}\frac{1}{q^2+k_g^2}d\mathbf{q}\ , \tag{1}$$

where k_BT is the Boltzman constant times the temperature, γ is the macroscopic surface tension $k_g^2=\rho_m g/\gamma$, where ρ_m is the *mass* density, and A_s is a circular region with a rectangular cutout in reciprocal space. The inner boundary of A_s is determined by the known resolution of the x-ray reflectometer such that x-rays scattered by capillary waves with wave vectors $\mathbf{q}$ outside of the inner boundary, and thus contained in A_s, are deflected outside the angular acceptance of a detector centered on the position for specular reflection.[9] This scattering reduces $R(Q_z)/R_F(Q_z)$ to less than unity. Since long wavelength capillary waves scatter at small angles, the σ measured by a detector with finite resolution is not affected by waves at small $\mathbf{q}$. Consequently σ^2 is specified in terms of only two adjustable parameters: the intrinsic width of the electron density profile σ_0 and the radius $q_{\max}$ of the outer perimeter of A_s.

Since the origin of both σ_0 and $q_{\max}$ are microscopic (on the scale of angstroms) their effects cannot be separated by measurements that are only sensitive to in-plane length scales greater than 500 Å. Nevertheless, previous work had argued the plausibility of various values of σ_0 for particular choices of $q_{\max}$. For example, assuming $q_{\max}\approx(\pi/r_{\mathrm{mol}})$, where the molecular radius of H_2O was taken to be 1.93 Å, Braslau *et al.*[5,6] were able to fit the measurements at one resolution from the H_2O surface and they obtained an intrinsic width of $\sigma_0=1.8\pm0.2$ Å. Using higher-purity H_2O Daillant *et al.*[4] *measured slightly smaller* values for σ, and consequently obtained satisfactory fits using a physically equivalent theoretical form with $\sigma_0\approx0$. Braslau *et al.* also measured the reflectivity from CCl_4 and CH_3OH, having surface tensions, approximately, $\frac{1}{3}$ that of H_2O, and demonstrated that if σ_0 were allowed to vary, the reflectivities from the surface of all three liquids were consistent with known surface tensions and plausible values for σ_0.[10] They also measured the reflectivity of CCl_4 using two different resolutions. Although the measured values of σ roughly agreed with the capillary-wave prediction, the values of σ_0 were not equal.

In this paper we present specular reflectivity from the surface of clean H_2O using three resolutions in the ratio of 6.25:2.5:1.0. The data for all three resolutions can simultaneously be fit with $\sigma_0=0$ and *one common value* of $q_{\max}=(\pi/1.4)$ Å^{-1}. In addition, we present diffuse-scattering measurements that agree with a theoretical form for capillary waves that has no significant adjustable parameters.[6,7] The combination of the resolution dependence of the specular reflection and the diffuse scattering demonstrates that capillary waves with wavelengths of the order of 400–80 000 Å contribute to the width of the water-vapor interface as expected from the macroscopic theory of Eq. (1).

EXPERIMENTAL

A Langmuir trough, milled from a solid piece of Teflon, was filled with water from a Millipore Milli-Q+ system.[11] The entire apparatus was sealed in an alumi-

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num box filled with high-purity nitrogen. The absolute surface tension, measured *in situ* by a Wilhelmy plate was $\gamma = 72.5 \pm 0.4$ dyn/cm at a temperature $T = 20 \pm 0.5$°C. The precision of repeated measurements on a given water surface was 0.01 dyn/cm. Surface purity was assured by requiring that changes in the surface tension accompany the sweep of a Teflon barrier across the surface were less than 0.1 dyn/cm for an area compression by a factor of 4.

The experiments were performed on beam line *X22b* at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using a liquid-surface reflectometer that has been described elsewhere.[5,12,13] For specular reflection, the wavelength $\lambda = 1.2569 \pm 0.0002$ Å and for diffuse scattering $\lambda = 1.3965 \pm 0.0002$ Å. The size of the beam was defined by a slit with dimensions $h_i \times w_i$ [(height)×(width)], where $h_i \approx 0.2$ mm and $w_i \approx 3.0$–4.0 mm, which was approximately 400 mm from the monochromator. The distance L from the monochromator to the sample and from sample to detector was approximately 600 mm. The measured angular spread was $\Delta\alpha \approx 6 \times 10^{-5}$ rad in the vertical and $\Delta\Phi \approx 1 \times 10^{-3}$ rad in the horizontal. The magnitude of h_i was chosen so that its length projected on the sample, was smaller than the length of the sample (about 85 mm). The detector slit could be placed so the detector accepted radiation at an angle β from the horizontal and at an azimuthal angle ϕ. The dimensions h_d and w_d of the detector slit were set larger than the incident slit dimensions so the reflected beam could pass into the detector.

Considering the illuminated area on the liquid surface to be a uniform source for the diffuse scattering, the full widths at half maximum of vertical and horizontal angular spread accepted by the detector are $\Delta\beta \approx h_d/L$ and $\Delta\phi = w_d/L$.[14] The wave vector difference between the scattered and incident radiation, or the wave-vector transfer, is given by $\mathbf{Q} = \mathbf{q}_{\text{out}} - \mathbf{q}_{\text{in}}$:

$$Q_z = (2\pi/\lambda)[\sin(\alpha) + \sin(\beta)] ,$$

$$Q_x = (2\pi/\lambda)\sin(\phi/2)[\cos(\beta) + \cos(\alpha)] ,$$

and

$$Q_y = (2\pi/\lambda)\cos(\phi/2)[\cos(\beta) - \cos(\alpha)] .$$

The specular condition, $\alpha = \beta$ and $\phi = 0$ is equivalent to $Q_x = Q_y = 0$. The interior dimensions of A_s, ΔQ_x and ΔQ_y are calculated from $\Delta\alpha$, $\Delta\beta$, and $\Delta\phi$.

RESULTS

To test the predicted dependence of σ^2 on the interior dimensions of A_s the angular dependence of specular reflectivity was measured with detector heights h_d of 0.8, 2.0, and 5.0 mm. The three data sets are plotted in Fig. 1 as $\ln[R(Q_z)/R_F(Q_z)]$ versus Q_z^2. As predicted by Eq. (1), reflectivity for the smaller slits decreases faster. The three data sets were simultaneously fit to the capillary-wave model, with $\sigma_0 = 0$, varying only $q_{\max}$. Since

$$\Delta Q_y \approx (2\pi/\lambda)\cos(\phi/2)\sin(\beta)\Delta\beta ,$$

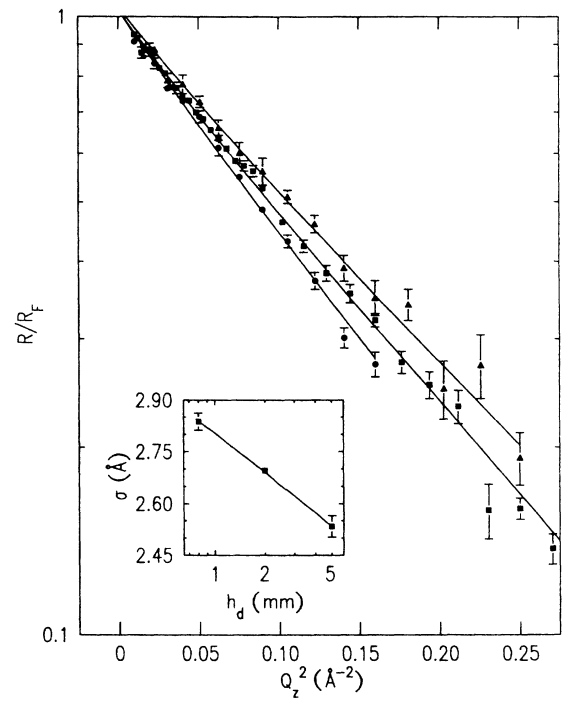

FIG. 1. Specular reflectivity data in the form of $R(Q_z)/R_F(Q_z)$ vs Q_z^2 for detector slit heights of 0.8 mm (●), 2.0 mm (■), and 5.0 mm (▲). The solid lines represent the best fit of the model discussed in the text. The inset shows the width of the surface profile plotted vs the detector slit height. The squares are derived from the fits to the data and the line is calculated from the theory at $Q_z = 0.4$ Å^{-1}.

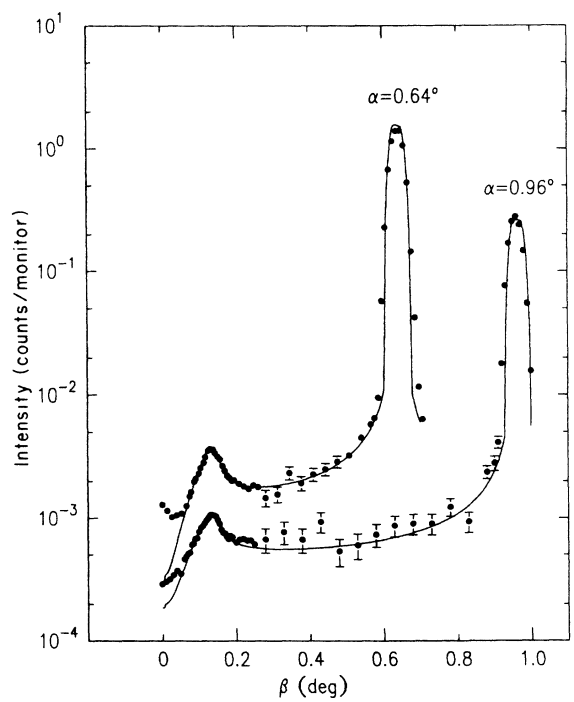

FIG. 2. Scattered intensity, in the plane of incidence, as a function of detector angle β for incident angles $\alpha = 0.64°$ and 0.96°. The peaks at $\beta = \theta_c \approx 0.13°$ are due to the surface scattering enhancement factor, the peaks at $\beta = \alpha$ are the specular reflectivity signals. The solid line is the theoretical prediction calculated with *no significant adjustable parameters.*

both the interior boundary of A_s and σ^2 vary with Q_z. The solid lines in Fig. 1 illustrating this fit correspond to $q_{\max}=(\pi/1.4\pm0.1$ Å) and a $\chi^2=1.03$. The inset to Fig. 1 displays calculated values of $[\sigma^2(Q_z)]^{1/2}$ calculated from this fit for $Q_z=0.4$ Å^{-1}.

In the specular position the reflectometer detects both the expected "specular signal," and diffuse scattering from windows, air, etc. Specular reflection is typically identified as the difference between scattering in the specular position and scattering at a small angle away from the specular position. This correctly subtracts away background that is approximately constant in angle. Since diffuse scattering from capillary waves varies as $1/(q^2+k_g^2)$, and k_g^2 is much smaller than our resolution, this procedure also subtracts part of the scattering from capillary waves. Taking that into account, the solid lines in Fig. 1 correspond to the calculated difference between the specular and off-specular signals.[15]

According to the capillary-wave model, the intensity removed from the specular reflectivity by scattering from a capillary wave with wave vector **q** appears as diffuse scattering at finite $\mathbf{Q}=(q_x,q_y,Q_z)$. To examine this, x-ray intensity was measured as a function of outgoing angles β, while keeping $\phi=0$ and the incident angle α fixed. Figure 2 illustrates data taken for $\alpha=0.64°$ and 0.96°. The solid line is determined by the model, to be described below, which contains no significant adjustable parameters. The deviations at small β correspond to small-angle scattering from the chamber window on the incident side of the trough. It is more prominent for smaller α.

The theoretical prediction for the diffuse scattering I_D is obtained by averaging the differential cross section $d\sigma/d\Omega=(r_e\rho)^2(A_0/\alpha)\Gamma f(\alpha)f(\beta)$ over the incident angular distribution and integrating over the angular acceptance of the detector. The cross sectional area of the incident beam is A_0 and the functions $f(\alpha)$ and $f(\beta)$ are the Fresnel surface scattering enhancement factors: $f(\beta)\approx(2\beta/\theta_c)^2\sqrt{R_F(\beta)}$ (where the critical angle for total external reflection, $\theta_c^2\equiv\rho e^2\lambda^2/\pi mc^2$). They approach zero for $\alpha,\beta\rightarrow0$, have a peak of amplitude 4 when $\alpha,\beta\approx\theta_c$, and level off to unity when $\beta\gg\theta_c$.[6,16] Taking $\Gamma\equiv(k_BT/\gamma)(q^2+k_g^2)^{-1}$:

$$I_D=[I_0/(A_0\Delta\alpha)]\int_{\alpha-\Delta\alpha/2}^{\alpha+\Delta\alpha/2}d\alpha\int_{-\Delta\phi/2}^{\Delta\phi/2}d\phi\int_{\beta-\Delta\beta/2}^{\beta+\Delta\beta/2}d\beta\, d\sigma/d\Omega\ , \tag{2}$$

where $\Delta\alpha$, $\Delta\beta$, and $\Delta\phi$ are the widths of the distributions of the respective angles and I_0 is the total incident flux.[17] The displayed fits include a small constant background on the order of 10% of the intensity of the peak at $\beta=\theta_c$. In the small-angle approximation $Q_x\approx(2\pi/\lambda)\phi$ and $Q_y\approx(\pi/\lambda)(\alpha^2-\beta^2)$ and the integral over ϕ can be done analytically. The solid lines in Fig. 2 are obtained by numerical integration of I_D and by adding a δ function at $\alpha=\beta$, of amplitude $A_\delta=\exp(-Q_z^2\sigma^2)$, where

$$\sigma^2=\frac{k_BT}{2\pi\gamma}\int_0^\infty q\,dq/(q^2+k_g^2)\ .$$

This term represents the true *specular reflection,* due to the gravitational cutoff of the $1/q^2$ fluctuations, that would be observed with infinite resolution.[18]

DISCUSSION

The agreement between the resolution dependence of σ^2 and the specular reflectivity data out to $Q_z\approx0.5$ Å^{-1} (i.e., $\beta\approx0.05$ rad) demonstrates that the macroscopic capillary-wave model is a good representation of the long-wavelength portion of the spectrum of surface excitations. In terms of the real-space fluctuations, this is equivalent to saying that the macroscopic description is a good representation of the height-height correlations in surface fluctuations over distances as short as the reciprocal of the coarsest resolution in $\Delta q_y\approx(2\pi/\lambda)(\beta\Delta\beta/2)$. For $Q_z\approx0.5$ Å^{-1}, $\beta\approx0.05$ rad, and $\Delta Q_z=(2\pi/\lambda)(\Delta\beta/2)\approx(2\pi/1.259$Å) (5.0 mm/600 mm). This corresponds to the length $1/\Delta q_y=1/(\beta\Delta Q_z)=480$ Å.

The agreement between theory and experiment—for both the *amplitude and the line shape*–for the diffuse scattering demonstrates that the macroscopic capillary-wave model correctly represents the height-height correlation function over a region in reciprocal space that is bracketed by the transverse resolution $\Delta q_x\approx(2\pi/\lambda)(\Delta\phi/2)$ in one direction and $q_y\approx(2\pi/\lambda)[\cos(\theta_c)-\cos(\theta)]$ in the other. These are typically $\Delta q_x\approx(2\pi/1.3965$ Å$)[4/(600\times2)]=0.015$ Å^{-1} and $q_y\approx(2\pi/1.3965$ Å$)(1.4\times10^{-4})=6.3\times10^{-4}$ Å^{-1}. The larger of these two corresponds to a characteristic length of 400 Å, in agreement with the length scale determined by specular reflection. The smallest wave vector for which diffuse scattering was measured is slightly larger than the spectrometer width $\Delta q_y\approx(2\pi/1.3965$ Å$)[\cos(0.96°)-\cos(0.9°)]$ (e.g., Fig. 2) corresponding to approximately 8×10^4 Å.

Although it would be interesting to know if the capillary-wave model can be extended to even shorter lengths, or larger wave vectors, this would require either diffuse scattering, or specular reflectivity measurements at larger incident angles. Both of these measurements are limited by some combination of the maximum x-ray flux that can be applied to the sample and the diffuse background scattering from other sources. In principal, the higher flux and better collimation expected from future synchrotrons will probably enable these results to be extended to shorter lengths. In the meantime, one of the more important aspects of the present data is that it establishes confidence in the ability to use x-rays to characterize the surface properties of simple liquids on the

length scales of a few hundred angstroms to a few micrometers. In contrast, optical light scattering explores the surface on length scales of a micrometer to a millimeter.[19]

Measurements such as those reported here can now be applied to complex liquid surfaces with confidence that excess diffuse scattering above what is predicted from the capillary-wave model, or decreased reflectivity beyond what is expected from thermally excited capillary waves, can now be interpreted in terms of other microscopic models. For example, it is possible that there will be studies of excess diffuse scattering from compressed Langmuir monolayers on the surface of H_2O that will yield information on the inhomogeneity of the monolayers in different parts of the two-dimensional phase diagram. There are numerous other possible systems where one might expect roughness beyond what is expected from capillary waves, and these can now all be studied with some confidence that the basic capillary wave effects can be understood.

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[17]We have chosen a constant, or square wave, angular intensity distribution. This is a good approximation in this case, however, the results are almost identical for a trapezoidal distribution suggesting that they are insensitive to the exact form of the distribution.

[18]In the small-Q_z limit this expression for A_δ corresponds to the sum rule $I_0 R_F A_\delta + \int_{\text{all space}} I_D = I_0 R_F$.

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