# X-Ray-Scattering Study of Capillary-Wave Fluctuations at a Liquid Surface

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A study of the scattering of x rays from the liquid-vapor interface of ethanol at room temperature is reported and compared in detail to predictions based on standard continuum capillary-wave theory. Quantitative agreement is obtained and, in particular, the asymptotic power laws in the diffuse scattering characteristic of the algebraic decay of the density-fluctuation correlations at the surface are verified. The root-mean-square fluctuation of the liquid surface is obtained as 6.9 ± 0.2 Å.

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A liquid-vapor or liquid-liquid interface possesses the property that the density-density correlations induced by capillary-wave fluctuations at the interface are long ranged (i.e., macroscopic), in contrast to density fluctuations in the *bulk* liquid, which are short ranged. This is a remarkable consequence of dimensionality.[1] In the case of two-dimensional crystals or certain liquid-crystal phases, it is well known that the displacement-displacement correlations increase logarithmically as a function of distance,[2,3] resulting in the loss of true Bragg peaks and their replacement by power-law singularities of the form $q^{-(2-\eta)}$ in the structure factor $S(q)$. For liquid interfaces, there is an analogous effect, namely, the true *specular* reflection from the interface (which owes its existence only to finite-size or gravitational-cutoff effects) merges continuously (as we shall see) with the power-law singularities in reciprocal space originating along the rod in reciprocal space normal to the interface (the "specular ridge"). $q$ now refers to the component of wave-vector transfer *parallel* to the interface, and the exponent $\eta$ depends *only* on the surface tension and on $q_z$, the wave-vector transfer normal to the interface. Such power laws in $S(q)$ have been seen in x-ray- and neutron-scattering experiments from liquid crystals,[2] lyotropic membranes,[3] and single-crystal surfaces and adsorbed monolayers,[4] but this behavior has hitherto only been explored in one study[5] of the diffuse scattering from water in the small-$q_z$ ($\eta \sim 0$) limit. An important practical consequence is that in an analysis of the nominal "specular" reflectivity from a liquid surface it is imperative to take into account the diffuse scattering from capillary fluctuations.

There have been several recent studies of the x-ray scattering from a liquid surface.[5-11] In the experiments of Braslau *et al.*[6] and of Schwartz *et al.*[5] the nominal specular reflectivity has been analyzed in terms of a mean-square surface roughness calculated as an integral over capillary waves *not* sampled by the instrumental resolution, and shown to have a logarithmic dependence on the resolution width. We shall analyze the data here in accordance with a previous theoretical formulation[12] which yields an analytical expression for the static structure factor of the liquid surface and includes the effect of instrumental resolution.[13] This formulation yields almost identical expressions to those of Ref. 6 for the nominal specular reflectivity. In addition, this formalism explicitly yields the power-law tails in the diffuse scattering which are compared here with experiment.

From the theory of capillary waves, if $h(\mathbf{r})$ is the $z$ component of the interface displacement at lateral position $\mathbf{r}$ relative to some arbitrary origin, the quantity $g(\mathbf{r}) = \langle [h(\mathbf{r}) - h(0)]^2 \rangle$ is given to a good approximation by[14]

$$g(\mathbf{r}) = 2\sigma^2 - BK_0(\kappa r)\,, \tag{1}$$

where $B = k_B T/\pi\gamma$, $\gamma$ is the surface tension at temperature $T$ ($B = 6.0$ Å$^2$ for ethanol at room temperature), and $\sigma^2$ is the total intrinsic mean-square surface displacement. In particular,

$$\sigma^2 = \tfrac{1}{4} B \ln[(q_u^2 + \kappa^2)/\kappa^2]\,, \tag{2}$$

where $\kappa$ is the gravitational cutoff given by $(\Delta\rho g/\gamma)^{1/2}$, $\Delta\rho$ is the difference in mass density across the interface, and $g$ is the acceleration due to gravity ($\kappa^2$ is 35 cm$^{-2}$ for ethanol at room temperature). $K_0(x)$ is the modified Bessel function[15] and $q_u$ is the upper wave-vector cutoff for the capillary waves. In the Born approximation, $S(\mathbf{q})$ is obtained[12] from $g(\mathbf{r})$ by taking the 2D Fourier transform in $q_x$-$q_y$ space of $\exp[-(q_z^2/2)g(r)]$. Since $K_0(\kappa r) \to 0$ as $r \to \infty$, Eq. (1) yields a purely specular component; however, $S(q)$ must always be folded with a finite instrumental resolution width in $q_x$-$q_y$ space which is usually much greater than $\kappa$, and hence we can discuss the total scattering by using the approximation

$$K_0(\kappa r) = -\gamma_E - \ln(\kappa r/2)\,, \tag{3}$$

where $\gamma_E = 0.5772$, which yields the algebraic decay in the surface density-density correlation function. $S(q)$ then has to be folded with the instrumental resolution in $q_x$-$q_y$ space. We have intentionally set the wave-vector resolution normal to the scattering plane (the $q_x$ direction) to be coarse so that the spectrometer effectively integrates over the entire wave-vector spectrum along $q_x$.

In the $q_y$ direction, the resolution is modeled as Gaussian (with standard deviation $\sigma_y$). The observed intensity in the detector can then be shown to be given by

$$I = I_0 \frac{q_c^4}{16}\frac{1}{q_z^3}\left[\frac{1}{2k_0\sin\alpha}\right]\exp[-q_z^2\sigma_{\rm eff}^2]\frac{1}{\sqrt{\pi}}\Gamma\left[\frac{1-\eta}{2}\right] \times {}_1F_1\left[\frac{1-\eta}{2};\frac{1}{2};\frac{q_y^2L^2}{4\pi^2}\right]|T(\alpha)|^2|T(\beta)|^2, \quad (4)$$

where $I_0$ is the incident beam intensity, $k_0$ is the incident wave vector, $q_c$ is the wave vector corresponding to the critical angle of incidence ($=2k_0\sin\theta_c$), $\Gamma(x)$ is the gamma function, ${}_1F_1(x;y;z)$ is the Kummer function,[13,15]

$$\eta = \tfrac{1}{2}Bq_z^2, \quad (5)$$

and

$$\sigma_{\rm eff}^2 = \sigma^2 + \tfrac{1}{2}B\gamma_E - \tfrac{1}{2}B\ln(2\pi/\kappa L). \quad (6)$$

In Eq. (6) $L$ is the effective coherence dimension along the surface (determined principally by the inverse of $\sigma_y$). If we use Eq. (2), and realize that $\kappa \ll q_u$, expression (6) for the *effective* surface mean-square roughness can be simplified to yield

$$\sigma_{\rm eff}^2 = \tfrac{1}{2}B\ln\left[\frac{e^{\gamma_E}}{2\pi}q_uL\right]. \quad (7)$$

The factors $|T(\alpha)|^2|T(\beta)|^2$ in Eq. (4) arise from the distorted-wave Born approximation,[12] since the Born approximation breaks down when either the incident or scattered grazing angle of incidence ($\alpha$ or $\beta$ in Fig. 1) is close to the critical angle. $T(\alpha)$ is the usual Fresnel transmission coefficient for a smooth surface given by

$$T(\alpha) = \frac{2\sin\alpha}{\sin\alpha + (\sin^2\alpha - \sin^2\theta_c)^{1/2}}, \quad (8)$$

with $\theta_c$ equal to the critical angle.

In the derivation of Eq. (4), we have assumed that the incident beam is completely intercepted by the liquid surface, and approximated the resolution width $\sigma_y$ and hence $L$ (which is in principle a function of $\alpha$ and $\beta$) by its value at the specular ridge ($\alpha = \beta$). We have also ignored the folding of the factors $|T(\alpha)|^2|T(\beta)|^2$ with the instrumental resolution in order to obtain an analytical expression for the scattered intensity.

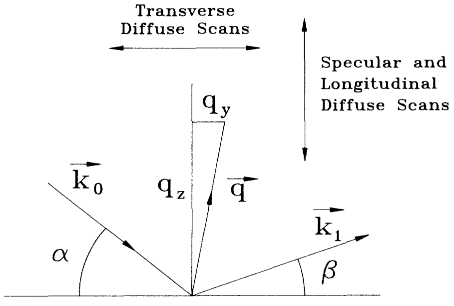

FIG. 1. Schematic reciprocal-space diagram for scattering experiments. The scans indicated are transverse (i.e., $q_y$ scans for constant $q_z$) or longitudinal ($q_z$ scans for constant $q_y$). Specular scans correspond to $q_y = 0$.

The asymptotic form of the Kummer function (for $q_yL \gtrsim 10$ and fixed $q_z$) in Eq. (4) predicts $S_{\rm obs}(q) \sim q_y^{\eta-1}$, which is a manifestation of the $\eta - 2$ power-law characteristic of all 2D systems, with one component of $q$ integrated over. For $q_y = 0$, on the other hand, $\alpha = \beta$ and ${}_1F_1((1-\eta)/2;\frac{1}{2};0) = 1$. We then obtain from Eq. (4) and identities relating $T(\alpha)$ to the Fresnel specular reflectivity $R_F(\alpha)$ the "effective specular reflectivity"

$$R = R_F\exp[-q_z^2\sigma_{\rm eff}^2]\frac{1}{\sqrt{\pi}}\Gamma\left[\frac{1-\eta}{2}\right]. \quad (9)$$

The factor $(1/\sqrt{\pi})\Gamma((1-\eta)/2)$ arises from the integration of the scattering over all $q_x$ and only differs from unity at large values of $\eta$.

In order to verify these predictions, we have studied the scattering of grazing-incidence x rays from a liquid ethanol surface. Ethanol was chosen because it is a good solvent for both water and organics, thus reducing the possibility of contamination of the liquid surface, and because it has a reasonably low surface tension (22 dyn/cm at room temperature). The sample was in the form of a $\sim$250-$\mu$m-thick film of liquid on the surface of a polished glass plate placed inside a leak-tight cell[16] with gold-plated Kapton windows for the incident and exit beams. The inside of the cell supporting the glass plate was maintained at 25.5 °C while the outside of the cell was maintained at 27.0 °C with the help of a thermoelectric device and a temperature controller to ensure that no liquid evaporated and condensed on the cell walls. The ethanol used was USP200 proof, and the cell, glass plate, and pipet used to introduce the liquid into the cell were thoroughly cleaned with a mixture of $H_2SO_4$ and $H_2O_2$ (Ref. 16) prior to the experiment. The experiment was performed using the liquid surface spectrometer on beam line X22B at the National Synchrotron Light Source. The operation of this spectrometer and the alignment procedure have been described in detail elsewhere.[8,16,17] The incident radiation was focused by a cylindrical mirror and diffracted horizontally by a Ge(111) monochromator crystal at $\lambda = 1.52$ Å. It was then tilted down to the liquid surface by means of a second Ge(111) monochromator crystal. The defining slits for the incident beam were 0.2 mm in the vertical direction (in the plane of scattering) and 2.0 mm in the horizontal direction, while those for the detector were 0.3 and 6.0 mm, respectively. The sample-detector distance was 610 mm. By suitable settings of $\alpha$ and $\beta$, scans were performed as a function of $q_z$ for fixed $q_y$ (specular and longitudinal diffuse scans) or as a function of $q_y$ for fixed $q_z$ (transverse diffuse scans) as shown in Fig. 1. The liquid sample thickness was measured by scanning the cell vertically. During the experiment this scan was performed periodically to confirm that no loss of liquid had occurred. No time-dependent effects were observed in the scattering due to gradual contamination of the surface.

Figure 2(a) shows the diffuse scattering intensity (normalized to the direct beam intensity) as obtained in transverse ($q_y$) scans for fixed values of $q_z$ ranging from 0.1 to 0.3 $\text{Å}^{-1}$. Also shown are the calculated scattering curves obtained from fits described below. In the fitting procedure to the five transverse scans only the background and $\sigma$ were allowed to vary. The background under the scattering curves was assumed to arise from bulk liquid scattering and can be described by a function of only $q_z$. The $q_y$ resolution function width $2\pi/L$ was calculated from the spectrometer resolution, i.e., slit settings. Excellent fits by the capillary-wave model were obtained with $\sigma = 6.9$ Å and a background which is well approximated by the form $2.9\times10^{-7}+3.5\times10^{-10}/q_z^2$ over the range of $q_z$ values studied [dashed lines, Fig. 2(a)]. Figure 2(b) shows the transverse scans plotted in a manner to illustrate the Kummer function form with respect to $q_y$ at several values of $q_z$. In the plot, the background-subtracted data have been corrected for variation in the illuminated area and normalized to unity at $q_y = 0$. One can see that Kummer function fits yield a good representation of the diffuse scattering both in the central (resolution-limited) region and in the "power-law" region. In particular, the exponent of the power-law tails, and the ratios of observed intensities between the "central" and "tail" regions (which depend sensitively on $\eta$ alone) are correctly obtained. For $q_z = 0.1$ $\text{Å}^{-1}$, the peak in the wing of the diffuse scattering (Yoneda scattering or "angel's wing"[12]) which arises from the factor $|T(\beta)|^2$ in Eq. (4) when $\beta \sim \theta_c$ is also correctly predicted. Also plotted is the direct beam profile converted (using the relationship $\Delta q_y = \frac{1}{2} q_z \Delta\beta$) into an effective transverse resolution function at $q_z = 0.1$ $\text{Å}^{-1}$, which shows no significant tail (e.g., due to slit scattering, etc.). This gives confidence that the observed power-law tails are indeed due to genuine diffuse scattering and are consistent with the model based on capillary-wave fluctuations. In Fig. 3 the longitudinal scattering is shown at $q_y = 0$ (specular) and at $q_y = 0.0005$ $\text{Å}^{-1}$ (diffuse). The only adjustable parameter is the incident beam intensity ($I_0$) which was obtained by fixing the reflectivity to unity at $q_z = 0.018$ $\text{Å}^{-1}$ just below the $q_c$ (0.0195 $\text{Å}^{-1}$) for ethanol. (We chose to adjust $I_0$ since the measured $I_0$, obtained with slightly different incident slits, gave a peak reflectivity of

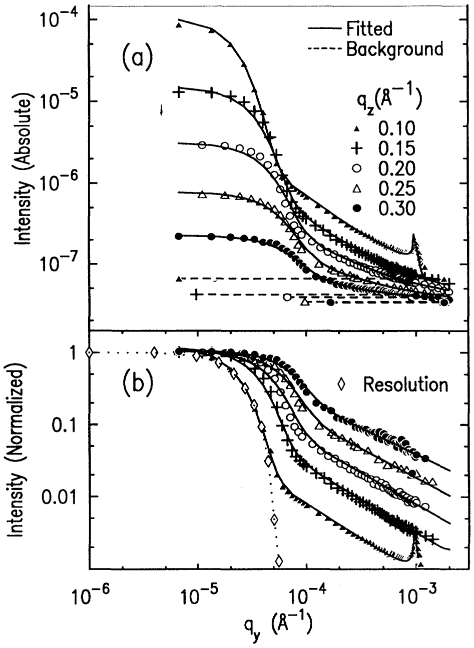

FIG. 2. (a) Log-log plot of the absolute scattered intensity (normalized to the direct beam) vs $q_y$ at several values of $q_z$. The solid curves represent the theoretical expression [Eq. (4)] added to the backgrounds (shown as dashed lines) as described in the text. (b) Log-log plot of the transverse diffuse scattering scans normalized to unity at $q_y = 0$ for different values of $q_z$. The intensities have been corrected for variation in illuminated area after subtraction of the fitted background. The solid curves represent the calculated scattering. The dashed curve indicates a scan of the profile of the main beam converted to an effective transverse resolution at $q_z = 0.1$ $\text{Å}^{-1}$.

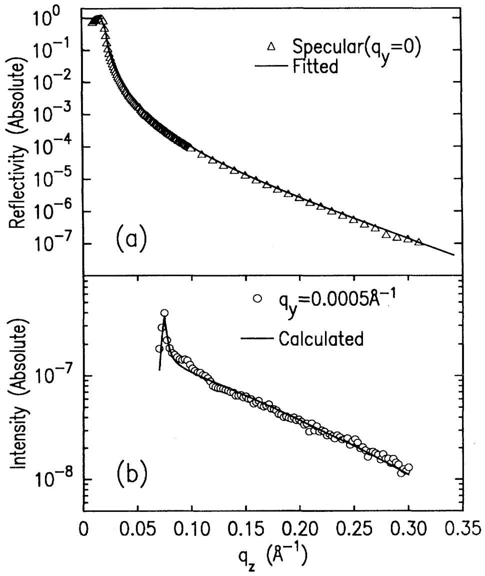

FIG. 3. (a) Measured and fitted "specular" reflectivity on an absolute scale. (b) Measured and calculated longitudinal diffuse scattering (normalized to direct beam) for $q_y = 0.0005$ $\text{Å}^{-1}$. The background has been subtracted from both of the spectra.

1.1 at $q_z = 0.018$ Å$^{-1}$.) Good agreement is obtained between the measured and calculated scattered intensities in the specular and diffuse scans as shown by the solid lines, where the specular scan has been used to refine $\sigma$ ($6.9 \pm 0.2$ Å). The background parameters have been fixed from the analysis of the transverse scans. The sharp peak [Fig. 3(b)] is again due to Yoneda scattering when $\beta$ passes through $\theta_c$ for this scan. The value obtained for $\sigma$ provides a value for $q_u \sim 0.50 \pm 0.3$ Å$^{-1}$, in agreement with the rough estimate of $\pi/d_m$,[1,6] $d_m$ being the molecular diameter (5.7 Å for ethanol).

In summary, we have shown that x-ray diffuse scattering from the surface of a typical liquid such as ethanol can be accounted for consistently in terms of the standard theory of capillary waves. A quantitative and satisfactory fit to all the scattering data has been obtained in terms of the root-mean-square height fluctuation at the surface, and a small background. All other parameters were fixed in terms of known physical constants. In particular, we have verified the algebraic decay of the density fluctuations at the surface of a liquid which leads to asymptotic power laws in the transverse diffuse scattering with a continuously varying exponent as given by Eq. (5).

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