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# Liquid surface order: X-ray reflectivity

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## Abstract

This note contains a brief summary of how the X-ray specular reflectivity technique can be used to measure electron density profiles across the bulk/vapor interface for a variety of liquids.

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## 1. Introduction

Following on extensive progress in our understanding of the properties of bulk matter, a good deal of interest has been directed towards the properties of surfaces and interfaces. Although interest in interfacial phenomena is not new, much of the experimental tools for studying them is new. These include atomic force and electron tunneling microscopy, the various forms of surface spectroscopy (SEXAFS, Auger, etc.) and synchrotron based X-ray scattering. This note is a summary of the invited oral presentation that one of us (PSP) made at the conference “Colloid and Interface Science: Trends and Applications” at Copamarina Beach, Puerto Rico in May 3–5 1995. In view of the fact that most of the results described there have already been published, as well as been reviewed this note is brief.

## 2. Background

It would be difficult to precisely date the onset of serious scientific interest in the nature of the liquid–vapor interface; however, we can note that Percus attributes the following form for the monotonic interfacial profile,  $\rho(z) = \rho_{\text{bulk}}\{1 - \tanh(z/\sigma)\}$  to theoretical mean field techniques published by van der Waals in 1894, where  $\sigma$  is a measure of the width of the interface [1]. In fact, when the influence of fluctuations (i.e., thermally excited capillary waves) in the location of the surface properties was recognized it became clear that a physically meaningful definition of interfacial width

must include a length scale  $\Delta L$  over which the fluctuations are averaged [2–6]. Since the surface is two-dimensional this leads to the logarithmical form

$$\sigma^2(\Delta L) \equiv (\Delta L)^{-2} \int_{\Delta L} d^2 r [h(r) - h(0)]^2 \sim (k_B T / \gamma) \ln(\Delta L / a), \quad (1)$$

where  $\gamma$  is the surface tension and  $a$  is a molecular dimension. For typical liquids, such as  $H_2O$ , the values of  $\sigma$  calculated from this expression are of the order 2–4 Å for  $\Delta L$  of the order of 0.1–1  $\mu m$ .

Although techniques such as laser based ellipsometry are sensitive to interfacial widths as small as these, wavelengths of the order of 1–2 Å make X-rays practically ideal for measuring structures characterized by such small  $\sigma$  [7, 8]. Although James discussed the phenomenon of X-ray reflectivity for studying interfaces in the earliest editions of his book [9], the technique was only developed into a practical tool for studying liquid surfaces within the past 10–15 yr [10–14]. In large part, this can probably be attributed to the development of synchrotron radiation X-ray sources. The basic idea is that for an incident angle<sup>1</sup>  $q$  and X-ray wavelength  $l$ , the ratio of the measured reflectivity  $R(\theta)$  to the ideal Fresnel reflectivity,  $R_F(\theta)$  from an abrupt-flat surface (i.e.  $\sigma = 0$ ) is approximately given by

$$\frac{R(\theta)}{R_F(\theta)} \approx |\Phi(Q)|^2, \quad (2)$$

where  $Q \equiv (4\pi/\lambda) \sin(\theta)$  and the surface structure factor is [15]

$$\Phi(Q) \equiv \int dz \frac{1}{\rho_{\text{bulk}}} \frac{d\langle \rho(z) \rangle}{dz} e^{iQz} \quad (3)$$

and  $\langle \rho(z) \rangle$  is obtained by averaging the surface fluctuations over an area defined by the reciprocal of the X-ray instrumental resolution [3, 16]. Assuming that the surface roughness can be described by Gaussian statistics

$$\frac{1}{\rho_{\text{bulk}}} \frac{d\langle \rho(z) \rangle}{dz} = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{z^2}{2\sigma^2}\right] \quad (4)$$

the ratio  $R(\theta)/R_F(\theta) \approx \exp(-Q^2\sigma^2)$ . Differences between this approximate result and a more accurate one are usually immeasurably small. This expression, including the logarithmic dependence on the X-ray resolution have been confirmed by X-ray reflectivity measurements of the angular dependence of  $R(\theta)$  from  $H_2O$  and other organic fluids consisting of relatively small molecules [5, 17].

There have been interesting debates about the relative importance of the height-fluctuations (Eq. (1)) and a presumed smearing of the interface due to local variations of the liquid density across the interface at any one position. For example, the mean field theory that Percus referred to (see above) would give rise to an interfacial

<sup>1</sup> The angles are defined such that, for  $\theta \equiv 0$ , the incident ray is parallel to the surface.

width even if the capillary waves were neglected. This is not the place to elaborate on the debate; however, we can point out that recent experiments by Ocko et al. [18] on the temperature dependence of the surface roughness of normal alkanes are consistent with a form  $\sigma^2 = \sigma_{\text{int}}^2 + (k_B T/\gamma) \ln(\Delta L)$  in which the  $\sigma_{\text{int}}$  could be interpreted as an intrinsic, or local roughness. This interpretation of the experimental results was possible because of the very strong temperature dependence of  $\gamma$ .

A second approximation implicit in the above is the neglect of correlations between the local position of the surface and that of the subsurface atoms, or molecules. The problem is most easily illustrated by considering the surfaces of the liquid and nematic-liquid crystal phase of liquid-crystal forming molecules like the cyano-biphenyls [19,20]. These molecules are  $\sim 20\text{--}30 \text{ \AA}$  long, and for some temperatures the individual molecules orient with their long axes normal the surface forming a relatively dense, homogenous layer whose thickness is approximately the length of one molecule, or pairs of molecules if they tend to dimerize as the cyanobiphenyls. The molecules are much longer than the amplitude of the surface fluctuations and structure of the surface layer is not significantly perturbed by the fluctuations. In this situation, the location of the second layer relative to the surface is relatively well defined. Interference effects between X-rays reflected from the first and second layer give rise to a structure in the angular dependence of  $R(\theta)$ . In some cases, the surface layering can propagate through a number of layers ( $n > 1$ ) such that the local interfacial profile might have a form like

$$\left. \frac{\rho(z)}{\rho_{\text{bulk}}} \right|_{\text{local}} = \frac{1}{2} [1 + \text{erf}(z/\sigma_0)] + \sum_{n=0,1,\dots} A_n \delta(z - nd), \quad (5)$$

where  $nd$  is the position of the  $n$ th layer,  $A_n$  is a decaying function of  $n$ , and  $\sigma_0$  is the local, or intrinsic width of the surface. The net profile  $\langle \rho(z) \rangle$  to be inserted in Eq. (3) would then be obtained by convolution of the “local” profile with a Gaussian smearing function representing the thermal fluctuations. The Fourier transformation of Eq. (5) would then lead to a peak in  $R(\theta)$  when  $Q \approx 2\pi/d \sim 0.2 \text{ \AA}^{-1}$ , or  $\theta = \sin^{-1}(\lambda/2d) \sim 1.5^\circ$  for  $d \sim 30 \text{ \AA}$  and  $\lambda = 1.5 \text{ \AA}$ . Reflectivities exhibiting such a peak have been observed from the surfaces of liquid crystals [19,20]; however, for microemulsions [21], ordered polymers, etc. the  $d$ -spacing can be considerably larger [22,23]. In some cases, especially for  $d \gtrsim 100\text{--}200 \text{ \AA}$ , neutron reflectivity is particularly useful [24–28].

As a rough rule of thumb we believe that one can generally expect monotonic liquid/vapor interface profiles for liquids consisting of molecules [6], or molecular aggregates for complex fluids, whose sizes are comparable, or smaller, than the amplitude of the thermal fluctuations in the surface position. This is the case for  $\text{H}_2\text{O}$  and small alkanes. On the other hand, when the molecule, or aggregate, is larger than the surface roughness, non-monotonic or layered surfaces might or might not occur, depending on the local molecular order near the surface. This point can be illustrated by results from molecular simulations of Chapela et al. on the interfaces of slab of liquid Ar that is held against a hard solid substrate by van der Waals attraction [29].

Chapela et al. plot the density as a function of distance along the surface normal. Near to the solid surface, where there are no fluctuations, the oscillations in density corresponding to 3–4 layers are prominent. On the other hand, at the far end of the slab, at the liquid/vapor interface, the density is smooth, decaying to zero in a monotonic fashion.

Current theoretical understanding is that for small non-metallic liquids the interfacial profiles at the liquid/vapor interface should be monotonic with no layering [6]. Unfortunately, it has not been possible to test this by direct measurement for atoms such as Ar, Xe, or for small molecules like H<sub>2</sub>O. The problem is that, in order to look for layering, the reflectivity must be measured to  $Q \gtrsim 2\pi/d$  which, for small molecules, corresponds to  $Q \gtrsim 2-3 \text{ \AA}^{-1}$ , corresponding to  $\theta \approx 14-15^\circ$  for  $\lambda = 1.5 \text{ \AA}$ . Unfortunately, the Fresnel reflectivity falls off very rapidly with increasing angle [13, 30, 31];

$$R(\theta) \approx [\sin(\theta_c)/2 \sin(\theta)]^4, \quad (6)$$

where  $\theta_c \approx 0.1^\circ-0.3^\circ$ , depending on the X-ray wavelength and the electron density of the material. For  $\theta = 15^\circ$ ,  $R(15^\circ) \sim 10^{-8}$ , however, the problem is made much worse by the roughness,  $\sigma$ , of the interface. From the discussion following Eq. (4),  $R(\theta)/R_F(\theta) \approx \exp[-(\sigma Q)^2]$  and for  $\sigma \approx 3.0 \text{ \AA}$  (as was typical for small molecules)  $R(15^\circ)/R_F(15^\circ) \approx \exp[-(3 \times 2.5)^2] \sim 10^{-24}$  and this is unmeasurably small.

There are two reasons why the prospect for studying atomic layering is more propitious for liquid metals. Firstly, in contrast to the case of non-metallic liquids, the theoretical predictions for liquid metals is that quantum mechanical interactions between the ions and the charged electron Fermi fluid stabilizes the free surface and gives rise to atomic layering [32–35]. Thus atomic layering is actually expected, where it was not expected for non-metallic liquids. Secondly, since the surface tension for liquid metals is nearly an order of magnitude larger for liquid metals than for non-metallic liquids, the contribution of thermally excited capillary waves to the mean square width of the interfacial profile,  $\sigma^2 \propto k_B T/\gamma$ , of metals is smaller by an order of magnitude. This means that the theoretical estimate for the effect of thermal fluctuations on the reflectivity from a liquid metal would be much less severe than for non-metallic liquids; i.e.  $R(15^\circ)/R_F(15^\circ) \gtrsim 10^{-3}$  and even if the predicted layering did not occur, the resultant  $R(15^\circ) \gtrsim 10^{-11}$  is large enough to be measurable. This has very recently been confirmed in independent experiments by Magnussen et al. for liquid Hg [36] and by Regan et al. for liquid Ga [37].

For both Hg and Ga the reflectivity was measured to large enough angles to show peaks at  $Q \approx 2\pi/d$ , where  $d$  is of the order of the atomic spacing in the bulk phases, i.e.  $2.2 \text{ \AA}^{-1}$  for Hg and  $2.45 \text{ \AA}^{-1}$  for Ga. There are qualitative differences between the reflectivities from the two metals and it does appear that their explanation will require something other than the theoretical models that have been developed to date [32–35]. Regan et al. [37] speculate that the differences might arise from differences in the nature of covalent bonding in these two liquid metals [38, 39].

### 3. Summary

In summary, the background for X-ray studies of the structure of liquid surfaces has been reviewed. Aside from the most recent results on liquid metals, all of the other work has been published and reviewed a number of times. Hopefully, the references listed here will guide the reader to a more complete discussion of the details.

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