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# X-ray diffuse scattering study of height fluctuations at the liquid–vapor interface of gallium

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**Abstract**

We report an experimental study of wavelength dependent interfacial tension of liquid Ga using X-ray surface diffusion scattering. The observed surface tension can be explained by Mecke–Dietrich formalism derived from a microscopic density functional theory when the known stratified liquid–vapor interfacial density profile of Ga and a so-called individual local pseudo-potential for the pair-interaction potential of liquid metal are used. The quantitative behavior of the surface tension as a function of wavelength is very sensitive to the forms of both the interfacial density profile and the asymptotic part of the pair-potential, and is different from that observed from several dielectric liquids reported previously (Nature 403 (2000) 871; Phys. Rev. Lett. 90 (2003) 216101).


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Liquid surfaces are rough at the atomic length scale. Contributions to the interfacial height fluctuations of a one component liquid are from thermal fluctuations and gravity. A fundamental problem in thermodynamics is to find an accurate effective Hamiltonian, $H$, for the description of the interfacial height–height correlation function. Phenomenological capillary wave theory has been used to derive the height–height correlation function, given, in the wave vector space, as

$$\langle z(q)z(-q)\rangle = \frac{1}{A}\frac{k_B T}{(\rho_l - \rho_v)g + \gamma q^2} = \frac{1}{A}\frac{k_B T}{H(q)}, \quad (1)$$

where $A$ is the area of interface, $g$ is the gravity, $q$ is the wave vector transfer, $\rho_l$ and $\rho_v$ are the densities of the liquid and vapor, respectively. In this representation, $\gamma$ is the macroscopic interfacial tension and is independent of $q$ [3]. Schwartz et al.

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have first tested Eq. (1) on the surface of water down to a sub-micron length scale [3]. Their measurements of X-ray surface diffuse scattering, using a second generation synchrotron source, off the height fluctuations at the liquid–vapor interface of water proved that the capillary wave model for surface roughness can be accurately extended to a length scale of 400 Å. This was two orders of magnitude shorter than what had been measured with laser light scattering previously.

Recently, the height–height correlation function for several dielectric liquids was measured up to $q$ values that are beyond $q_{\max} \equiv 2\pi/R$ ($R$ is at the first maximum of the pair distribution function), and the results indicated that the capillary wave representation of the Hamiltonian is not valid at a length scale near the bulk correlation length. Mecke and Dietrich presented a $H(q)$ derived from a microscopic density functional theory for an inhomogeneous liquid [4], and predicted that, by defining a wavelength-dependent surface tension, $\gamma(q)$, the Hamiltonian can be written as

$$H(q) \equiv q^2\gamma(q). \tag{2}$$

This wavelength-dependent surface tension is sensitive both to the interfacial density profile and the pair interaction potential of the liquid. Their theory agreed with the measured height correlation functions of various dielectric liquids satisfactorily, when interfacial density profiles appropriate for those liquids and a pair interaction in the liquid asymptotically decaying as $1/r^6$ were used to derive $\gamma(q)$. The resulting $\gamma(q)/\gamma(0)$ was found to decrease as $q$ approach $q_{\max}$, reach a minimum value when $q/q_{\max} \approx 0.2 - 0.1$, and then increase strongly as $q$ increases.

In this report, we describe the interfacial height–height correlation function of liquid Ga determined by an X-ray diffuse scattering measurement. The liquid–vapor interfacial density profile of a liquid metal is stratified, that is, non-monotonic, and the asymptotic falloff of the effective pair interaction potential has a very different form from that of a dielectric liquid [1,2]. Remarkably, we find that the observed $\gamma(q)$ for liquid Ga is similar to that for the dielectric liquids previously reported, namely $\gamma(q)/\gamma(0)$ is also found to decrease monotonically to a minimum near $q_{\max}$ and then increase strongly thereafter. Nevertheless, the location and magnitude of the minimum of $\gamma(q)/\gamma(0)$ for the former differ significantly from that for the latter, and are very sensitive to both the shape of the density profile and the asymptotic form of the effective pair interaction potential.

The X-ray surface diffuse scattering measurement for liquid Ga was carried out at ChemMatCARS, Sector 15ID at the Advanced Photon Source, Argonne National Laboratory. The high-vacuum sample chamber used in the measurement and the detailed sample preparation procedure have been described elsewhere [5,6]. In this experiment, liquid Ga was kept at 35 °C and at $5 \times 10^{-10}$ Torr. The experimental setup is illustrated in Fig. 1 and detailed performance of the liquid surface spectrometer was reported elsewhere [7,8]. X-ray beam ($\lambda = 0.8504$ Å) was steered down to the liquid surface with a Si(1 1 1) crystal at a grazing angle, $\alpha$, of 0.13°, smaller than the critical angle of liquid Ga (0.19°).

Surface diffuse scattering data were collected in an in-plane geometry (as a function of in-plane angle, $\phi$) with a fixed pickup angle, $\beta$, of 3°. Sinha et al. [9] showed that if the incident and pickup angles are kept small (so that the wave vector transfer along the normal of the surface, $q_z$, is negligible compared to that along the plane $q_{xy}$), then the intensity of the diffuse scattering, $I_{\text{diff}}$, is directly proportional to the height–height correla-

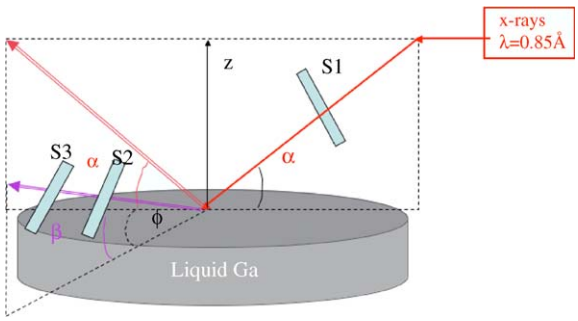


Fig. 1. Schematics for the experimental setup. X-ray diffuse scattering was measured in an in-plane geometry as a function of $\phi$ with fixed grazing incident angle, $\alpha$, and pickup angle, $\beta$. S1 represents horizontal and vertical collimation slits for the incident beam, and S2 and S3 represent two sets of horizontal and vertical collimation slits, respectively, for the detector.