Wavelength Dependence of Liquid-Vapor Interfacial Tension of Ga

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The wave-vector dependence of the liquid-vapor interfacial tension of Ga, $\gamma(q)$, has been determined from diffuse x-ray scattering measurements. The ratio $\gamma(q)/\gamma(0) = 1$ for $q < 0.05$ Å^{-1} decreases to 0.5 near $q = 0.22$ Å^{-1}, and increases strongly for larger q. The observed form for $\gamma(q)/\gamma(0)$ is consistent with the prediction from the Mecke-Dietrich theory when the known stratified liquid-vapor interfacial density profile of Ga and a pseudopotential based pair interaction with appropriate asymptotic ($r \to \infty$) behavior are used. The detailed behavior of $\gamma(q)/\gamma(0)$ depends on the particular forms of both the interfacial density profile and the asymptotic falloff of the atomic pair interaction.

There has been a recent flurry of interest in improving the representation of the effective Hamiltonian descriptive of the liquid-vapor interface [1,2]. One convenient definition of the effective Hamiltonian relates it to the observable interface height-height correlation function $\langle z(0)z(x, y)\rangle$ or its Fourier transform $\langle z(q)z(-q)\rangle$. The capillary wave description of fluctuations of a liquid-vapor interface of area A in the Earth's gravitational field G leads to a height-height correlation function with the spectrum

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

in which q is the magnitude of the wave vector in the plane of the interface, ρ_l and ρ_g are the densities of the liquid and vapor, respectively, and γ is the interfacial tension [1–5]. This representation of the Hamiltonian is valid only for q small compared to $q_{max} \equiv 2\pi/r_{max}$, with r_{max} the position of the nearest-neighbor maximum in the pair correlation function. We note, however, that the far right hand side of Eq. (1) interprets the denominator of the middle term as the excess free energy, or effective Hamiltonian $H(q)$, associated with the interface deformation with wavelength $2\pi/q$, so that the equality between the far left and the far right hand sides of Eq. (1) provides a general definition of $H(q)$ independent of the capillary wave description. One of the fundamental problems in the theory of the liquid-vapor interface is the development of a form for $H(q)$ that is valid over a wide range of density, temperature, and fluctuation wavelength for systems with either density independent or density dependent interactions, and for systems that have interfacial density distributions that are either monotone or nonmonotone.

The classical van der Waals description of the liquid-vapor interface [6] identifies the density fluctuations in the bulk phases as the generator of a smooth monotone density distribution between liquid and vapor phases, while the capillary wave description of the liquid-vapor interface attributes the monotone density profile entirely to the average over thermally excited distortions of a discontinuous interface between liquid and vapor phases [3,4]. A combination of these analyses that uses the van der Waals description to define an intrinsic liquid-vapor density profile, the undulations of which are described by capillary wave excitations, implicitly assumes that the van der Waals analysis is valid for distances smaller than the bulk liquid correlation length, and the capillary wave description for distances greater than that correlation length. This approach neglects bulk liquid fluctuations with scale length greater than the correlation length. Moreover, the correlation length near the triple point is only a very few molecular diameters, about or smaller than the length scale where one expects that the conventional capillary wave excitation approximation to the liquid-vapor interface Hamiltonian must break down. Consequently, this hybrid approach to the effective Hamiltonian does not describe accurately the transition region that connects the two domains of important fluctuations in the inhomogeneous system.

A superior analysis, advanced by Mecke and Dietrich [1], uses a density functional representation of the inhomogeneous liquid to derive $H(q)$. They assume that the interfacial density profile monotonically decays from liquid to the vapor with a width of about two molecular diameters near the freezing temperature, and that the pair interaction in the liquid has the asymptotic form r^{-6}. It is then predicted that the effective wavelength dependent surface tension, defined by $\gamma(q) \equiv H(q)/q^2$, is a nonmonotonic function of q. Specifically, $\gamma(q)$ is found to decrease as q approaches q_{max}, with a minimum value when $q/q_{max} \approx 0.2$–0.1; thereafter, $\gamma(q)$ increases strongly as q increases. Stecki [2] has also constructed an effective Hamiltonian for the liquid-vapor interface by using the direct correlation function obtained from molecular dynamics simulations of a Lennard-Jones fluid and a particular parametrization of the density fluctuations. Stecki's results predict that $\gamma(q)$ becomes smaller as q approaches the inverse of a few molecular diameters

and that $\gamma(q)/\gamma(0)$ increases to greater than unity at large q. The behavior of $\gamma(q)$ predicted by both theoretical analyses is consistent with experimental studies reported by Fradin et al. [7] and Mora et al. [8] of diffuse x-ray scattering from the liquid-vapor interfaces of water [7] and several organic liquids [8]. All of these have liquid-vapor interfacial density profiles that are monotonic near the freezing temperature, and the asymptotic form of the pair interaction for all has the form r^{-6}. For water the data show that $\gamma(q)/\gamma(0) \approx 0.25$ when $q/q_{max} \approx 0.4 \text{ Å}^{-1}/2 \text{ Å}^{-1} = 0.2$, noting that the first peak in the structure function of liquid water is at $q_{max} \approx 2 \text{ Å}^{-1}$.

The liquid-vapor interfacial density profile of a metal is stratified (nonmonotonic), the effective ion-core–ion-core interaction depends on the electron density, hence also the ion density and thereby position in the interface, and the asymptotic form of the effective pair interaction has a very different form from that in a dielectric liquid [9–14]. It is then reasonable to expect a difference in the dependence of $\gamma(q)$ on q of a metal and a dielectric.

We describe below an experimental study of the wavelength dependence of the liquid-vapor interfacial tension of Ga, as determined by measurement of diffuse x-ray scattering from the liquid-vapor interface. We find that, despite the stratification of the liquid-vapor interface and the different asymptotic form for the effective pair potential, the observed wavelength dependence of the liquid-vapor interfacial tension of Ga is similar to that of the dielectric liquids previously studied. We show that the observed behavior is consistent with the Mecke-Dietrich analysis when an account is taken of the stratification of the Ga liquid-vapor interface and the functional form of the interaction in a liquid metal.

The high vacuum sample chamber used in these experiments has been described elsewhere [15]. The diffuse scattering measurements were taken in sensibly the same fashion as described by Fradin et al. [7]. The sample of liquid Ga was prepared from 99.99999% pure metal ingot; liquid Ga was introduced through a capillary feeder system into the previously evacuated $(5 \times 10^{-10}$ torr) sample chamber. The temperature of the sample was fixed at 35 °C. The x-ray wavelength was 0.8504 Å. Prior to initiation of x-ray scattering measurements, the liquid Ga surface was subjected to Ar ion sputtering for several days. After the sputtering, there remained a few very small patches of contamination on the surface, mostly located close to the edges of the sample and out of the x-ray footprint. Throughout the collection of data the surface of the sample was monitored by a video camera attached to the vacuum chamber, and the absence of patches of contamination from the x-ray footprint was continuously verified. Previous x-ray reflectivity studies have shown that this procedure yields accurate data for the uncontaminated surface [15].

The diffuse x-ray scattering was collected by fixing the incident angle to be 0.13°, which is smaller than the

critical angle (0.19°) for total external reflection. The q resolution of our measurements was determined by the small opening of the horizontal slits installed before the detector; it is calculated to be 0.002 Å^{-1}. We used large detector pickup angles ($\beta = 1°$, 1.5°, and 3°) to minimize the collection of background scattering from the direct beam. The empty chamber background x-ray scattering was measured by moving the sample out of the x-ray beam, keeping the relative angle between the direct beam and the detector fixed. The bulk scattering was measured with the incident and pickup angles set at 0.35°. A large tail arising from specular reflection is found at small q. We normalized the bulk scattering intensity to the surface scattering intensity at the principal diffraction peak of liquid Ga and then, using the fact that $S(q)$ has a finite limiting value of $S(0)$, we replace the high intensity tail at the low q side of the data set with the average intensity of bulk scattering around $q = 0.5$ Å^{-1}. For $\beta = 1°$ and 1.5°, the direct beam background was thereby rescaled by factors of 0.65 and 0.8, respectively. For $\beta = 3°$, the background was always much weaker than the surface scattering intensity, so no rescaling was needed. For all β the diffuse scattering intensity was proportional to q^{-2} up to about 0.05 Å^{-1}. At higher q, up to the detection limit set by bulk scattering, positive deviation from the q^{-2} decay is clearly seen.

Figure 1 displays the measured diffuse scattering patterns for three pickoff angles. The data shown have been corrected for polarization and geometric factors, with the latter determined by integrating over the illuminated area and the solid angle set by the slits before the detector. The contributions from both the bulk liquid scattering and the
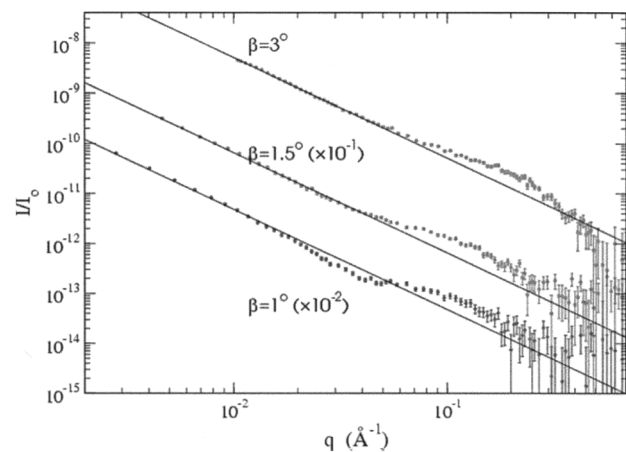

FIG. 1. Diffuse scattering from the liquid-vapor interface of Ga at 35 °C. The measured intensity of diffuse scattering is shown for three pickoff angles: 1°, 1.5°, and 3°. For clarity, the intensity data for 1° and 1.5° have been displaced by multiplication by 0.1 and 0.01, respectively. Different vertical slit sizes were used at the different pickoff angles. The three solid lines show the q^{-2} dependence predicted by the capillary wave theory.

background scattering around the direct beam have been subtracted from the surface scattering intensity.

Figure 2 shows the q-dependent surface tension pattern calculated from the diffuse scattering pattern. The values of $\gamma(q)/\gamma(0)$ were first calculated from $1/[I(q)q^2]$, and then normalized to unity at small q. For $\beta = 1°$, there is a small peak of $\gamma(q)/\gamma(0)$ around $q = 0.03$ Å^{-1}, which we attribute to extraneous scattering not removed by our background subtraction procedure for this case with the largest ratio of background to desired signal. Other than that, the functional forms of $\gamma(q)/\gamma(0)$ for each pickoff angle β agree well with each other. The value of $\gamma(q)/\gamma(0)$ is one within the estimated experimental error for q up to about 0.08 Å^{-1}. The value of $\gamma(q)/\gamma(0)$ then decays smoothly to about 0.5 near $q = 0.22$ Å^{-1}. The data taken with $\beta = 3°$ show a clear increase of $\gamma(q)/\gamma(0)$ at higher q; the data taken with $\beta = 1°$ and 1.5° are too noisy for q greater than 0.3 Å^{-1} to conclusively show that trend.

Although the general dependences of $\gamma(q)/\gamma(0)$ on q for water and several organic liquids and gallium are similar, there are important quantitative differences, specifically the locations and amplitudes of the minima; these do not appear to have any systematic dependence on the molecular diameter.

Our measurements probe the distribution of atoms along the normal to the liquid-vapor interface on a length scale that averages over the strata in the density distribution. Nevertheless, there remains a quantitative difference between the averaged liquid-vapor interfacial density profile of a metal and that of a dielectric. Specifically, the averaged stratified liquid-vapor interfacial density profile for Ga [9,14] has a width of only a few tenths of an atomic diameter, an order of magnitude smaller than the width of the liquid-vapor interface of a dielectric. And, as already noted, the forms of the effective atom-atom interaction of a metal and a dielectric are different.
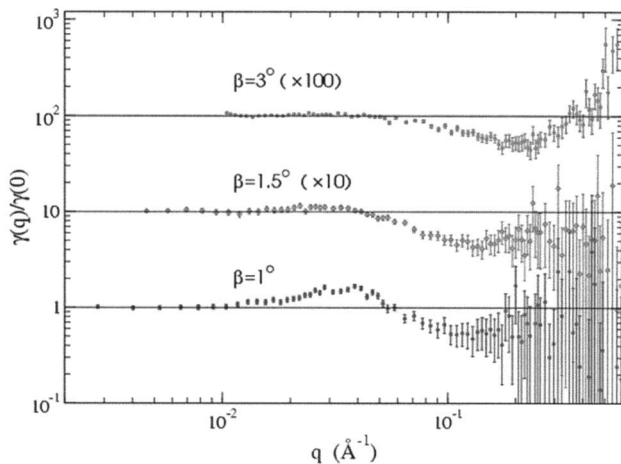
It is the asymptotic ($r \to \infty$) form of the pair interaction that determines the capillary wave spectrum. The asymptotic falloff of the atom-atom interaction is adequately characterized as r^{-6} for a dielectric, but is more complex for a metal. The ion-core–ion-core dispersion interaction is shielded by the electron dielectric function and it is not evident that this term will be asymptotically dominant. The effective ion-core–ion-core interaction generated by pseudopotential theory neglects the dispersion interaction and is of the screened Coulomb form, but the screening depends on the dielectric function and does not have a simple form [16]. We have made several comparisons between the predicted behavior of $\gamma(q)$ as a function of q and our experimental data (Fig. 3). When the averaged liquid-vapor interfacial density profile of Ga is used in the Mecke-Dietrich formalism with either an r^{-6} interaction or the effective interaction derived from pseudopotential theory, the calculated values of $\gamma(q)$ are not in agreement with the experimental data (not shown in Fig. 3). When the known stratified interfacial density profile of Ga is used with an r^{-6} interaction, $\gamma(q)$ is predicted to be independent of q up to about 0.3 Å^{-1} and to increase dramatically thereafter, in disagreement with the experimental data. When that interfacial profile is used with an exponentially screened Coulomb interaction, $\gamma(q)$ is predicted to be independent of q up to about 0.05 Å^{-1} and to decrease dramatically thereafter, in disagreement with the experimental data. When the known stratified interfacial density profile is used with the energy independent model pseudopotential (EIMP) that accurately predicts that stratification [9,17,18], $\gamma(q)$
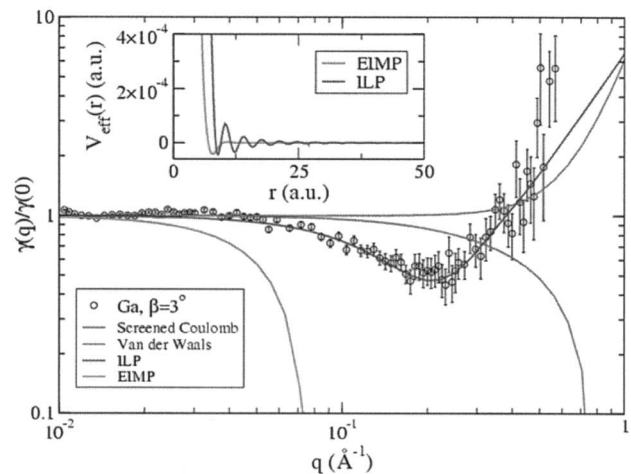
FIG. 3. Comparison of the normalized q-dependent surface tension of Ga determined experimentally with that calculated using the Mecke-Dietrich formalism with several model potentials and a stratified intrinsic interfacial density profile. The interfacial density profile used was obtained from a fit to the x-ray reflectivity from the Ga liquid-vapor interface as a function of angle of incidence. The inset compares the effective atom-atom interactions derived from the EIMP pseudopotential and the so-called individual local pseudopotential.

FIG. 2. Normalized q-dependent surface tension calculated from the diffuse scattering intensity data displayed in Fig. 1. For clarity, the inferred values of $\gamma(q)/\gamma(0)$ for pickoff angles of 1.5° and 3° have been multiplied by 10 and 100, respectively.

is independent of q only up to about 0.02 Å^{-1} and decreases dramatically thereafter, in disagreement with the experimental data. However, when the stratified interfacial density profile is used with the so-called individual local pseudopotential (ILP) [19] (see inset of Fig. 3) the calculated and observed forms of $\gamma(q)/\gamma(0)$ can be brought into good agreement with a suitable choice of parameters. Overall, we infer that the Mecke-Dietrich theory captures the general features of the dependence of $\gamma(q)$ on q, but the details of that dependence are sensitive to the particular forms of both the interfacial density profile and the asymptotic form of the atom-atom interaction.

What can be said concerning the adequacy of the asymptotic form of the effective potential derived from pseudopotential theory? It has been shown in earlier work that several different pseudopotentials, based on different approximations, predict the stratification of the density profile in the liquid-vapor interface of a metal, albeit with differing precision [9–13,20]. We are confident that the ILP will predict, with reasonable accuracy, the stratification of the liquid-vapor interface of Ga, since it is the density dependence of the one-body contribution to the energy that appears in the density functional formulation of pseudopotential theory that generates the stratification. As to the bulk liquid structure, previously reported calculations show that different choices for the pseudopotential lead to somewhat different effective pair potentials, all of which provide quite good predictions for the bulk liquid pair correlation function. This latter observation is not surprising given that the bulk liquid pair correlation function is largely determined by the short-range repulsive part of the pair potential (hence the reasonable description provided by the unphysical hard core interaction). It appears that the pseudopotential that provides the most accurate description of the density profile in the liquid-vapor interface of Ga does not accurately represent the asymptotic form of the atom-atom interaction, and that measurement of $\gamma(q)$ provides a means of testing the accuracy of the effective pair potential in the large separation region.

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