

DIFFUSE SCATTERING OF MERCURY-ELECTROLYTE INTERFACE

B. Runge, A. Elsen, S. Festersen, O. H. Seeck¹, B. M. Murphy, O. M. Magnussen

Christian-Albrechts-Universität zu Kiel, IEAP, Leibnizstraße 19, D-24098 Kiel, Germany

¹DESY, HASYLAB, Notkestraße 85, D-22607 Hamburg, Germany

Surface X-ray scattering methods belong to the very few experimental approaches that provide access to data on the nano-scale structure and dynamics of liquid surfaces. These methods can also be expanded to liquid-liquid interfaces which play a major role in emulsions, colloids, micelles, and biological membranes. While reflectivity measurements provide information about the laterally averaged electron density perpendicular to the surface of a sample [1], measuring the diffuse scattering intensity reveals the lateral correlations on the sample surface. Analyzing structure at liquid surfaces is complicated by the fact that the diffuse scattering which is driven by capillary waves is peaked at the specular condition and therefore no real reflected beam can be measured with realistic resolution.

The capillary waves and therefore the diffuse scattering are strongly dependent on temperature and surface tension [2] with the latter varying pronounced with the applied electrode potential. For the liquid mercury surfaces former studies revealed a temperature dependent behavior that is not in agreement with standard capillary wave theory [3].

In our experiments we recorded diffuse scattering data from the mercury-electrolyte (0.01 M NaF) interface under simultaneous potential and temperature control. Up to now diffuse surface scattering studies were only reported for a few free liquid surfaces, while for liquid-liquid interfaces measurements of this type have not been reported yet.

The data was collected at PETRA III at the beam line P08 on the LISA liquid surface diffractometer [4] at photon energy of 25 keV. To minimize the curvature of the interface the sample was about 50 mm in diameter, giving the best ratio from surface area to signal loss due to absorption from to the electrolyte. At the temperatures 4°C, 23°C and 40°C and at several different potentials against a Hg/Hg₂SO₄ electrode a reflectivity was recorded to ensure that the surface stayed clean and to gain information about the surface structure. Directly after the reflectivity measurements diffuse scattering data were recorded at 0.3 Å⁻¹, 0.9 Å⁻¹ and 1.5 Å⁻¹ (Figure 1).

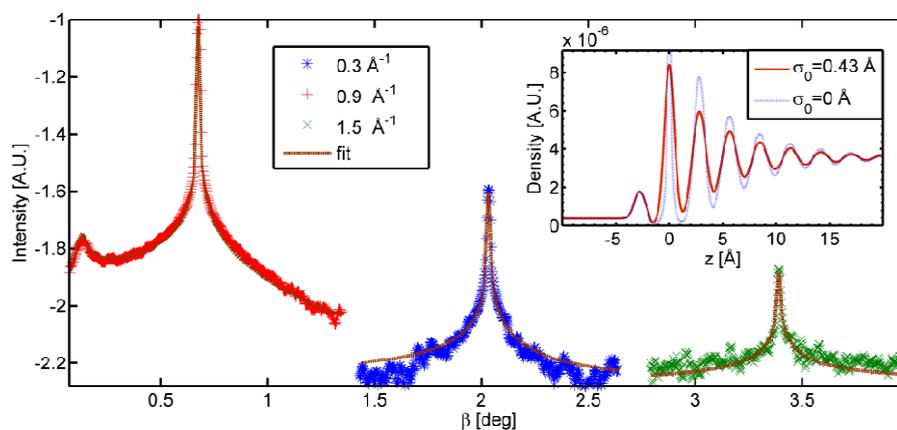


Figure 1: Diffuse scattering spectra at different q_z values. The temperature was 23°C and the applied potential was -0.85 V versus a Hg/Hg₂SO₄. The continuous line shows a simultaneous fit to all spectra with one set of parameters. The inset shows the electron density of the fit ($\sigma_0=0.43$ Å) and an electron density resulting if the additional roughness is not included ($\sigma_0=0$ Å).

Comparing the diffuse scattering data sets at different temperatures and a potential of -0.85 V they show deviation from theory that can be modeled in a first attempt as an additional roughness σ_0 in the surface structure factor, i.e., the intrinsic electron density profile, whereas the diffuse scattering can be modeled according to theory [5] using surface tension values for the Hg/NaF system reported in literature [6](Figure 1). This roughness results in a broadening of each mercury layer which increases as the temperature increases (Figure 2).

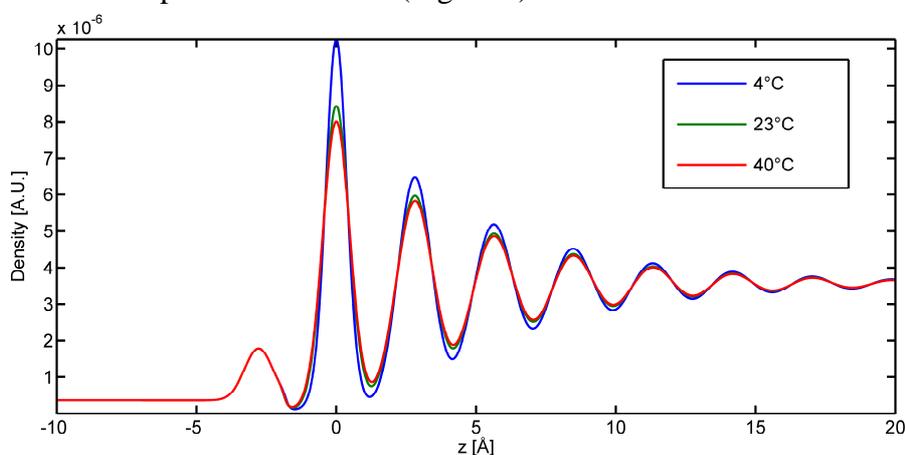


Figure 2: Intrinsic electron densities of the mercury-electrolyte interface based on the values of the fits to the diffuse scattering at three different temperatures. As one can clearly see the width of each mercury layer increases with increasing temperature.

Preliminary potential dependent data show a tendency which is in agreement with former results [7], which we plan to verify in future measurements.

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