Water in contact with extended hydrophobic surfaces: Direct evidence of weak dewetting

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Earlier grazing-incidence X-ray diffraction (GIXD) experiments at HASYLAB’s beamline BW1 had shown\textsuperscript{[1]} that all-hydrophobic long n-alkanes such as \textit{n}-C\textsubscript{36}H\textsubscript{74} may form a 2D-crystalline monolayer at the air-water interface. The electron density of such a monolayer is almost the same as that of water (\(\rho_{\text{alkaneML}}/\rho_{\text{water}} = 1.02\)), giving very little vertical contrast. It was thus a surprise when, more recently\textsuperscript{[2]}, probing the vertical electron density profile of such a monolayer with X-ray reflectivity, we observed pronounced interferences (Fig. 1A).

A free-form inversion\textsuperscript{[3]} of the reflectivity data yields an electron density profile (shown as a full line in Fig. 1B) that exhibits (a) the density of the bulk water, (b) a dip to ca. 0.9\(\rho_{\text{water}}\) (marked green), (c) the density expected for the close-packed alkanes, (d) a density level of only ca. 0.7\(\rho_{\text{water}}\) further away from the water interface, and (e) the low density of the gas phase above. To reconcile feature (d) with the earlier GIXD work\textsuperscript{[1]} (reproduced in the present study) we must assume an only 70\% coverage for the I-phase detected by GIXD, and that it is interspersed by small non-diffracting disordered (though close packed) II-regions that contribute to the density only close to the water interface, as schematically depicted in Fig.1C.

In this connection we note that (i) the deep interferences of Fig. 1A can only be modelled coherently (model calculations confirm that an incoherent superposition of two components would wash out the interferences) and (ii) an extensive search using both models and the free-form method\textsuperscript{[3]} yielded no other solutions \(\rho(z)\). In different preparations, at different temperatures, the details of feature (d) showed some variation. In contrast, the dip (b) was reproduced well in different preparations. Model calculations show that the dip (b) is essential in producing the deep interferences. The integrated area of the dip is \(D_{\text{exp}} \approx 0.9\) Å at 5\(^\circ\)C and it increases by some 20\% as temperature is increased to 35\(^\circ\)C.

No such dip is observed with monolayers of amphiphilic molecules such as, \textit{e.g.}, the long alcohol 1-triacontanol (C\textsubscript{30}H\textsubscript{61}OH).

To gain further insight we have performed molecular dynamics (MD) simulations\textsuperscript{[2,4]} on a periodic alkane-water system (C\textsubscript{36}H\textsubscript{74}/H\textsubscript{2}O/C\textsubscript{36}H\textsubscript{74}). According to the simulations \(D\) results from a narrow and deep electron density deficit (Fig. 3a) indicating that the broader and shallower dip found experimentally is due to the smearing of the interface caused by capillary waves. The MD value \(D_{\text{MD}} \approx 1.2\) Å is about 20\% larger than the measured value, \(D_{\text{exp}} \approx 1\) Å. In Fig. 1B the dotted line shows the density \(\rho(z)\) extracted MD, smeared by 3 Å rms. for comparison with \(\rho(z)\) inverted from the reflectivity data (solid line).

For the system (C\textsubscript{35}H\textsubscript{71}OH/H\textsubscript{2}O/C\textsubscript{35}H\textsubscript{71}OH), MD yields \(D_{\text{MD}} \approx 0\) in agreement with the reflectivity result.

Based on theoretical considerations, dewetting (drying) of large apolar species in water has been suggested to play a significant role for their mutual hydrophobic interaction\textsuperscript{[5,6]}. This study has provided the first experimental evidence, showing such dewetting at a large apolar surface floating on water\textsuperscript{[7]}. The dewetting phenomenon extends less than 15 Å into the bulk water phase.

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Fig. 1 A: X-ray reflectivity of a C$_{36}$H$_{74}$ monolayer on water, normalized to the Fresnel reflectivity calculated for an ideal water surface, versus scattering vector $Q_z = 4 \pi \sin(\alpha) / \lambda$ where $\alpha$ is the grazing angle of incidence. The points are exp. data and the line corresponds to the solid line in (B).

B: Electron density inverted from the data shown in A (solid line, zone I+II; the red and blue solid lines are error bands) and MD-simulated electron density (dotted line, zone I).

C: Schematic illustration of the experimental results. The lighter blue shading illustrates the density deficient contact zone.

References