

Ordering of a Liquid at a Solid Interface

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We have made the first real-space observation of ordering of a liquid at a solid interface using the Xe Al system and High-Resolution Electron Microscopy (HREM) [1]. HREM was carried out using the high-resolution, high-voltage electron microscope (JEM-ARM 1000, JEOL Ltd.) at the National Institute for Materials Science in Tsukuba, Japan, operating at 1 MeV.

After implantation, inert gases, insoluble in most materials, precipitate in nanometer size cavities. At room temperature, Xe in Al can be solid or liquid depending on the cavity size (pressure). HREM of room temperature, fluid xenon in faceted cavities in aluminum has revealed the presence of as many as three well-defined layers within the fluid at each facet.

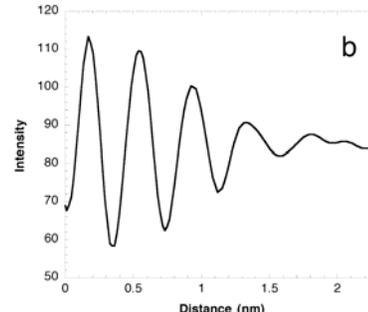
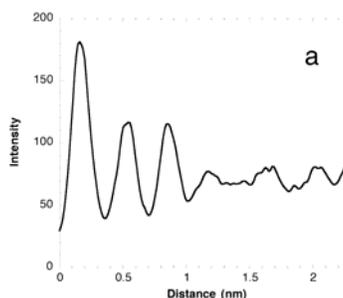
High resolution transmission electron micrograph of faceted cavities in aluminum containing Xe. The Xe in the two large cavities is fluid; in the small cavity at the right of the figure the Xe is solid. The scale marker indicates 2.5 nm.



To interpret this intensity variation, atomic configurations extracted from MD simulation of fluid Xe in contact with a $\langle 111 \rangle$ Al surface were used as input to HREM image simulation. In both experiment and simulation three clear fringes are observed. The origin of the fringes in the simulated image is the layering of Xe atoms at the interface. Positions of the minimum in electron intensity in the image (bright fringes) correspond to the positions of the maximum in the Xe density in the MD simulations. This indicates that contrast in the experimental image results from the three layers of Xe at the interface. This is the first real-space, experimental observation of layering at a fluid/solid interface.

a) Intensity variation as a function of distance within the cavity in a direction normal to the facet indicated by the arrow in the top figure. This figure shows the presence of three fringes.

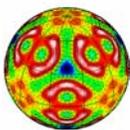
b) Intensity variation in a simulated HRTEM image of an interface between fluid Xe and solid Al. Input for the image simulation was obtained from a molecular dynamics simulation. This also shows three fringes



Interfacial ordering is controlled by the Xe density and cavity size. Using molecular dynamics, we have found that in a three-dimensionally confined system of sufficiently small size, it is possible for complete three-dimensional liquid ordering where the apparent crystallographic structure is determined by the geometry of the cavity. Xe in a 2 nm cubic cavity would condense into the body-centered cubic phase rather than the normal face-centered cubic phase. In this case, structure is determined by confinement.

This observation verifies suggestions from modeling and X-ray scattering experiments that liquids order at a flat interface. This effect would explain observation of crystal structures, such as precipitates of bcc copper, that do not occur in unconfined systems. Liquid ordering is of fundamental and technological importance for any phenomena controlled by interactions at a liquid-solid interface. It increases friction, alters electrochemical reactions and controls solidification of a melt.

Ordering in a fluid inert gas confined by flat surfaces, S. E. Donnelly, R. C. Birtcher, C. W. Allen, S. E. Donnelly, I. Morrison, K. Furuya, M. Song, K. Mitsuishi and U. Dahmen, Science, 2002. 296(5567): p. 507-510.



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