

Supplementary Information

Theoretical Methods

Molecular dynamics simulations of liquid thin films over model ionic lattice surfaces have been conducted with the DL_POLY software.[1] The general setup consists of an orthorhombic cell of dimensions $32 \times 32 \times 80$ Å in which a surface comprising five atomic layers (total width 8 Å) is positioned in the xy plane. Above this, a liquid film approximately 40 Å thick is placed above this surface, leaving ~ 32 Å of vacuum along the z direction. The surfaces themselves are simple FCC arrangements (e.g. as for NaCl) of unit charge ions with a lattice constant of 4 Å. The liquid films comprise either 1450 water molecules or 341 isopropanol molecules – for water, the SPC/E model of Berendsen *et al.* is used,[2] while for isopropanol the model of Kahn and Bruce is employed.[3] For the alcohol, all C–H and O–H bonds were treated as constraints to allow the use of a larger timestep. In the interests of simplicity in this model study, the non-Coulombic part of the interactions between the liquid molecules and any surface atom is assumed to be of the Lennard-Jones 12-6 type, with $\sigma = 3.0$ Å and $\epsilon = 0.6$ kJ mol⁻¹. For each liquid simulations over five different surfaces are performed; the original charged lattice as described above (H/PHIL), a lattice where the charges of all atoms have been removed to leave a purely Lennard-Jones surface (H/PHOB), and three simulations where charges have been removed from small patches of atoms on each surface (PATCH/4, PATCH/12, and PATCH/24).

All simulations were run with a cutoff of 15 Å for the short range potential and the real-space part of the Ewald sum (reciprocal space terms encompass 16 k -vectors in each Cartesian axis with convergence parameter $\alpha = 0.23833$) in the Hoover NVT ensemble at 300 K with relaxation time $\tau = 0.1$ ps. The Yeh-Berkowitz correction was applied to remove periodic artefacts influencing the system in the z direction.⁴ Preliminary zero-Kelvin minimisation

stages with timesteps ranging from 1×10^{-7} to 1×10^{-4} were conducted in order to generate suitable starting configurations for production runs. Trajectories of 10 ns length were generated for each individual liquid / surface combination with a timestep of 1.0 fs. All quantities are calculated over the last 5 ns of the simulation.

Surface	Peak 1	Peak 2	Peak 3
H/PHIL	7.70±2.0	25.02±2.7	9.30±2.3
PATCH/4	8.96±2.2	24.25±2.5	8.59±2.7
PATCH/12	12.24±2.0	21.68±2.4	7.91±2.1
PATCH/24	15.39±2.8	19.66±2.9	6.59±2.0
H/PHOB	0.56±0.7	31.78±2.2	8.90±2.4
$z_{min}, \text{Å}$	0.0	3.75	4.58
$z_{max}, \text{Å}$	3.75	4.58	6.2

Table 1 Populations of molecules in the individual peaks of the triplet observed for the first adsorbed layer in the case of pure isopropanol.

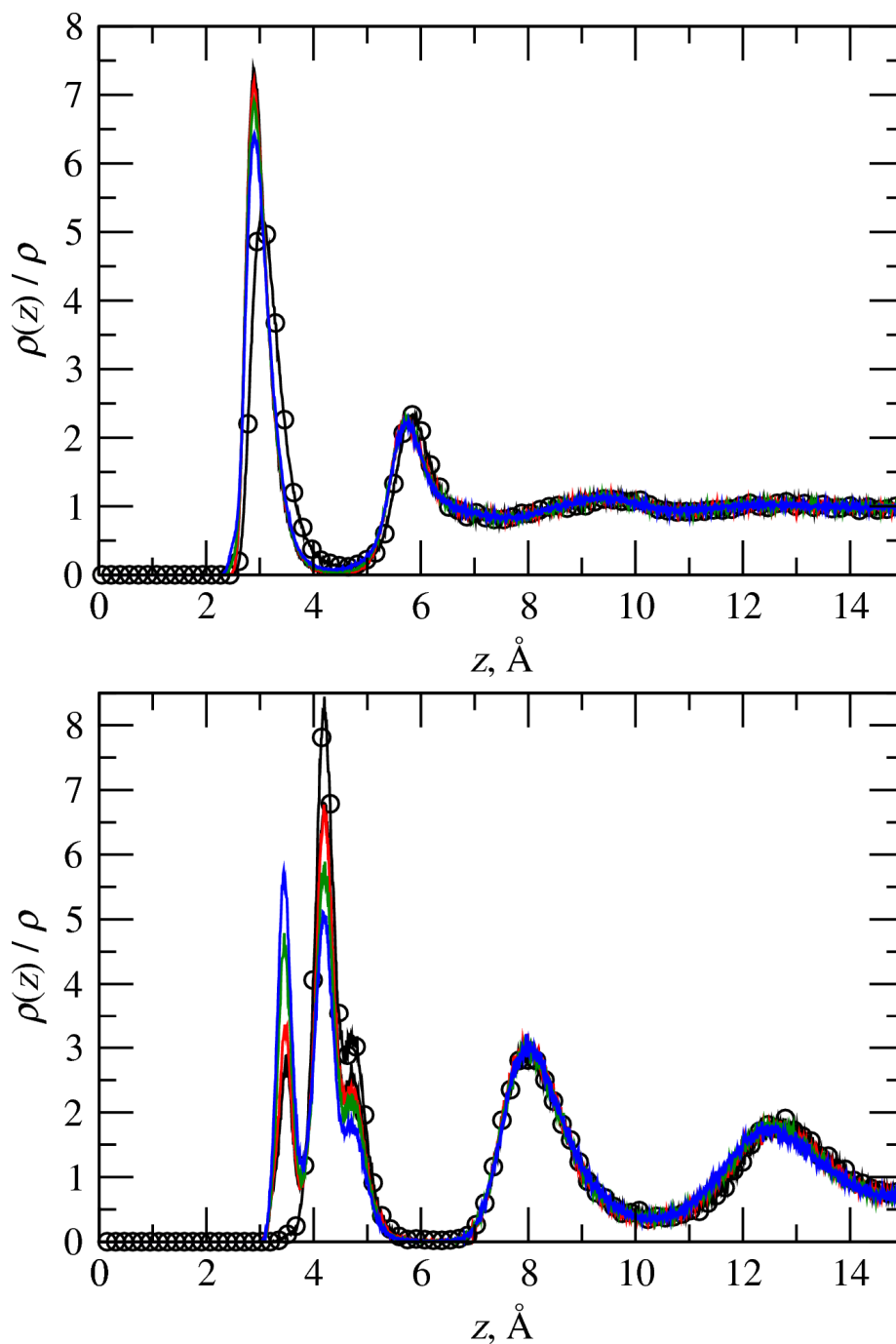


Figure 1 Normalised z-density profiles for water (top) and isopropanol (bottom) over the various surface types; H/PHIL (solid black line), PATCH/4 (red), PATCH/12 (green), PATCH/24 (blue), and H/PHOB (black line with circles). Clear oscillations of the liquid density along the surface normal are seen for all surface types up to ~ 12.5 Å owing simply to the termination of the liquid phase by the presence of the surface.

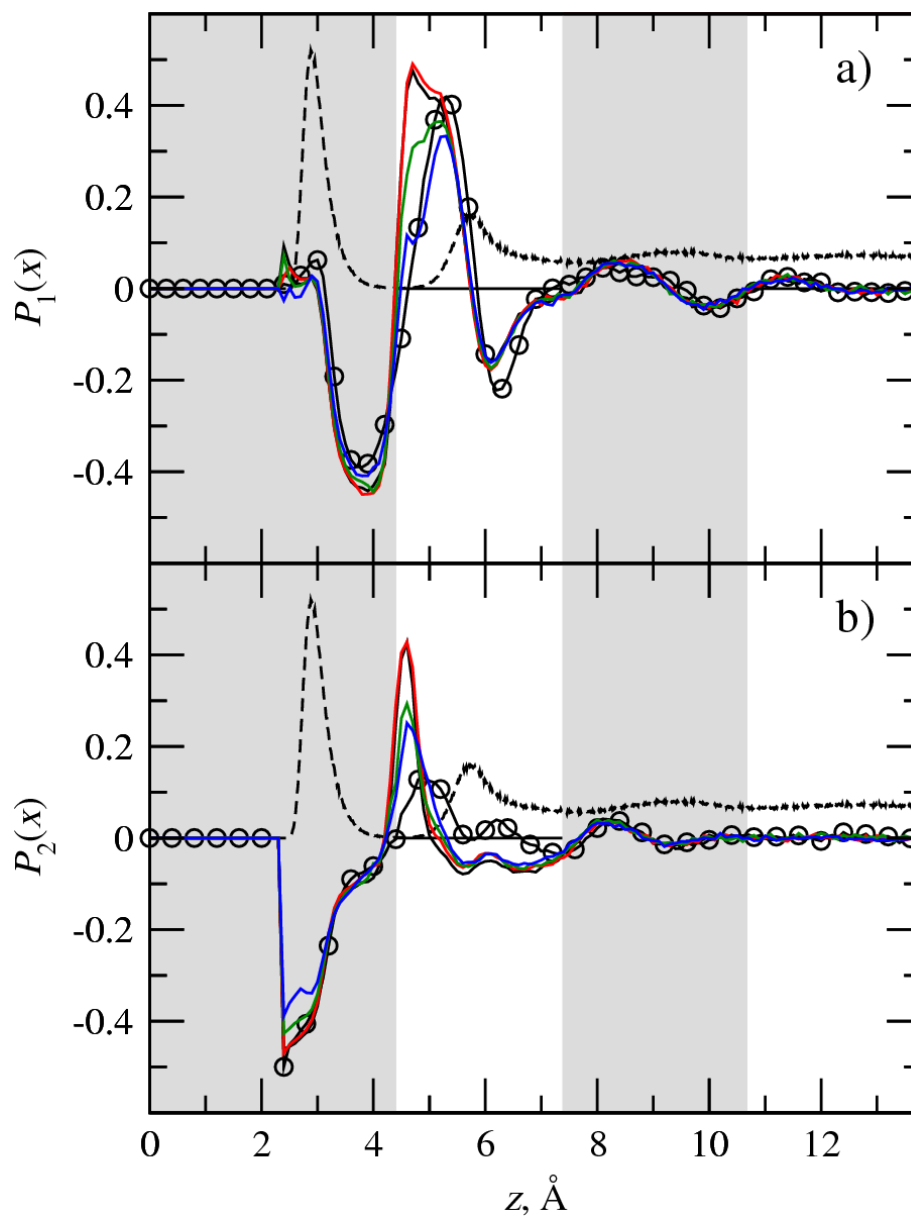


Figure 2 First- (a) and second-order (b) Legendre polynomials for the water systems calculated as a function of z ($z = 0$ corresponds to the topmost layer of atoms in the surface); H/PHIL (solid black line), PATCH/4 (red), PATCH/12 (green), PATCH/24 (blue), and H/PHOB (black line with circles). Layers as inferred from the z -density profile (dashed black line) are indicated by alternating grey/white background.

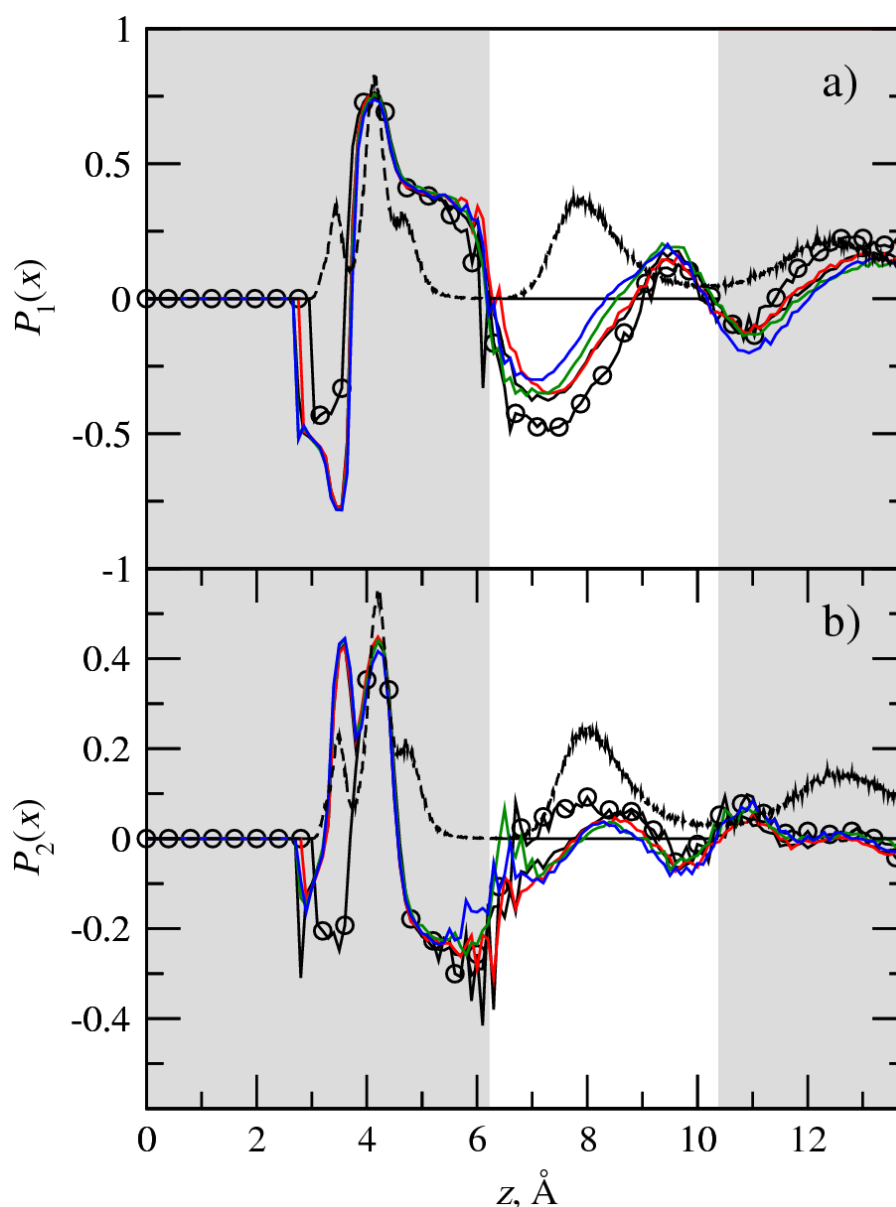


Figure 3 First- (a) and second-order (b) Legendre polynomials for the isopropanol systems calculated as a function of z ($z = 0$ corresponds to the topmost layer of atoms in the surface); H/PHIL (solid black line), PATCH/4 (red), PATCH/12 (green), PATCH/24 (blue), and H/PHOB (black line with circles). Layers as inferred from the z -density profile (dashed black line) are indicated by alternating grey/white background.

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- 2 J. C. Berendsen, J. R. Grigera, T. P. Straatsma, *J. Phys. Chem.* **1987**, *91*, 6269–6271.
- 3 K. Kahn, T. C. Bruice, *J. Comp. Chem.* **2002**, *23*, 977–996..
- 4 I. Yeh, M. L. Berkowitz, *J. Chem. Phys.* **1999**, *111*, 3155–3162.