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Supplementary information for “Structure and dynamics of nanoconfined water between surfactant monolayers”

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Intrinsic surface construction

We have used a straightforward grid-based method to construct intrinsic surfaces that capture the monolayer-water and air-water interfaces that exist in the system. This method allows for natural partitioning between the monolayer-water and air-water interfaces. The number of grid bins must be chosen *a priori* and has a qualitative effect on the features of the water intrinsic density profiles. To choose a suitable number of bins, we calculated the water intrinsic density for a range of different grid resolution values. We found that a resolution of $2.6 \times 2.6 \text{ \AA}$ (using a 40×40 grid) encapsulates the expected behaviour of the confined water

layer. It shows a peak in the water density that we would expect from the headgroup-water pair distribution function and shows the monotonic decay of water density at the air-water interface. Figure 1 below shows why a finer or coarser grid is not appropriate. The coarser 20×20 grid (violet) does not partition the air-water and monolayer-water interfaces and a finer 60×60 grid (turquoise) describes a non-physical decay of water density at the air-water interface (see inset plot) as some monolayer-water interface is erroneously partitioned into the air-water contribution. In the 20×20 grid, the air-water interface is not accounted for since the grid bins are too wide. When using a 60×60 grid, parts of the intrinsic surface that should be classified as covered by monolayer domains are instead partitioned into the air-water interface.

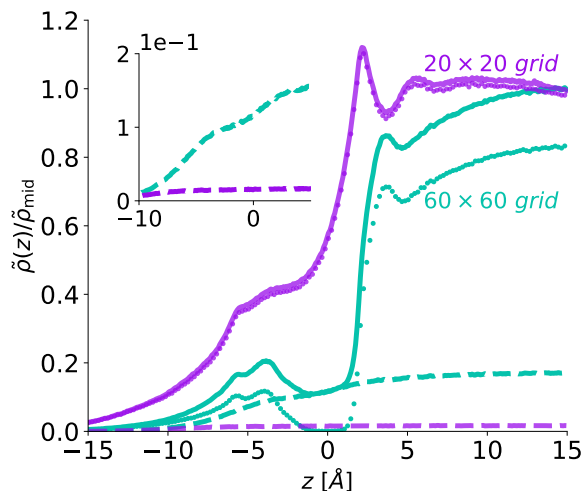


Figure 1: Normalized intrinsic density of the denser ($A_{\text{CTAB}} = 49 \text{ \AA}^2$) monolayer in the ASYM2 system for different grid sizes. Shown here are the total intrinsic density (solid lines), the monolayer-water interface density (dotted lines) and the air-water interface density (dashed lines). The coarse 20×20 grid (violet) does not partition the air-water and monolayer-water interfaces. The fine 60×60 grid (turquoise) describes a non-physical decay of water density at the air-water interface (see inset plot).

Pair distribution functions

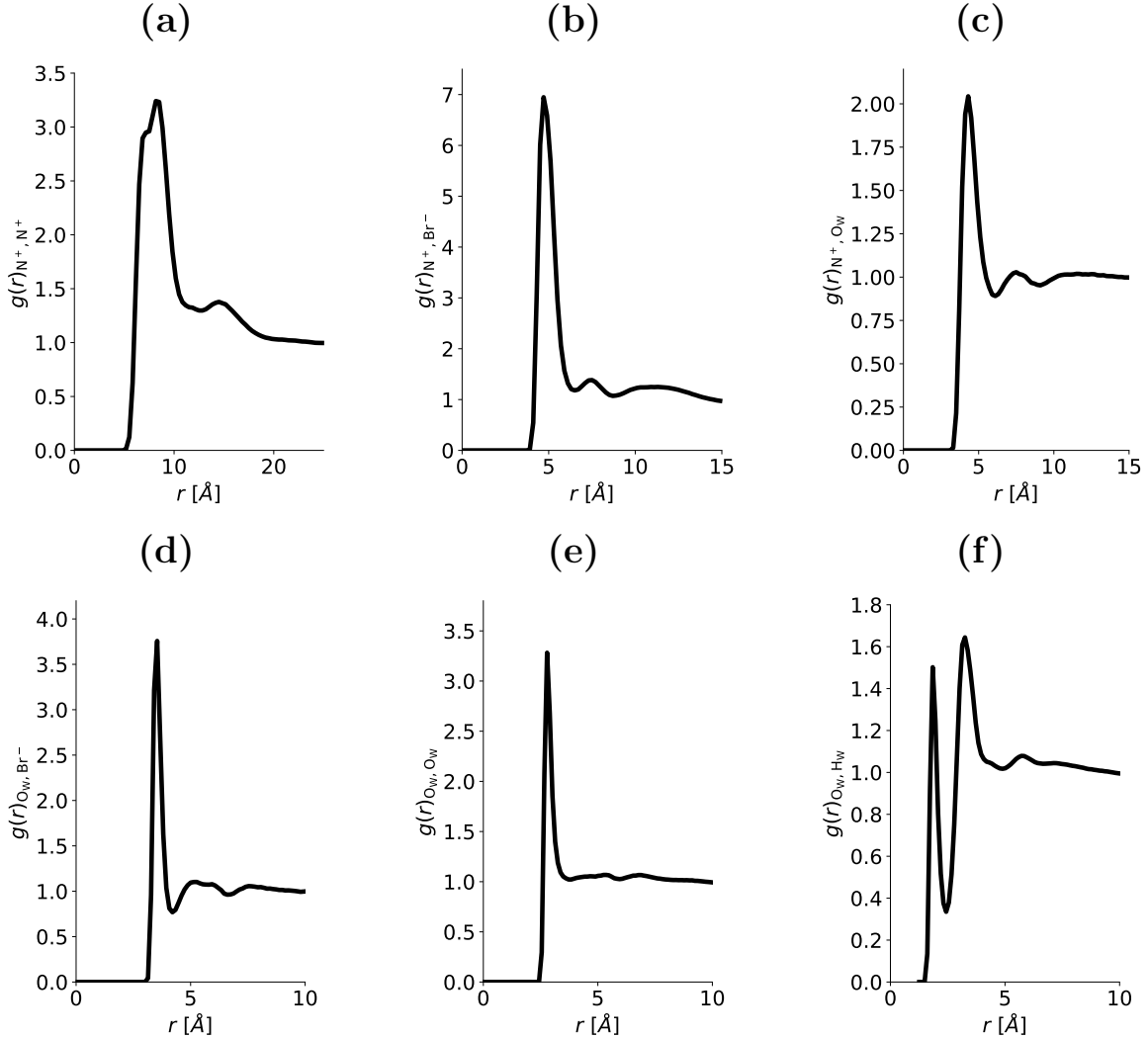


Figure 2: Pair distribution functions for (a) onium-onium, (b) onium-bromide, (c) onium-water oxygen, (d) water oxygen-bromide, (e) water oxygen-water oxygen, and (f) water oxygen-water hydrogen pairs.. Presented here are the results from the SYM52 system. The observable positions of the turning points and intensity of the peaks do not change appreciably over the range of A_{CTAB} considered in this work.

The important features of SI Figure 2(a), (e) and (f) are discussed in the main text. The positions of the global maximum and first local minimum of $g(r)_{N^+, Br^-}$ are found at 4.7 Å and 6.4 Å, respectively. The analogous results for $g(r)_{N^+, O_w}$ occur at slightly shorter distances: 4.3 Å and 6.1 Å. For the water oxygen-bromide pair, the $g(r)_{N^+, Br^-}$ maximum occurs at 3.5 Å and the first local minimum 4.2 Å.

Intrinsic orientational distribution of water molecules

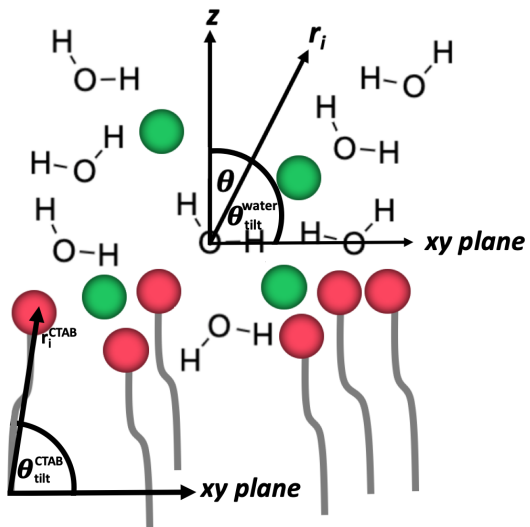


Figure 3: Schematic describing the angle $\theta \equiv \hat{\mathbf{z}} \cdot \hat{\mathbf{r}}_i$ used to characterize the orientation of confined water molecules. Coloring scheme analogous to Fig. 1 in the main text: CTAB alkyl tails are colored gray, CTAB headgroups are red and bromide anions are green. The water and CTAB tilt angles referred to in SI Fig. 11. are also shown.

Equilibrium properties of the CTAB monolayers

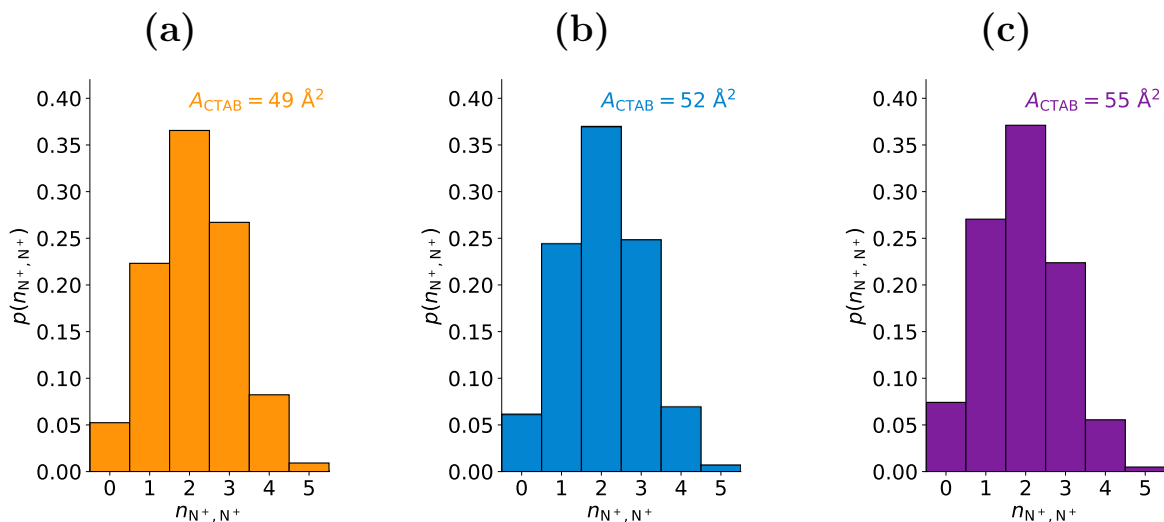


Figure 4: Normalized inter-headgroup coordination number probability distributions for (a) $A_{\text{CTAB}} = 49 \text{ \AA}^2$ monolayer in ASYM2, (b) both $A_{\text{CTAB}} = 52 \text{ \AA}^2$ monolayers in SYM52 (overlaid), and (c) $A_{\text{CTAB}} = 55 \text{ \AA}^2$ monolayer in ASYM2.

Intrinsic density profiles

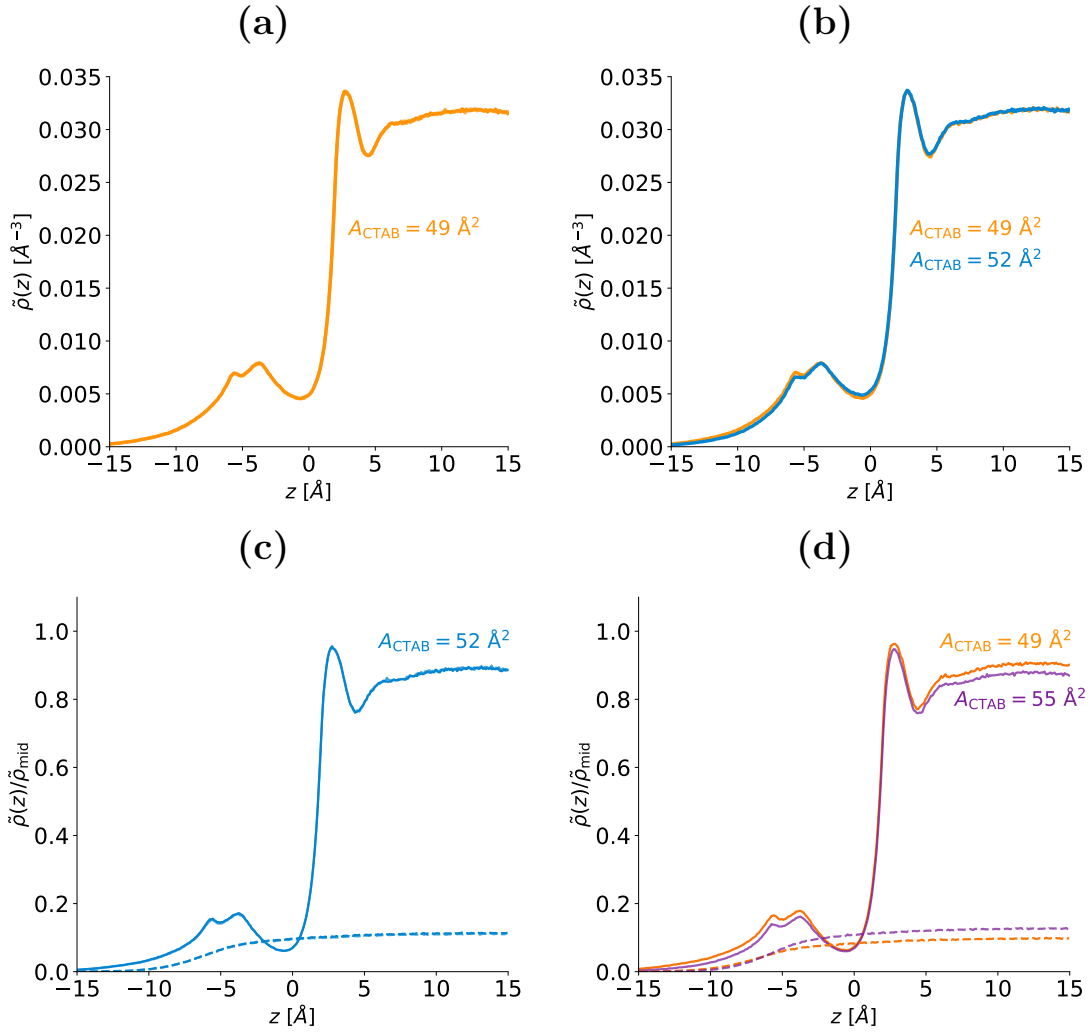


Figure 5: Intrinsic density of water in (a) SYM49 and (b) ASYM. Intrinsic density of water partitioned into monolayer-water and air-water interfacial components in (c) SYM52 and (d) ASYM2.

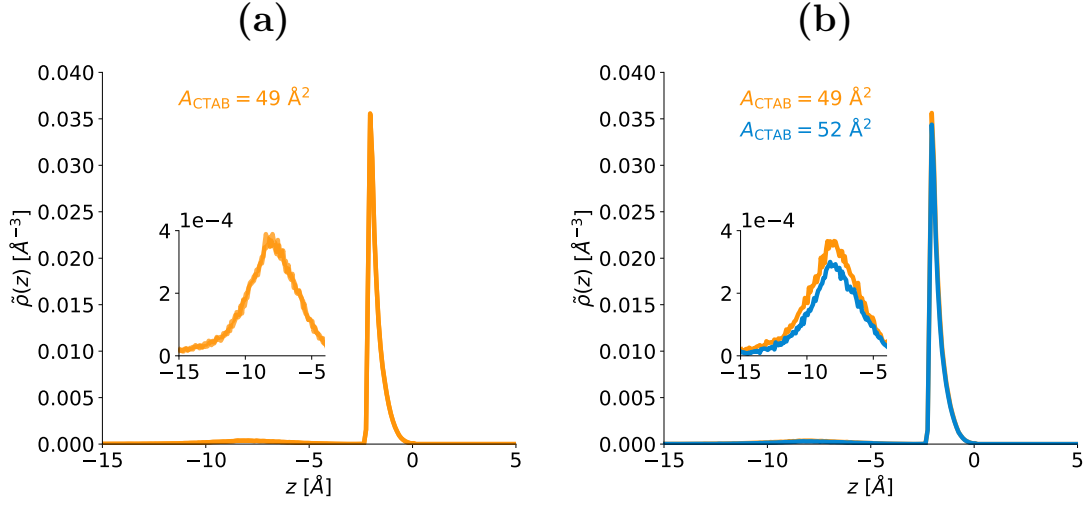


Figure 6: Intrinsic onium (N^+) density in (a) SYM49 and (b) ASYM. The inset figures highlight the small, secondary peak in the intrinsic density centered at $z \approx -8$ \AA .

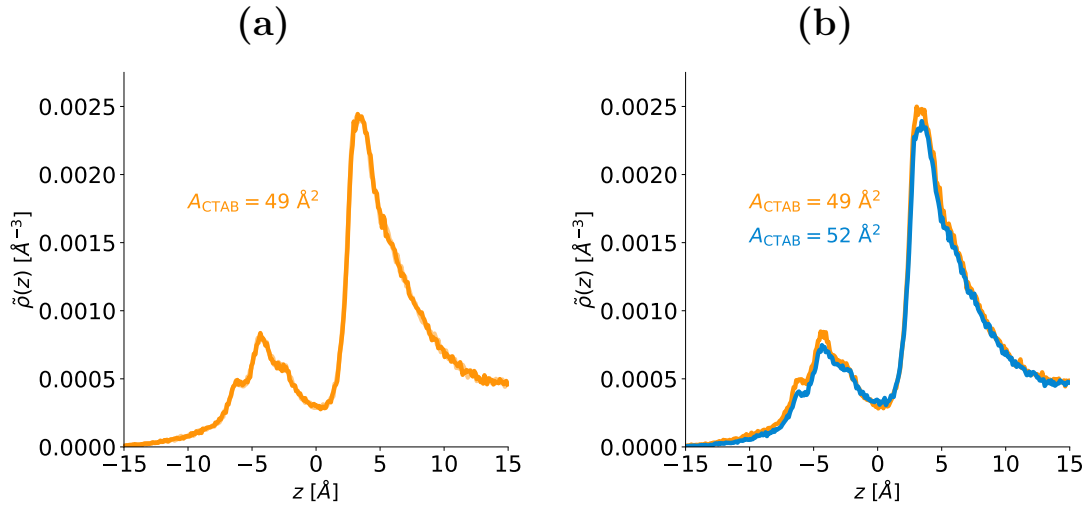


Figure 7: Intrinsic bromide density in (a) SYM49 and (b) ASYM.

Dynamics of the confined water

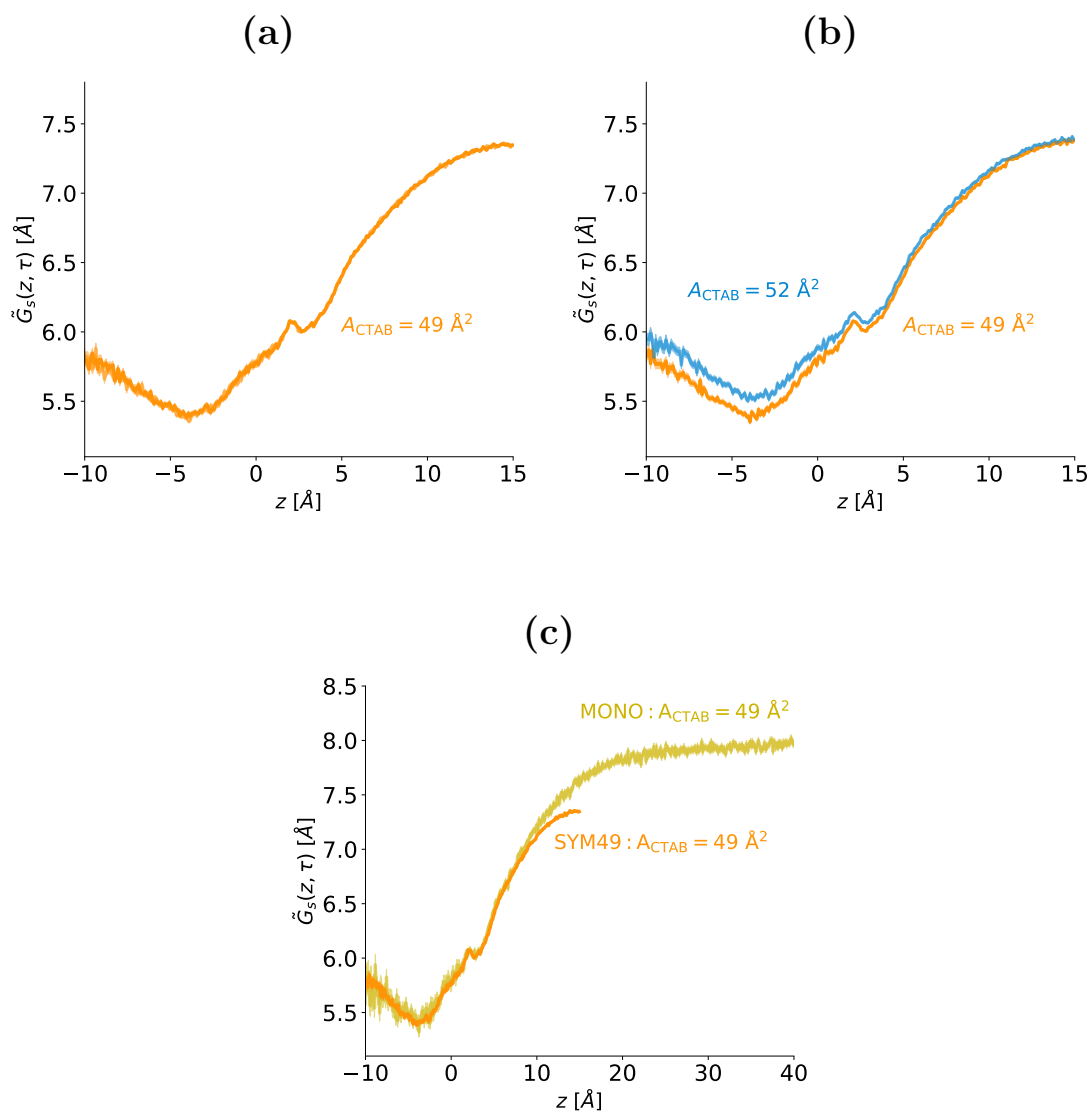


Figure 8: Intrinsic van Hove self-correlation function distributions for water in (a) SYM49, (b) ASYM (c) and MONO compared to SYM49.

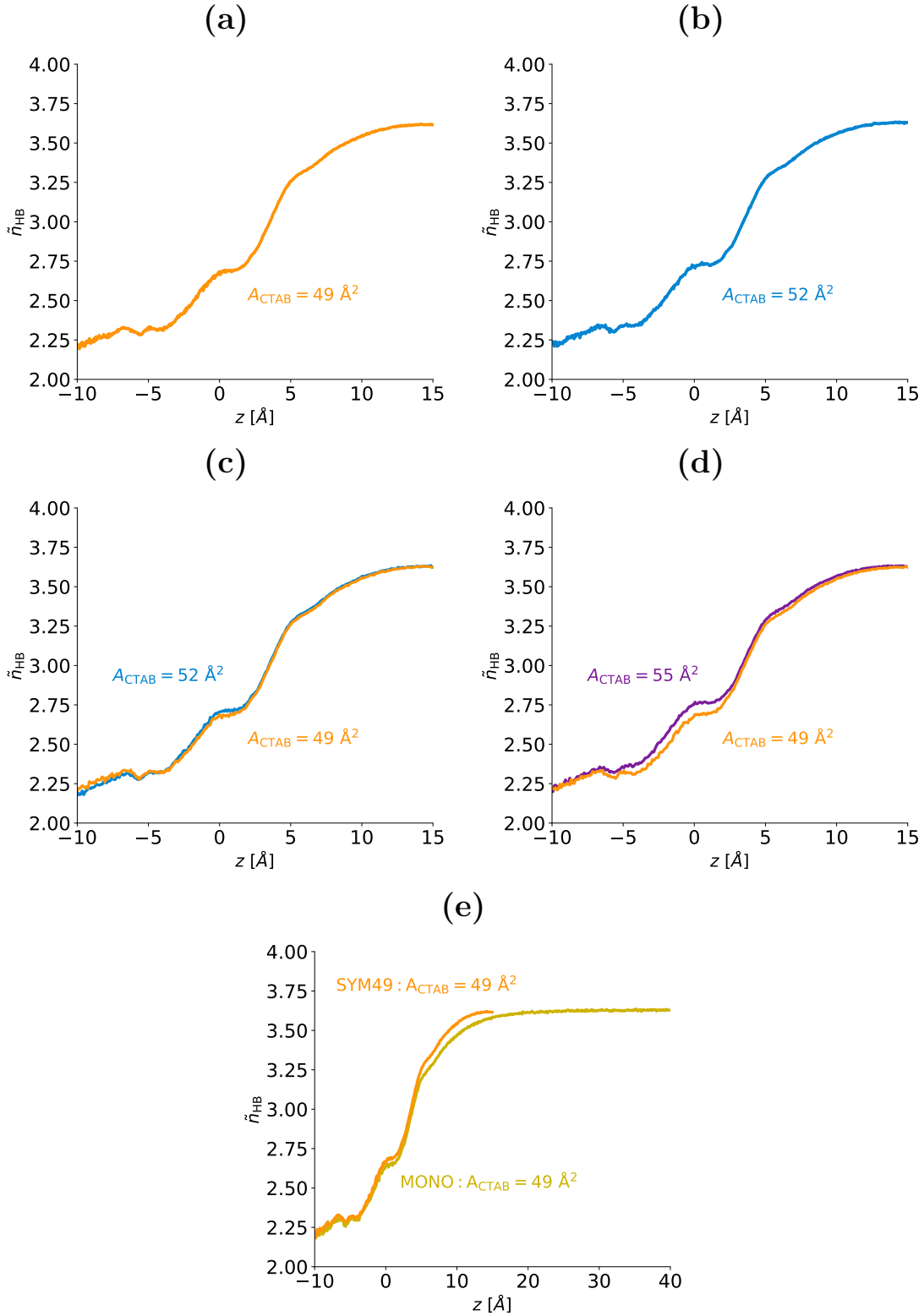


Figure 9: Intrinsic average degree of hydrogen bonding in (a) SYM49, (b) SYM52, (c) ASYM, (d) ASYM2 and (e) MONO compared to SYM49. MONO reduces \tilde{n}_{HB} slightly more than SYM49 at the interface (both have $A_{\text{CTAB}} = 49 \text{ \AA}^2$): attributed to higher roughness of MONO ($5.3 \pm 0.3 \text{ \AA}$, some bromide counterions diffuse away from the monolayer.)

Angular distributions

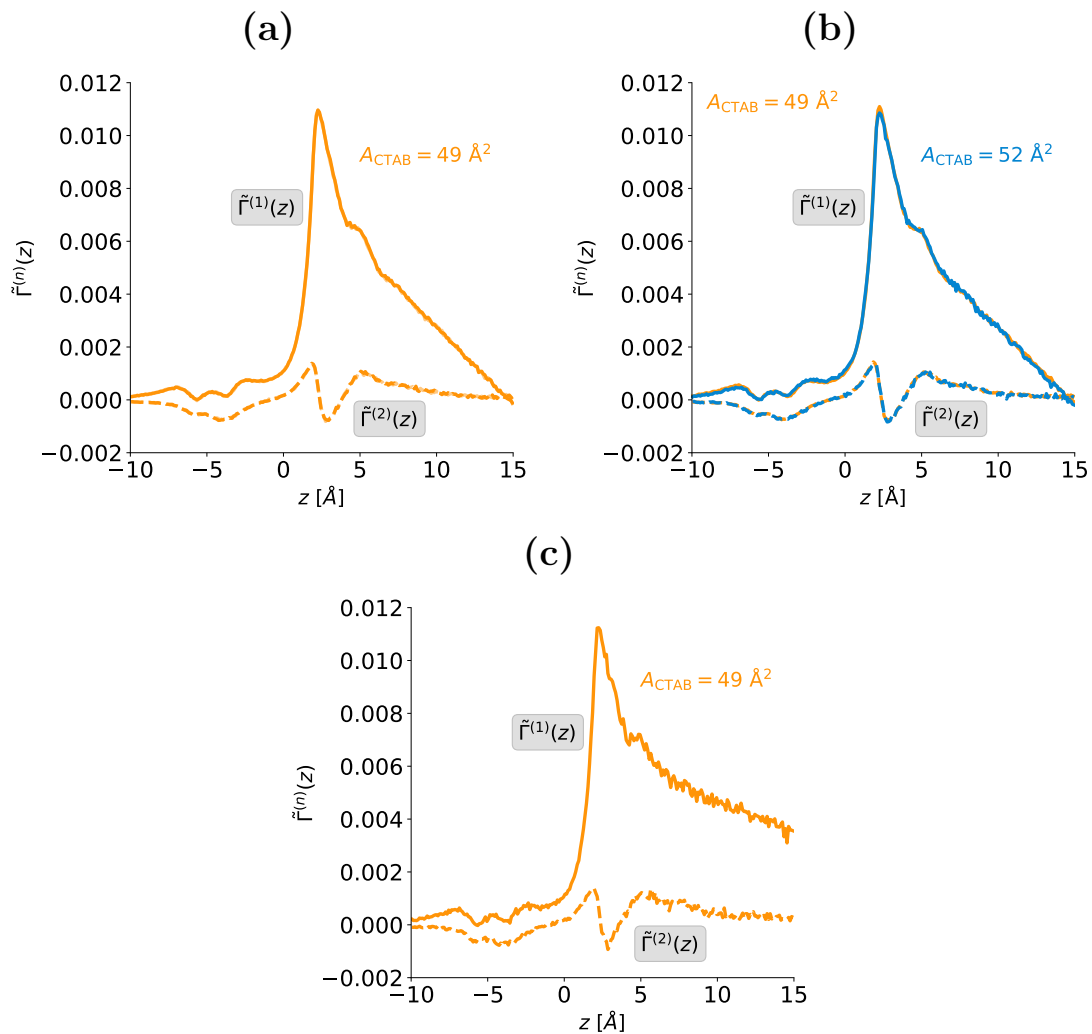


Figure 10: Intrinsic orientational profiles of the confined water in (a) SYM49, (b) ASYM and (c) MONO. First moment ($\tilde{\Gamma}^{(1)}(z)$, solid lines) and second moment ($\tilde{\Gamma}^{(2)}(z)$, dashed lines) are both shown.

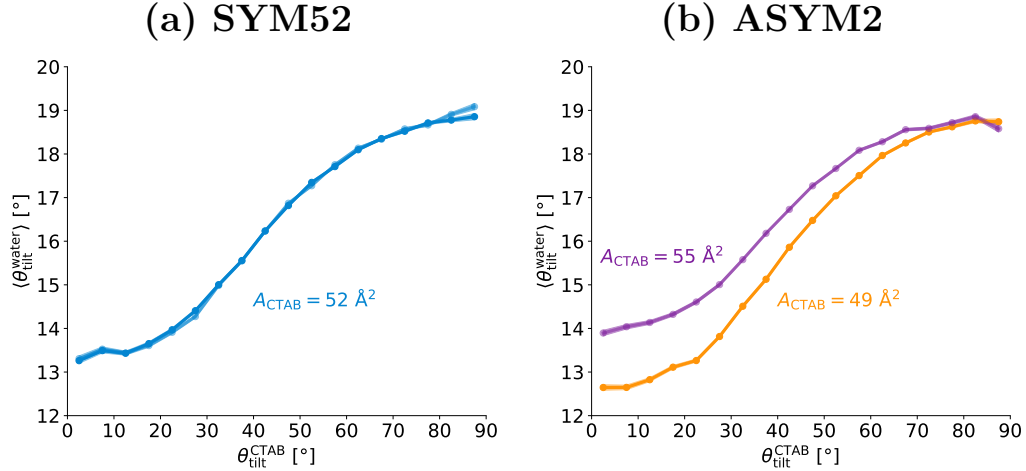


Figure 11: Average water tilt angle as a function of CTAB tilt angle in (a) SYM52 and (b) ASYM2. A CTAB tilt angle $\theta_{\text{tilt}}^{\text{CTAB}} = 0$ corresponds to the CTAB molecule lying flat along the water-monolayer interface, and $\theta_{\text{tilt}}^{\text{CTAB}} = 90$ corresponds to the CTAB molecule oriented along the monolayer normal, with its headgroup pointing into the confined water layer. The water tilt angle $\theta_{\text{tilt}}^{\text{water}} = 90$ describes a water molecule with its oxygen atom pointing towards the monolayer, and a water tilt angle $\theta_{\text{tilt}}^{\text{water}} = 0$ describes a water molecule with its dipole axis lying in the xy plane. These angles are depicted in SI Fig. 3.

Table 1: Total mean system energies at equilibrium and standard deviation.

System	Total energy [kcal mol ⁻¹]
SYM49	-89385 ± 251
SYM52	-88756 ± 252
ASYM	-89053 ± 246
ASYM2	-88749 ± 248

The total energy of the various systems has the rank order SYM49 < ASYM < SYM52 \approx ASYM2, which follows the trend in average A_{CTAB} of the confining monolayers. The interaction of water with the headgroups is favourable. Therefore an increased packing density of the monolayers results in a lower total energy.