Supplementary material:
The intrinsic structure of hydrophobic surfaces: the oil-water interface

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I. TRANSVERSE AREA DEPENDENCE OF THE DENSITY PROFILES

Within the intrinsic sampling method (ISM) [1, 2], an intrinsic surface (IS) \( z = \xi(x, y) \) is identified from the molecular positions of each species, and described through its Fourier component \( \hat{\xi}(q) \). The statistical properties of these IS components, for each wavevector \( q \), are obtained from the sampling over a large set of molecular configurations along the molecular dynamics. The thermal fluctuations of the IS are the capillary waves (CW) of the liquid surface lead to null averages \( \langle \hat{\xi}(q) \rangle = 0 \), and mean square amplitudes \( \langle |\hat{\xi}(q)|^2 \rangle \) which depend on \( |q| \). The total mean amplitude of the CW fluctuations is

\[
\Delta \equiv \langle \xi^2 \rangle - \langle \xi \rangle^2 = \sum_{q \geq q_l} \langle |\hat{\xi}(q)|^2 \rangle,
\]

and it depends on the sampled area through the lower bound for the CW wavevectors. In a simulation box with square transverse section, and the usual periodic boundary conditions, this low-\( q \)-cutoff is \( q_l = 2\pi/\sqrt{A} \).

The mean density profile is the average

\[
\rho(z, A) = \frac{1}{A} \left\langle \sum_{i=1}^{N} \delta(z - z_i) \right\rangle,
\]

over the sampled molecular configurations, and it should become increasingly smoother with larger \( A \). The dependence of \( \rho(z, A) \) with the area is often waived, but it may set a serious problem when comparing the results of computer simulations with different box sizes, particularly for water or other structured interfaces. This problem may be avoided with the intrinsic density profiles

\[
\hat{\rho}(z) = \frac{1}{A} \left\langle \sum_{i=1}^{N} \delta(z - z_i + \xi(x_i, y_i)) \right\rangle.
\]

The blurring created by the CW fluctuations is eliminated in \( \hat{\rho}(z) \), which gives a much sharper view of the molecular structure at the interface, and it is independent of the sampled area \( A \).

The capillary wave theory (CWT) [3] assumes that \( \rho(z, A) \) is the convolution of \( \hat{\rho}(z) \) with a Gaussian of width \( \Delta(A) \),

\[
\rho(z, A) = \frac{1}{\sqrt{2\pi\Delta(A)}} \int dz' \hat{\rho}(z + z') e^{-\frac{(z')^2}{2\Delta(A)}},
\]

and that the mean square CW amplitudes are described by

\[
\langle |\hat{\xi}(q)|^2 \rangle \approx \frac{kT}{A\gamma q^2},
\]

\[A \gamma \approx \frac{a^2}{2\Delta(A)} \] for a Gaussian profile.

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in terms of the thermodynamic surface tension $\gamma$. Taking the continuous limit for the sum in (1) gives [3]

$$
\Delta(A) = \frac{kT}{4\pi\gamma} \ln \left( \frac{A}{A_m} \right),
$$

(6)

where $A_m$ is an effective molecular cutoff for the CW spectrum.

The results of the ISM confirm such logarithmic dependence of $\Delta(A)$ with the sampled area [1], and therefore give direct access to the constant $A_m$, which may be defined directly from equating the right hand sides of eqs. (1) and (6). Also the ISM results for $\langle |\tilde{\xi}(q)|^2 \rangle$ make clear that there is no sharp upper-limit for the CW spectrum. Instead, it is observed that as $q$ approaches $2\pi/\sigma$, in terms of the molecular diameter, the mean square CW amplitudes fall continuously below their classical prediction (5). That may be described by a wavevector dependent surface tension $\gamma(q) \equiv \frac{kT}{A\langle |\tilde{\xi}(q)|^2 \rangle q^2}$. Therefore, $A_m$ in eq. (3) reflects an effective upper cutoff which derives from a smooth damping of the CW fluctuations at molecular level [4].

The direct access to $A_m$ from simulation results is particularly interesting when we compare the dodecane/water and the free vapor/water interfaces, since the different molecular sizes of the water and the alkane should show up in the values of the effective cutoff $A_m$ at each of these interfaces. In the Fig. 1 of the article we present the average and the intrinsic density profiles for the dodecane-water and interface at 300 K, obtained with a simulation box of transverse area $A = (13\sigma)^2$. These profiles are compared with those of the water-vapor, and dodecane vapor interfaces. As analyzed in our letter, the intrinsic profiles of water are very similar at the oil-water interface and at the free water surface. The same similarity appears between the two the density profiles, $\rho_w(z, A)$ and $\rho'_w(z, A)$ (see Figure), which is consistent with eq.(4) since we obtain that the calculated mean square fluctuation of the intrinsic surface of water is very similar in the o/w ($\Delta_w = 0.18\sigma^2$) and the free interface ($\Delta'_w = 0.19\sigma^2$). Hence, for our of $A$, the gaussian convolutions of the intrinsic profiles result in very similar mean density profiles.

However, we note that the surface tension of the free water surface for the SPC/E model at 300 K, $\gamma_w = 0.0584 N/m$, is slightly higher than the dodecane-water surface tension $\gamma_{ow} = 0.0523 N/m$. The difference is small but with the same simulation box size we should expect that the lower stiffness of the oil/water interface produces larger CW fluctuations, with $\Delta_w(A)$ approximately 12% larger than $\Delta'_w(A)$. Instead we find $\Delta_w \lesssim \Delta'_w$. This apparent contradiction is solved by the fact that the free water surface is stiffer that oil-water surface, but the CW fluctuations in the water surface extend up to shorter wavelength when they are not restricted by the contact with the larger dodecane molecules. From eqs. (1) and (6), our ISM gives $A_m \approx 6.9\sigma^2$ at the free water surface, and $A_m \approx 9.6\sigma^2$ for water at the dodecane-water interface. With our value of $A = 139\sigma^2$, the difference in the molecular cutoff $A_m$ still compensates the difference in the surface tensions. Only for larger simulation boxes we would observe that $\rho'_w(z, A)$, at the dodecane-water interface becomes smoother than $\rho_w(z, A)$, at the water-vapor surface, reflecting the stiffer character of the later.
The terms change for the intrinsic surfaces calculated for the dodecane molecules. The oil/vapor interface surface tension $\gamma_{vo} = 0.020\,\text{N/m}$, is much lower than the above value for the oil/water interface. For the alkane molecules the main effect of being close to the water surface is to flatten their molecular distribution at all the scales, from the molecular size (slightly more structured intrinsic density profiles) to the CW fluctuations observed within the simulation box size. All that contributes to get $\rho_{vo}(z, A)$ clearly smoother than $\rho_o(z, A)$, as shown in the figure.

All together, we have to stress the relevance of the molecular structure to understand the dependence of the density profiles with the sampled area in fluid interfaces. For the typical size of the computer simulations boxes, the predictions of the classical CWT may be qualitatively affected by the value of the molecular cutoff $A_m$. The ISM gives direct access to this quantity, and to the intrinsic density profiles which represent a much shaper view of the interfacial structure than that provided by the usual density profiles.

II. ADDITIONAL RESULTS FOR THE INTRINSIC STRUCTURE OF THE HEXANE-WATER INTERFACE

We present in the following results for the intrinsic properties of the hexane-water interface at 300 K. The simulations were performed using the models discussed in the letter, i.e., the TraPPE forcefield for the alkane molecules and the SPC/E model for water. The system consisted of 496 hexane molecules and 2794 water molecules. The box dimensions were $(L_x, L_y, L_z) = (36.77, 36.77, 300.86)\,\text{Å}$. The intrinsic analysis was performed over configurations obtained from canonical molecular dynamics simulations. The production time was 1 ns.

The intrinsic density profile for water at the alkane surface is represented in figure 2. We find that the intrinsic structure of water is insensitive to the presence of the hexane phase. This observations is compatible with the results we have obtained for dodecane (see main paper), despite the fact that the length of the hexane molecule is considerably shorter than that of dodecane. These changes in the molecular structure of the molecules have of course an impact on the structure of the liquid, but this does not seem to affect the structure of water at the interface. All this lead us to conclude that the results presented in the letter apply to a wide range of alkane systems. Hence, the behavior described in our paper seems to be a generic feature of water at hydrophobic interfaces.

We have also quantified the rigidity of the hexane-water interface. The rigidity of the interface depends mainly of the distance of the thermodynamic state to the drying transition. In the main paper we show that the dodecane-water interface at 300 K is far from the drying transition, which occurs above 500 K. For hexane the drying temperature will decrease with respect to that of dodecane. Preliminary calculations indicate this temperature is above 400K, showing that at 300 K the hexane-water interface is still far from drying. The rigidity of the hexane-water interface can be obtained using the methodology discussed in the letter. Figure 3 shows the corresponding inverse dispersion of the
FIG. 3: Inverse dispersion of the fluctuations of the water-hexane interface as a function of the square of the wave vector. The results for the water-dodecane interface are included for comparison.

fluctuations of the hexane-water interface. A fitting of the simulation data similar to the one performed for dodecane shows that the intrinsic gap width and the transverse correlation length are $1.41 \sigma$ and $1.3-1.6 \sigma$ respectively. These results are very similar to the ones obtained for dodecane. The main conclusion from this analysis is that the hexane-water interface is also very rigid at ambient temperature. Overall our results indicate that the oil-water interface at ambient temperature undergoes very small fluctuations.