Supplementary Information

Correction: Characterizing surface wetting and interfacial properties using enhanced sampling (SWIPES)

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1 Comparing \( h_{\text{COM}} \) and \( h \)

In this appendix, we present the derivation which leads to Eq. 1. Consider the model setup illustrated in Fig. S1. The simulation box is a fixed-volume orthorhombic box with side lengths \( L_x, L_y, \) and \( L_z \) maintained at constant temperature, \( T \). It contains \( N_{\text{tot}} \) water molecules in contact with a solid surface \( a \) of length \( l_{S,x} \) that runs from \( x_{S,0} \) to \( x_{S,1} \) along the \( x \)-axis. Its surface is normal to the \( z \)-axis and the separation between opposing faces across periodic boundary conditions is \( l_z \). We will refer to the space between the two faces of the solid surface as the \textit{inner} region, and the space outside as the \textit{outer} region. The vapor-liquid interface in the inner region is located at \( x = H \), the position of its midpoint.

For a single-component system of point masses (or rigid molecules, whose positions are identified by their centers of mass), \( \langle x_{\text{COM}} \rangle_{\kappa,N^*} \) for the entire system is related to the total number density profile at equilibrium, \( \rho(x,y,z) \), by

\[
\langle x_{\text{COM}} \rangle_{\kappa,N^*} \equiv \frac{1}{N_{\text{tot}}} \int_V dV \rho(x,y,z)
\]  

(1)

where the integral is taken over the entire simulation box (volume \( V \)) and the dependence of \( \rho \) on the biasing parameters \( \kappa \) and \( N^* \) is suppressed for clarity.

Assuming that \( \rho \) is constant along \( y \) due to periodic boundary conditions,

\[
\langle x_{\text{COM}} \rangle_{\kappa,N^*} = \frac{L_y}{N_{\text{tot}}} \int_0^{L_x} dx \int_0^{L_z} dz \rho(x,z)
\]  

(2)

In evaluating Eq. 2, we distinguish between several different regions of the simulation box to simplify the calculation. First, we assume that \( l_{S,x} \) is large enough there are regions to the left and right of the inner vapor-liquid interface in which

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Figure S1: Illustration of the model system employed to estimate the accuracy of using \( x_{\text{COM}} \) to track the location of the vapor-liquid interface.
the density is unaffected by the inner vapor-liquid interface or edges of the surface, and is therefore constant along \( x \). Denote the density of the liquid and vapor in these "bulk" inner regions by \( \rho_{L,S}(z) \) and \( \rho_{V,S}(z) \), respectively. We assume that deviations of the density field away from these profiles due to the presence of the inner vapor-liquid interface are confined to the region from \( x_A(N^*) \) to \( x_B(N^*) \). Provided that the inner vapor-liquid interface maintains its shape as \( N^* \) increases, \( \Delta x_{AB} = x_B - x_A \) is constant and \( x_A(N^*) \propto H(N^*) \). To account for edge effects, we place the Gibbs dividing surface between the inner and outer liquid phases at \( x_{S,0} \) and assume that the edge effects are confined to the region \( x_{S,0} \pm 2\Delta x_{S,0} \) with width \( 2\Delta x_{S,0} \). We use the same approach at the right edge of the slab and confine the inhomogeneity to the region \( x_{S,1} \pm \Delta x_{S,1} \). The corresponding surface excesses are \( \Gamma_L \) and \( \Gamma_V \), respectively. The probe volume, \( v \), is chosen such that it encompasses the region \( x = x_{S,0} - \Delta x_{S,0} \) to \( x = x_{S,1} + \Delta x_{S,1} \).

Breaking the simulation box into regions as described above,

\[
\langle x_{COM}\rangle_{K,N^*} = \frac{L_y}{N_{tot}} \left[ \int_{x_{S,0} - \Delta x_{S,0}}^{x_{S,0}} dx \int_0^{L_z} dz \rho(x,z) + \int_{x_{S,0} + \Delta x_{S,0}}^{x_{S,0}} dx \int_0^{L_z} dz \rho(x,z) \right] \]

\[
+ \left[ \int_{x_{S,0} + \Delta x_{S,0}}^{x_{S,1} + \Delta x_{S,1}} dx \int_0^{L_z} dz \rho_{L,S}(z) + \int_{x_{S,1} - \Delta x_{S,1}}^{x_{S,1}} dx \int_0^{L_z} dz \rho_{V,S}(z) \right]
\]

After taking the derivative with respect to \( N^* \), it can be shown that

\[
\frac{h_{COM}}{h} = \frac{d\langle x_{COM}\rangle_{K,N^*}}{dH} \frac{dH}{dN^*} = 1 - \frac{\langle x_{COM}\rangle_{K,N^*}}{N_{tot} \langle x_{COM} \rangle_{K,N^*}} - (1 - \zeta) \left[ 1 - \frac{(N_e(N^*)_{K,N^*}}{N_{tot}} \right] - \frac{\Delta x_{S,0} \rho_{L,b}}{L_x} \frac{\Delta x_{S,1} \rho_{V,b}}{L_x} \rho_{tot} \]

\[
- \zeta \frac{\rho_{V,b}}{\rho_{tot}} \frac{\bar{\rho}_{V,S} l_{S,x}}{\rho_{V,b}} + \rho \left( 1 - \frac{l_{S,x}}{L_x} \right) \right]
\]

where \( A_o = L_y L_z \) is the outer cross-sectional area, \( \rho_{tot} \equiv N_{tot}/V \) is the average density, \( \Gamma_L \) and \( \Gamma_V \) are the surface excesses at either end of the surface,

\[
\Gamma_L \equiv \int_{x_{S,0} - \Delta x_{S,0}}^{x_{S,0}} dx \left[ \bar{\rho}_o(x) - \rho_{L,b} \right] + \int_{x_{S,0}}^{x_{S,0} + \Delta x_{S,0}} dx \left[ \bar{\rho}_i(x) - \rho_{L,S} \right],
\]

\[
\Gamma_V \equiv \zeta \int_{x_{S,1} - \Delta x_{S,1}}^{x_{S,1}} dx \left[ \bar{\rho}_i(x) - \rho_{V,S} \right] + \int_{x_{S,1}}^{x_{S,1} + \Delta x_{S,1}} dx \left[ \bar{\rho}_o(x) - \rho_{V,b} \right],
\]

\( \zeta = l_z/L_z \) is the fraction of the box along \( z \) that is between the surfaces, \( r \equiv \Delta \bar{\rho}_S/\Delta \bar{\rho}_b = \langle \rho_{L,S} - \rho_{V,S} \rangle/\langle \rho_{L,b} - \rho_{V,b} \rangle \) is the ratio of differences in average density between the inner and outer regions, \( \bar{\rho}_{L,S} = \frac{1}{L_z} \int_{l_z} dz \rho_{L,S}(z) \) and \( \bar{\rho}_{V,S} = \frac{1}{L_z} \int_{l_z} dz \rho_{V,S}(z) \) are the average densities in the bulk inner regions, and \( \bar{\rho}_i(x) = \frac{1}{L_z} \int_{l_z} dz \rho(x,z) \) and \( \bar{\rho}_o(x) = \frac{1}{L_z} \int_{l_z} dz \rho(x,z) \) are the densities averaged over the inner and outer cross-sectional areas (respectively).

If we assume that the vapor and liquid densities are uniform and equal to their bulk values (\( \rho_{V,b} \) and \( \rho_{L,b} \), respectively), then \( \rho_{V,S} = \rho_{V,b} \) and \( \rho_{L,S} = \rho_{L,b} \); since edge effects are therefore also neglected, \( \Delta x_{S,0} = \Delta x_{S,1} = 0 \) and \( \Gamma_L = \Gamma_V = 0 \). Eq. 4 then greatly simplifies to

\[
\frac{h_{COM}}{h} = 1 - \alpha \lambda - (1 - \alpha) \frac{\rho_{V,b}}{\rho_{tot}}
\]

where \( \alpha \equiv l_{S,z}/L_z = 1 - \zeta \) is the fraction of the box occupied by the solid surface along \( z \), and \( \lambda \equiv 1 - (N_e(N^*)_{K,N^*}/N_{tot}) \) is the fraction of molecules outside the observation volume. Lastly, for fluids far from their triple point (such as water at ambient conditions), \( \rho_{V,b} \ll \rho_{tot} \) when the liquid occupies a substantial part of the simulation box. and therefore the last term in Eq. 5 is negligible. This leads to Eq. 1 of the main text: \( h_{COM}/h \approx 1 - \alpha \lambda \).