<div align="center">

Supplementary Information

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

</div>

<div align="center">

Sean M. Marks, Hao Jiang, Zachariah Vicars, Suruchi Fialoke,
Amish J. Patel*
(amish.patel@seas.upenn.edu)

Department of Chemical and Biomolecular Engineering, University of Pennsylvania
Philadelphia, PA 19104, USA

</div>

1 Comparing h_{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_{tot} water molecules in contact with a solid surface a of length $l_{\mathrm{S},x}$ 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 *inner* region, and the space outside as the *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), $\langle x_{\mathrm{COM}} \rangle_{\kappa,N^*}$ for the entire system is related to the total number density profile at equilibrium, $\rho(x, y, z)$, by

$$\langle x_{\mathrm{COM}} \rangle_{\kappa,N^*} \equiv \frac{1}{N_{\mathrm{tot}}} \int_V \mathrm{d}V \, x \rho(x, y, z) \tag{1}$$

where the integral is taken over the entire simulation box (volume V) and the dependence of ρ on the biasing parameters κ and N^* is suppressed for clarity. Assuming that ρ is constant along y due to periodic boundary conditions,

$$\langle x_{\mathrm{COM}} \rangle_{\kappa,N^*} = \frac{L_y}{N_{\mathrm{tot}}} \int_0^{L_x} \mathrm{d}x \int_0^{L_z} \mathrm{d}z \, x \rho(x, z) \tag{2}$$

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

---

*To whom correspondence should be addressed
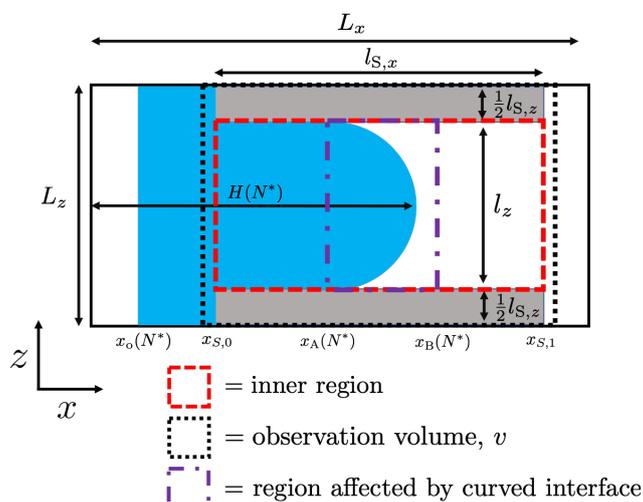
Figure S1: Illustration of the model system employed to estimate the accuracy of using x_{COM} to track the location of the vapor-liquid interface.

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 $\rho_{\mathrm{L},S}(z)$ and $\rho_{\mathrm{V},S}(z)$, 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 $x_{\mathrm{A}}(N^*)$ to $x_{\mathrm{B}}(N^*)$. Provided that the inner vapor-liquid interface maintains its shape as N^* increases, $\Delta x_{\mathrm{AB}} = x_{\mathrm{B}} - x_{\mathrm{A}}$ is constant and $x_{\mathrm{A}}(N^*) \propto H(N^*)$. 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 $x_{S,0} \pm \Delta x_{S,0}$ 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 Γ_{L} and Γ_{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,

$$
\langle x_{\mathrm{COM}} \rangle_{\kappa, N^*} = \frac{L_y}{N_{\mathrm{tot}}} \left[\underbrace{\int_0^{x_{S,0} - \Delta x_{S,0}} \mathrm{d}x \int_0^{L_z} \mathrm{d}z\, x\rho(x,z)}_{\text{to the left of the surface}} + \underbrace{\int_{x_{S,0} - \Delta x_{S,0}}^{x_{S,0} - \Delta x_{S,0}} \mathrm{d}x \int_0^{L_z} \mathrm{d}z\, x\rho(x,z)}_{\text{left edge of surface}} \right.
$$

$$
+ \underbrace{\int_{x_{S,0} + \Delta x_{S,0}}^{x_{\mathrm{A}}(N^*)} \mathrm{d}x \int_0^{L_z} \mathrm{d}z\, x\rho_{\mathrm{L},S}(z)}_{\text{"bulk" liquid between surface}} + \underbrace{\int_{x_{\mathrm{A}}(N^*)}^{x_{\mathrm{B}}(N^*)} \mathrm{d}x \int_0^{L_z} \mathrm{d}z\, x\rho(x,z)}_{\text{inner vapor-liquid interface}} + \underbrace{\int_{x_{\mathrm{B}}(N^*)}^{x_{S,1} - \Delta x_{S,1}} \mathrm{d}x \int_0^{L_z} \mathrm{d}z\, x\rho_{\mathrm{V},S}(z)}_{\text{"bulk" vapor between surface}}
$$

$$
\left. + \underbrace{\int_{x_{S,1} - \Delta x_{S,1}}^{x_{S,1} + \Delta x_{S,1}} \mathrm{d}x \int_0^{L_z} \mathrm{d}z\, x\rho(x,z)}_{\text{right edge of surface}} + \underbrace{\int_{x_{S,1} + \Delta x_{S,1}}^{L_x} \mathrm{d}x \int_0^{L_z} \mathrm{d}z\, x\rho(x,z)}_{\text{to the right of the surface}} \right] \quad (3)
$$

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

$$
\frac{h_{\mathrm{COM}}}{h} \equiv \frac{\mathrm{d}\langle x_{\mathrm{COM}}\rangle_{\kappa,N^*}/\mathrm{d}N^*}{\mathrm{d}H/\mathrm{d}N^*} = 1 - \frac{(\Gamma_{\mathrm{L}} + \Gamma_{\mathrm{V}})A_{\mathrm{o}}}{N_{\mathrm{tot}}} - (1 - \zeta r)\left[1 - \frac{\langle N_v \rangle_{\kappa,N^*}}{N_{\mathrm{tot}}} - \frac{\Delta x_{S,0}}{L_x}\frac{\rho_{\mathrm{L},b}}{\rho_{\mathrm{tot}}} - \frac{\Delta x_{S,1}}{L_x}\frac{\rho_{\mathrm{V},b}}{\rho_{\mathrm{tot}}} \right]
$$

$$
- \zeta\frac{\rho_{\mathrm{V},b}}{\rho_{\mathrm{tot}}}\left[\frac{\bar{\rho}_{\mathrm{V},S}}{\rho_{\mathrm{V},b}}\frac{l_{\mathrm{S},x}}{L_x} + r\left(1 - \frac{l_{\mathrm{S},x}}{L_x}\right) \right] \quad (4)
$$

where $A_{\mathrm{o}} = L_y L_z$ is the outer cross-sectional area, $\rho_{\mathrm{tot}} \equiv N_{\mathrm{tot}}/V$ is the average density, Γ_{L} and Γ_{V} are the surface excesses at either end of the surface,

$$
\Gamma_{\mathrm{L}} \equiv \int_{x_{S,0} - \Delta x_{S,0}}^{x_{S,0}} \mathrm{d}x\,\left[\bar{\rho}_{\mathrm{o}}(x) - \rho_{\mathrm{L},b} \right] + \zeta \int_{x_{S,0}}^{x_{S,0} + \Delta x_{S,0}} \mathrm{d}x\,\left[\bar{\rho}_{\mathrm{i}}(x) - \bar{\rho}_{\mathrm{L},S} \right],
$$

$$
\Gamma_{\mathrm{V}} \equiv \zeta \int_{x_{S,1} - \Delta x_{S,1}}^{x_{S,1}} \mathrm{d}x\,\left[\bar{\rho}_{\mathrm{i}}(x) - \bar{\rho}_{\mathrm{V},S} \right] + \int_{x_{S,1}}^{x_{S,1} + \Delta x_{S,1}} \mathrm{d}x\,\left[\bar{\rho}_{\mathrm{o}}(x) - \rho_{\mathrm{V},b} \right],
$$

$\zeta = l_z/L_z$ is the fraction of the box along z that is between the surfaces, $r \equiv \Delta\bar{\rho}_S/\Delta\rho_b = (\bar{\rho}_{\mathrm{L},S} - \bar{\rho}_{\mathrm{V},S})/(\rho_{\mathrm{L},b} - \rho_{\mathrm{V},b})$ is the ratio of differences in average density between the inner and outer regions, $\bar{\rho}_{\mathrm{L},S} = \frac{1}{l_z}\int_{l_z} \mathrm{d}z\, \rho_{\mathrm{L},S}(z)$ and $\bar{\rho}_{\mathrm{V},S} = \frac{1}{l_z}\int_{l_z} \mathrm{d}z\, \rho_{\mathrm{V},S}(z)$ are the average densities in the bulk inner regions, and $\bar{\rho}_{\mathrm{i}}(x) = \frac{1}{l_z}\int_{l_z} \mathrm{d}z\, \rho(x,z)$ and $\bar{\rho}_{\mathrm{o}}(x) = \frac{1}{L_z}\int_0^{L_z} \mathrm{d}z\, \rho(x,z)$ 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 ($\rho_{\mathrm{V},b}$ and $\rho_{\mathrm{L},b}$, respectively), then $\bar{\rho}_{\mathrm{V},S} = \rho_{\mathrm{V},b}$ and $\bar{\rho}_{\mathrm{L},S} = \rho_{\mathrm{L},b}$; since edge effects are therefore also neglected, $\Delta x_{S,0} = \Delta x_{S,1} = 0$ and $\Gamma_{\mathrm{L}} = \Gamma_{\mathrm{V}} = 0$. Eq. 4 then greatly simplifies to

$$
\frac{h_{\mathrm{COM}}}{h} = 1 - \alpha\lambda - (1 - \alpha)\frac{\rho_{\mathrm{V},b}}{\rho_{\mathrm{tot}}} \quad (5)
$$

where $\alpha \equiv l_{\mathrm{S},z}/L_z = 1 - \zeta$ is the fraction of the box occupied by the solid surface along z, and $\lambda \equiv 1 - \langle \tilde{N}_v \rangle_{\kappa,N^*}/N_{\mathrm{tot}}$ is the fraction of molecules outside the observation volume. Lastly, for fluids far from their triple point (such as water at ambient conditions), $\rho_{\mathrm{V},b} \ll \rho_{\mathrm{tot}}$ 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: $h_{\mathrm{COM}}/h \approx 1 - \alpha\lambda$.