SUPPLEMENTARY INFORMATION

Gas–Liquid Phase Equilibrium of a Model Langmuir Monolayer Captured by a Multiscale Approach

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1 3D reference simulations

1.1 Radial distribution functions of w-H and w-w pairs

As was discussed in the paper, w particles prefer H segments as neighbors over their own species. We verify
this observation by calculating the radial distribution functions (rdf) of w-H and w-w pairs as given in Fig S1a.
It is seen that the first peak in rdf is more pronounced for H-w pairs (solid line) and takes place at a smaller
radial distance with respect to that of the w-w pairs (dash-dotted line). The average hydration number as a
function of radial distance is calculated as
\[ N_w(r) = 4\pi \rho_w \int_0^r r'^2 g(r') dr', \] (S1)
and presented in Fig. S1b for H and w particles. It clearly shows that for small radial distances (say less than
1.3σ), H segments have a larger hydration number than w particles.

Figure S1 (a) Pair correlation functions of H-w (solid line) and w-w (dash-dotted line) pairs. (b) Average
number of neighboring w particles located until distance r, \( N_w(r) \), for H groups (solid line) and w (dash-dotted
line) particles.

1.2 Force-matching scheme

In order to calculate the CG force field \( F_{\text{CG}}(r) \) numerically, we consider a cut-off distance \( r_c \) beyond which
the radial force is assumed to be zero. The interval \([0, r_c]\) is meshed with equidistantly spaced grid points
\( \{r_i; i = 1, ..., \nu\} \) at \( r_i/r_c = (i - 1)/(\nu - 1) \) so that \( r_1 = 0 \) and \( r_\nu = r_c \). We consider a function space \( \{f_i\} \) of
linear spline basis functions as
\[
\begin{align*}
  f_i(r) &= \begin{cases} \\
    \frac{r - r_{i-1}}{r_{i+1} - r_i} ; & r_{i-1} < r \leq r_i, \quad i > 1 \\
    \frac{r_{i+1} - r_i}{r_{i+1} - r_{i-1}} ; & r_i < r \leq r_{i+1}, \quad i < \nu \\
    0 ; & \text{otherwise},
  \end{cases}
\end{align*}
\] (S2)
and take \( F_{\text{CG}}(r) \) to be represented by \( \nu \) coefficients \( \{F_i\} \) as
\[ F_{\text{CG}}(r) = \sum_{i=1}^\nu F_i f_i(r). \] (S3)
This representation implies that \( F_{\text{CG}}(r) \) is a piecewise continuous linear function, and the coefficients \( \{F_i\} \) are
the radial forces at the grid points \( \{r_i\} \) as
\[ F_i = F_{\text{CG}}(r_i), \] (S4)
subjected to the boundary condition of \( F_\nu = 0 \). In the following, we discuss how to calculate coefficients \( \{F_i\} \) by matching the forces in the CG system with the reference system through minimizing the residual \( \chi^2(\mathbf{F}) \). By
plugging Eq. S3 into Eq. 15, we rewrite the CG force $F_I$ in terms of coefficients $\{F_i\}$ as

$$F_I = \sum_{i=1}^{v} F_i a_{iI}, \quad (S5)$$

where

$$a_{iI} = \sum_{J=1, J \neq I}^{N_{int}} f_i(|R_I - R_J|) \frac{R_J - R_I}{|R_I - R_J|}, \quad (S6)$$

is known since it is only dependent on projected surfactant center-of-masses and the function space $\{f_i\}$. Combining Eqs. S5 and 15 results in a linear least-squares problem as

$$\chi^2(\{F_i\}) = \left\langle \frac{1}{2N_{int}} \sum_{I=1}^{v} \left| \sum_{i=1}^{v} F_i a_{iI} - f_I \right|^2 \right\rangle, \quad (S7)$$

where the coefficients $\{F_i\}$ are to be determined numerically. To this end, we solve equivalently an overdetermined linear system of equations obtained by equalizing $x$ and $y$ components of the total force ($f_I$) exerted on each surfactant center-of-mass at each reference configuration with the corresponding CG force ($F_I$) in terms of fitting coefficients $\{F_i\}$. After some trial and errors, we set the cut-off distance to $r_c = 10\sigma$ (not to be confused with $r_{cut}$ in the manuscript) and consider a nonuniform radial mesh with 358 grid points as $\{r_i / \sigma\} = \{0, 1.1, 1.125, ..., 9.975, 10\}$. We note that intermolecular distances with very small separation (say less than $1.1\sigma$ in our cases) are rarely sampled, and hence one can not accurately estimate the value of the forces $\{F_i\}$ in this region. That is why we have considered only one coarse mesh in the interval $[0, 1.1]$ and safely assumed $F_1 = F_2$. We approximate the solution in a block-averaging approach where we partition configurations into disjoint blocks each of which consists roughly of 80000 equations (e.g. for a simulation consisting of 400 surfactants, 50 blocks with the size of 100 each). We then solve the overdetermined linear system of equations in each block by using the LSQR algorithm and subsequently average the results of $\{F_i\}$ over different blocks.

2 Gibbs ensemble Monte Carlo (GEMC)

2.1 Particle displacement

To sample equilibrium configurations within each simulation box we perform displacements of randomly selected particles in a randomly selected region according to the following acceptance probability

$$\mathcal{P}_{\text{disp},\kappa} = \min \left( 1, \exp \left[ -\beta \Delta U^\kappa_{\text{disp}} \right] \right), \quad \kappa = \{le, g\}, \quad (S8)$$

where $\Delta U^\kappa_{\text{disp}}$ denotes the change in the internal energy of phase $\kappa$ due to the particle displacement.

2.2 Area exchange

For the area change trial moves, we perform a random walk in $\ln(A^{le} / A^{g})$ with the acceptance probability $\mathcal{P}_{\text{area}}$, described by

$$\mathcal{P}_{\text{area}} = \min \left( 1, \left( \frac{A^{le} + \Delta A}{A^{le}} \right)^{N^{le}+1} \left( \frac{A^{g} - \Delta A}{A^{g}} \right)^{N^{g}-1} \exp \left[ -\beta \left( \Delta U^{le}_{\text{area}} + \Delta U^{g}_{\text{area}} \right) \right] \right), \quad (S9)$$

where $\Delta A$ is the area change in region $le$ (and hence $-\Delta A$ is the area change in region $g$) and $\Delta U^\kappa_{\text{area}}, \kappa = \{le, g\}$, is the change in the internal energy of phase $\kappa$ associated with that area change. These trial moves result in the pressure equality of the two coexisting phases.
2.3 Particle exchange

Finally, we transfer a randomly selected particle from a randomly selected phase to the other to ensure the chemical equilibrium between two coexisting regions. The acceptance probability of removing a particle from phase \( le \), and inserting that in phase \( g \) is given by \(^7,8\)

\[
\mathcal{P}_{\text{ex}} = \min \left( 1, \frac{N_{le}^g A^g}{(N^g + 1)A^l} \exp \left[ -\beta \left( \Delta U_{\text{ex}}^{le} + \Delta U_{\text{ex}}^g \right) \right] \right)
\]

(S10)

where \( \Delta U_{\text{ex}}^\kappa, \kappa = \{le, g\} \), is the change in the internal energy of box \( \kappa \) associated with the particle insertion for \( g \) and particle removal for \( le \) phases.

2.4 Implementation details

We considered two periodic simulation boxes each with initial dimensions as \( 50\sigma \times 50\sigma \). A total number of 500 particles are equally distributed between the two boxes. For each MC step, we perform 500 particle displacements (with the acceptance rate of \( 40 \pm 5\% \)), 10 area change and 10 particle exchange trial moves in a random order. For the first \( 5 \times 10^4 \) steps, we only perform particle displacements within the individual boxes without any area change or particle exchange moves. Subsequently, we perform \( 1.5 \times 10^5 \) full MC steps, including particle exchange and area change moves. During this interval, we monitor the densities in the two boxes to make sure they are constant (but with a different value at each box, in case of coexistence) within the statistical fluctuations. Finally, we sample equilibrium configurations once every 20 steps for the next \( 10^5 \) MC steps.

3 Density functional theory (DFT)

In this section, we discuss different building blocks of our 2D DFT approach, and the numerical methods for calculating coexistence properties, density profiles across the G-LE dividing line and the corresponding line tensions.

3.1 Chemical potential of the hard-disc fluid

To obtain an expression for the chemical potential of the hard-disc fluid, and hence its free energy, we write down the Gibbs-Duhem relation for a constant temperature process as \(^9\)

\[
d\Pi_{\text{hd}} = \rho d\mu_{\text{hd}}, \quad T = \text{cst.}
\]

(S11)

Subtracting the same equation applied to an ideal gas at the same density, multiplying by \( \beta = 1/k_B T \) and dividing by \( d\rho \) results in

\[
\frac{\partial \beta \mu_{\text{hd}}^{ex}}{\partial \rho} \bigg|_{T} = \frac{1}{\rho} \frac{\partial \beta \Pi_{\text{hd}}^{ex}}{\partial \rho} \bigg|_{T}
\]

(S12)

where \( \rho_{\text{hd}}^{ex} \) and \( \mu_{\text{hd}}^{ex} \) are excess properties of the hard-disc fluid. By using the ideal gas law and the hard-disc equation of state \(^{10}\) (Eq. 29), we obtain \( \beta \rho_{\text{hd}}^{ex} \) as

\[
\beta \Pi_{\text{hd}}^{ex}(\rho) = \beta \Pi_{\text{hd}} - \beta \Pi_{\text{hd}}^{id} = \frac{\rho}{(1-\eta)^2} - \rho, \quad \eta = \frac{\pi}{4} \rho d^2.
\]

(S13)

Integrating Eq. S12, we obtain

\[
\beta \mu_{\text{hd}}^{ex}(\rho) - \beta \mu_{\text{hd}}^{ex}(\rho_0) = \int_{\rho_0}^{\rho} \frac{1}{\eta'} \left( \frac{\partial \beta \Pi_{\text{hd}}^{ex}}{\partial \rho'} \right) \bigg|_{T} d\eta',
\]

(S14)

and by replacing Eq. S13 into this integral we get

\[
\beta \mu_{\text{hd}}^{ex}(\rho) - \beta \mu_{\text{hd}}^{ex}(\rho_0) = \left[ -\ln(1-\eta) + \frac{1}{1-\eta} - \frac{2\eta - \eta^2}{(1-\eta)^2} \right] \eta \bigg|_{\eta_0}.
\]

(S15)
In the limit where \( \rho_0 \to 0 \) (and hence \( \eta_0 \to 0 \)), the hard-disc fluid behaves like an ideal gas and \( \beta \mu_{hd}^{ex}(\rho_0) \to 0 \), therefore the excess chemical potential can be evaluated from Eq. S15 as
\[
\beta \mu_{hd}^{ex}(\rho) = -\ln(1 - \eta) + \frac{3\eta - 2\eta^2}{(1 - \eta)^2}.
\] (S16)

Finally, the full chemical potential is obtained by adding the ideal gas contribution and then reads
\[
\beta \mu_{hd}(\rho) = \beta \mu_{hd}^{ex}(\rho) + \beta \mu_{hd}^{id}(\rho) = \ln \Lambda^2 \rho - \ln(1 - \eta) + \frac{3\eta - 2\eta^2}{(1 - \eta)^2},
\] (S17)
where \( \Lambda \) is the thermal de Broglie wavelength.

### 3.2 Coefficient \( \alpha \) and disc diameter \( d \)

The coefficient \( \alpha \) is calculated as \( 21.43 \pm 0.74 \varepsilon \sigma^2 \) by using tabulated values of \( U^{\text{att}}(r) \) and carrying out the following integral by using the trapezoidal rule
\[
\alpha = -\int_0^{r_c} 2\pi r U^{\text{att}}(r) dr,
\] (S18)
with \( r_c \) from above. Similarly, \( d_{BH}(T) \) is numerically calculated from Eq. 27 by using tabulated values of the repulsive branch of the interaction potential \( U^{\text{rep}}(r) \), and its values at different temperatures are shown in Fig. S2.

![Figure S2](image)

**Figure S2** Hard disc diameter, \( d_{BH}(T) \), for 2D fluid of surfactant center-of-masses at different temperatures.

### 3.3 Coexistence properties and phase diagram

To calculate the coexisting densities \( \rho^*_g \) and \( \rho^*_l \) at given \( T \) we basically follow the procedure described earlier by us in another context. \(^{11}\) Within the region of coexistence the spinodal equation, following from Eq. 34 (etc.)
\[
\frac{d^2 f}{d\rho^2} = \frac{d\mu}{d\rho} = \frac{16k_B T (4 + \pi d^2 \rho)}{\rho (4 - \pi d^2 \rho)^3} - \alpha = 0
\] (S19)
can be solved analytically for two spinodal densities \( \rho_{spi}^g < \rho_{spi}^l \). The value for the chemical potential we are looking for must assume this value at some yet to be determined \( \rho^* \) located between the spinodal densities. Because pressures and chemical potentials are identical for the coexisting states (binodal), the desired \( \rho^* \in [\rho_{spi}^g, \rho_{spi}^l] \) has the feature – known as Maxwell’s construction – that a net area \( \Delta I \) in the \( \mu-\rho \)-diagram vanishes. More formally,
\[
\Delta I(\rho^*) \equiv I_- (\rho^*) - I_+ (\rho^*) = 0
\] (S20)
with partial areas defined by

\begin{align}
I_-(\rho^*) &= \int_0^{\rho^*} \max[0, \mu(\rho) - \mu(\rho^*)] d\rho, \\
I_+(\rho^*) &= \int_{\rho^*}^1 \max[0, \mu(\rho^*) - \mu(\rho)] d\rho.
\end{align}

(S21) (S22)

Calculating $\rho^*$ thus amounts to finding the root of a known scalar function $\Delta I(\rho^*)$ of a single variable $\rho^*$, which is computationally inexpensive. Since $I_-(\phi_{el}^{\text{spi}}) = I_+(\phi_{el}^{\text{spi}}) = 0$ and $I_-(\phi_{g}^{\text{spi}}) > 0$ and $I_+(\phi_{g}^{\text{spi}}) > 0$, there is exactly one such root $\rho^* \in [\phi_{el}^{\text{spi}}, \phi_{g}^{\text{spi}}]$. With this root $\rho^*$ at hand we know the value of the chemical potential in the coexisting phases, $\mu^* \equiv \mu(\rho^*) = \mu(\rho^*)$ for $\kappa \in \{g, le\}$, and herefrom the coexisting densities $\rho^*_\kappa$ as well. The pressures $p^*_\kappa = p(\rho^*_\kappa)$ are identical by construction, because

\begin{equation}
\Pi_g - \Pi_{le} = -f(\rho^*_g) + \rho^*_g \mu^*_g + f(\rho^*_{le}) - \rho^*_{le} \mu^*_le = \int_{\rho^*_{le}}^{\rho^*_g} \mu(\rho) d\rho - (\rho^*_g - \rho^*_{le}) \mu(\rho^*) = \Delta I(\rho^*) = 0
\end{equation}

(S23)

actually proving and hereby employing the Maxwell construction of equal areas $I_-$ and $I_+$.

### 3.4 Density profile and line tension

For a given $T$, the value of the chemical potential at coexistence, $\mu \equiv \mu^*_el = \mu^*_g$, will be used to solve Eq. 43, which we repeat here as

\begin{equation}
\mu_{\text{hd}}(\rho^{i+1}(y)) = \mu - \int dr' U^{\text{att}}(|r - r'|) \rho^i(y').
\end{equation}

(S24)

We consider a semi-infinite rectangular domain in the $xy$-plane, with a length of $y_{\text{max}} = 100\sigma$ in the $y$-direction and a very large length ($L \to \infty$) in the $x$-direction. For a spherically symmetric potential $U^{\text{att}}(r)$ with a cut-off $r_c$, Eq. S24 can be written as

\begin{equation}
\mu_{\text{hd}}(\rho^{i+1}(y)) = \mu - \int_0^{2\pi} \int_0^{r_c} r' U^{\text{att}}(r') \rho^i(y + r' \sin \theta) dr' d\theta.
\end{equation}

(S25)

We mesh the interval $[0, y_{\text{max}}]$ with 201 equally spaced grid points in the $y$-direction (and hence resolve the density profile in this region). For the regions beyond this domain, which correspond to the gas and liquid bulk phases with uniform densities, we assume

\begin{equation}
\begin{cases}
\rho(y) = \rho(0), & y < 0 \\
\rho(y) = \rho(y_{\text{max}}), & y > y_{\text{max}}.
\end{cases}
\end{equation}

(S26)

The iterations are then started by a nonuniform density profile, e.g. half of the grid points taking the value of $\rho_l$ and the other half $\rho_g$. For each grid point $y_j$, the double integral in the right-hand-side (RHS) of Eq. S25 is evaluated (by knowing $\rho^i$ profile from the previous iteration) numerically using trapezoidal method where we considered 101 grid points in the $r$-direction (to mesh the interval $[0, r_c]$) and 51 grid points in the $\theta$-direction. The values of $\mu_{\text{hd}}(\rho^{i+1}(y_j))$ are then used to solve Eq. 30 for $\rho^{i+1}(y_j)$. We continue iterations until meeting the stopping criterion as

\begin{equation}
\int_0^{y_{\text{max}}} (\rho^{i+1}(y) - \rho^i(y))^2 dy \leq 10^{-6} \int_0^{y_{\text{max}}} \rho^i(y)^2 dy,
\end{equation}

(S27)

denote the converged density profile as $\rho(y)$. We note that the convergence was achieved in our cases with roughly 7 iterations.

The grand potential, $\Omega$, we calculate using this $\rho(y)$, and performing the integral in Eq. 45 over the 2D domain as

\begin{equation}
\Omega = L \int_0^{y_{\text{max}}} [f_{\text{hd}}(\rho(y)) - \mu \rho(y)] dy + \frac{L}{2} \int_0^{y_{\text{max}}} g(y) \rho(y) dy,
\end{equation}

(S28)

where $g(y)$ is the integral on the right hand side of Eq. S25, i.e.,

\begin{equation}
g(y) = \mu - \mu_{\text{hd}}(\rho(y)).
\end{equation}

(S29)
The line tension $\gamma_{\text{line}}$ simply follows from Eq. 46 as

$$\gamma_{\text{line}} = \frac{\Omega}{L} + \Pi_{\text{max}} \tag{S30}$$

where $\Pi \equiv \Pi^e = \Pi^g$ is the pressure of the coexisting phases.

References