# Supplementary Information for: Effective Interaction Potentials for Model Amphiphilic Surfactants Adsorbed at Fluid-Fluid Interfaces.

Ahmad Moghimikheirabadi\*1, Leonard M. Sagis<sup>1,2</sup>, and Patrick Ilg<sup>3</sup>

<sup>1</sup>Polymer Physics, Department of Materials, ETH Zürich, CH-8093 Zürich, Switzerland. Fax:+41 44 632 10 76; Tel: +41 44 633 92 32; E-mail: ahmad.moghimikheirabadi@mat.ethz.ch

<sup>2</sup>Food Physics Group, Wageningen University, Bornse Weilanden 9, 6708 WG Wageningen, The Netherlands.

<sup>3</sup>School of Mathematical, Physical and Computational Sciences, University of Reading, Reading, RG6 6AX, UK.

### 1 Pressure tensor calculations

Irving and Kirkwood's definition of the tangential pressure for a planar interface, using the molecular approach is given by<sup>1</sup>:

$$P_{T}(z) = \langle \mathbf{n}_{M}(z) \rangle \mathbf{k}_{B}T$$

$$- \frac{1}{L_{x}L_{y}} \left\langle \sum_{I=1}^{N_{M}-1} \sum_{J>I}^{N_{M}} \sum_{a=1}^{\lambda(I)} \sum_{b=1}^{\lambda(J)} \frac{R_{\text{com},IJ}^{x} r_{IaJb}^{x} + R_{\text{com},IJ}^{y} r_{IaJb}^{y}}{2r_{IaJb}} u_{ab}'(r_{IaJb})$$

$$\frac{1}{\left| R_{\text{com},IJ}^{z} \right|} \theta \left( \frac{z - R_{\text{com},IJ}^{z}}{R_{\text{com},IJ}^{z}} \right) \theta \left( \frac{R_{\text{com},IJ}^{z} - z}{R_{\text{com},IJ}^{z}} \right) \right\rangle$$
(S1)

where  $n_M(z)$ ,  $N_M$  and  $\lambda(I)$  are the molecular COM number density, the number of molecules (o, w, H<sub>5</sub>T<sub>5</sub>) and number of atoms within the  $I^{\text{th}}$  molecule respectively.  $R^{\alpha}_{\text{com},IJ}$  denotes the distance between the  $J^{\text{th}}$  and  $I^{\text{th}}$  COM in the  $\alpha$  direction,  $R^{\alpha}_{\text{com},IJ} = R^{\alpha}_{\text{com},J} - R^{\alpha}_{\text{com},I}$  and  $r^{\alpha}_{IaJb}$  stands for the distance between the  $b^{\text{th}}$  atom within the  $J^{\text{th}}$  molecule and the  $a^{\text{th}}$  atom within the  $I^{\text{th}}$  molecule in the  $\alpha$  direction,  $r^{\alpha}_{IaJb} = r^{\alpha}_{Jb} - r^{\alpha}_{Ia}$ ;  $u_{ab}$  is interaction potential between atoms of type a and b (where a and b can be o, w, H, T) and  $\theta$  is the unit step function.  $P_N(z)$  can be obtained by replacing  $R^{x}_{\text{com},IJ}r^{x}_{IaJb} + R^{y}_{\text{com},IJ}r^{y}_{IaJb}$  with  $2R^{z}_{\text{com},IJ}r^{z}_{IaJb}$  in Equation (S1). In this perspective, there is no explicit contribution from intra-molecular interactions (i.e. bonded and non-bonded interaction potentials within surfactant molecules) in the pressure tensor.

Using the atomic approach, the expression for the tangential component of the pressure tensor takes the form<sup>2</sup>:

$$P_{\mathrm{T}}(z) = \langle \mathbf{n}_{A}(z) \rangle \mathbf{k}_{\mathrm{B}}T - \frac{1}{L_{x}L_{y}} \left\langle \sum_{i=1}^{N_{A}-1} \sum_{j>i}^{N_{A}} \frac{(r_{ij}^{x})^{2} + (r_{ij}^{y})^{2}}{2r_{ij}} u_{ij}'(r_{ij}) \right.$$

$$\left. \frac{1}{\left| r_{ij}^{z} \right|} \theta\left( \frac{z - r_{i}^{z}}{r_{ij}^{z}} \right) \theta\left( \frac{r_{j}^{z} - z}{r_{ij}^{z}} \right) \right\rangle$$
(S2)

where  $n_A(z)$ ,  $N_A$  and  $r_{ij}^{\alpha}$  are the atomic number density, the number of atoms (o, w and surfactant segments H, T) and the distance between the *j*<sup>th</sup> and the *i*<sup>th</sup> atoms in the  $\alpha$  direction,  $r_{ij}^{\alpha} = r_j^{\alpha} - r_i^{\alpha}$  respectively.  $P_N(z)$  can be obtained by replacing  $(r_{ij}^x)^2 + (r_{ij}^y)^2$  with  $2(r_{ij}^z)^2$  in Equation (S2). The numerical implementation of this expression is easier than Equation (S1) but one has to incorporate intra-molecular interaction contributions in the pressure tensor as well. However, for a system in equilibrium, these two routes must give the same ensemble averages<sup>3-5</sup>.

We have divided the simulation box into 500 slabs in the z direction for both number density and pressure tensor calculations. In the molecular (or atomic) approach, the molecules I and J (or the atoms i and j) contribute to the local pressure in the slab located at z, if the slab contains the line that connects them. As a consequence of using periodic boundary condition, all the pair distances have been calculated using the minimum image convention.

### 2 Force matching scheme

We approximate the forcefield **F** by assuming a central pairwise interaction potential which is only a function of the scalar distance between CG sites  $^{6-10}$ :

$$U(\mathbf{R}^{N_{\text{int}}}) = \sum_{I=1}^{N_{\text{int}}} \sum_{J>I}^{N_{\text{int}}} U_{\text{CG}}(x(\mathbf{R}_I, \mathbf{R}_J)) \quad , \quad x(\mathbf{R}_I, \mathbf{R}_J) = |\mathbf{R}_I - \mathbf{R}_J|$$
(S3)

The corresponding CG force is then

$$\mathbf{F}_{I}(\mathbf{R}^{N_{\text{int}}}) = \sum_{J=1,\neq I}^{N_{\text{int}}} F_{\text{CG}}(x(\mathbf{R}_{I}, \mathbf{R}_{J})) \frac{\mathbf{R}_{I} - \mathbf{R}_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|}$$
(S4)

where  $F_{CG}(x) = -\frac{dU_{CG}(x)}{dx}$ . Now we set a cut-off distance  $x_{cut}$  for our CG force field and mesh the interval  $[0, x_{cut}]$  into d - 1 subintervals with grid points  $\{x_i; i = 1, ..., d\}$  where  $x_1 = 0$  and  $x_d = x_{cut}$ . We consider a function space consisting of linear spline basis functions  $\{f_i; i = 1, ..., d\}$ :

$$f_i(x) = \begin{cases} \frac{x - x_{i-1}}{x_i - x_{i-1}}, & x_{i-1} < x \le x_i \\ \frac{x_{i+1} - x}{x_{i+1} - x_i}, & x_i < x \le x_{i+1} \\ 0, & \text{otherwise} \end{cases}$$
(S5)

to which  $F_{CG}(x)$  belongs through a linear relation:

$$F_{\rm CG}(x) = \sum_{i=1}^{d} \phi_i f_i(x) \tag{S6}$$

which means  $F_{CG}(x)$  is a continuous forcefield, linear within each subinterval  $[x_i, x_{i+1}]$  with the knot values  $\{\phi_i\}$  at the grid points  $\{x_i\}$ . Combining Equations (S6) and (S4) together gives a linear relation for  $\mathbf{F}_I$  in terms of the fitting parameters  $\{\phi_i\}$  i.e.

$$\mathbf{F}_{I} = \sum_{J=1,\neq I}^{N_{\text{int}}} \sum_{i=1}^{d} \phi_{i} f_{i} (|\mathbf{R}_{I} - \mathbf{R}_{J}|) \frac{\mathbf{R}_{I} - \mathbf{R}_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|} = \sum_{i=1}^{d} \phi_{i} \mathbf{a}_{iI}$$
(S7)

where

$$\mathbf{a}_{iI} = a_{iI}^{x} \hat{\mathbf{i}} + a_{iI}^{y} \hat{\mathbf{j}} = \sum_{J=1,\neq I}^{N_{\text{int}}} f_{i}(|\mathbf{R}_{I} - \mathbf{R}_{J}|) \frac{\mathbf{R}_{I} - \mathbf{R}_{J}}{|\mathbf{R}_{I} - \mathbf{R}_{J}|}$$
(S8)

can be calculated directly from the coordinates of chain COMs and the basis functions. Plugging Equation (S7) into the expression for the residual  $\chi^2(\mathbf{F})$ , gives us a relation in terms of the fitting parameters  $\{\phi_i\}$ :

$$\chi^{2}(\mathbf{F}) = \chi^{2}(\phi_{1}, ..., \phi_{d}) = \frac{1}{2N_{\text{int}}} \left\langle \sum_{I=1}^{N_{\text{int}}} |\sum_{i=1}^{d} \phi_{i} \mathbf{a}_{iI} - \mathbf{f}_{I}|^{2} \right\rangle$$

$$= \frac{1}{2N_{\text{int}}n_{t}} \sum_{t=1}^{n_{t}} \sum_{I=1}^{N_{\text{int}}} |\sum_{i=1}^{d} \phi_{i} \mathbf{a}_{iI,t} - \mathbf{f}_{I,t}|^{2}$$
(S9)

A normal solution of the least-squares problem (S9) can be determined by minimizing the residual  $\chi^2(\mathbf{F})$  with respect to the  $\{\phi_i\}$  vector, which results in a  $d \times d$  linear system of equations. The solution can also be obtained equivalently by solving an overdetermined linear system of equations of the form :

$$\begin{bmatrix} a_{11,1}^{x} & \cdots & a_{d1,1}^{x} \\ a_{11,1}^{y} & \cdots & a_{d1,1}^{y} \\ \vdots & \ddots & \vdots \\ a_{1N,n_{t}}^{x} & \cdots & a_{dN,n_{t}}^{x} \end{bmatrix} \begin{bmatrix} \phi_{1} \\ \vdots \\ \phi_{d} \end{bmatrix} = \begin{bmatrix} f_{1,1}^{x} \\ f_{1,1}^{y} \\ \vdots \\ f_{N,n_{t}}^{x} \end{bmatrix}$$
(S10)

in a least-squares sense<sup>6–10</sup>. The matrix equation (S10) ( $\mathbf{A}\Phi = \mathbf{f}$ ), is a  $2N_{\text{int}}n_t \times d$  linear system of equations formed by equalizing the total force exerted on each CG site in terms of the unknown parameters { $\phi_i$ } with the total force on the corresponding surfactant obtained from the reference simulation, projected onto the *xy*-plane.

Based on the sample size  $n_t$  (which must be sufficiently large) and the number of surfactants adsorbed at each interface plane  $N_{int}$ , storing the **A** matrix may require more than available computational memory so we approximate the solution through using a block averaging (BA) procedure<sup>7–9</sup>. In the BA procedure, the  $n_t$  reference samples are partitioned into the  $n_b$  disjoint blocks such that the **A** matrix is full rank in each block (which guarantees uniqueness of the solution  $\{\phi_i\}$  for each block). Subsequently, the matrix equation (S10) is solved for each block using the LSQR<sup>11,12</sup> algorithm (which is an iterative method for solving sparse linear equations and least squares) and the results for the  $\{\phi_i\}$  are averaged over all blocks.

After some trial and errors, the cut-off distance is set to  $x_{cut}/\sigma = 5.0$ . A non-uniform grid (92 in total) with a coarser grid mesh at near zero intermolecular separation is considered such that  $\{x_i/\sigma\} = \{0, 0.5, 0.55, \dots, 4.95, 5.0\}$ . Total number of reference configurations  $n_t = 5000$  with each block consisting of roughly 12000 equations (e.g. 500 blocks of 10 configurations each, for the case of N = 1200 surfactants) is used in our BA procedure.

The CG interaction potential is a piecewise second order polynomial spline function (with continuous first order derivatives at  $x_i$  nodes) which is calculated by integrating Eq. S6 as

$$U_{\rm CG}(x) = \int_{x}^{x_{\rm cut}} \sum_{i=1}^{d} \phi_i f_i(x') dx',$$
 (S11)

and  $U_{CG}(x) = 0$  for  $x > x_{cut}$  (no shift is needed as  $U_{CG}(x_{cut}) = 0$  by construction).

## 3 Calculation of the coarse-grained pressure

While the evaluation of the standard virial expression (second term on the right hand side of Eq. 12) is routinely done in molecular simulations, the last term in Eq 12 resulting from density-dependent effective interactions deserves special attention. For isotropic and spatially homogeneous systems, this contribution can be expressed as <sup>13,14</sup>

$$\Pi_{\rm cor}(\Gamma) = \pi \Gamma^3 \int_0^\infty rg(r) \frac{\partial U_{\rm CG}(r;\Gamma)}{\partial \Gamma} dr, \tag{S12}$$

where  $\frac{\partial U_{CG}(r;\Gamma)}{\partial \Gamma}$  is to be determined for evaluating  $\Pi_{cor}(\Gamma)$ . To this end, we fit a smooth surface to discrete data points  $\{U_{CG}(r_i,\Gamma_j)\}$  obtained from MS-CG for different surface concentrations  $\Gamma_i$ , where  $\Gamma_i \in \{0.117, 0.156, 0.195, 0.234\}$ . The surface fittings are done using MATLAB R2017b bicubic spline interpolations and the results for both symmetric and asymmetric surfactants are plotted in Fig. S1.



Figure S1 Fitted interaction potential surfaces for (a) symmetric and (b) asymmetric surfactants.

Using the fitted interaction potential surfaces,  $\frac{\partial U_{CG}(r;\Gamma)}{\partial \Gamma}$  is evaluated at different surface concentrations for both symmetric and asymmetric surfactants as depicted in Fig. S2.



**Figure S2**  $\frac{\partial U_{CG}(r;\Gamma)}{\partial \Gamma}$  for (a) symmetric and (b) asymmetric surfactants at different surface concentrations.

The results for  $\partial U_{CG}/\partial \Gamma$  are then used to calculate  $\Pi_{cor}$  by evaluating the integral on the R.H.S of the Eq. S12 numerically, as is shown in the Fig. S3.



Figure S3 Corrections to the surface pressure due to the density dependence of the CG interaction potentials.

For the last two data points (the lowest surface concentrations) in both symmetric and asymmetric cases, we have used  $\frac{\partial U_{CG}}{\partial \Gamma}$  evaluated at  $\Gamma = 0.117$  to calculate the integral in Eq. S12. Finally, we turn to the error estimation of the coarse-grained pressure. We note that the uncertainty in  $\Pi_{cor}$  is significantly larger than in the standard virial contribution since the latter can be calculated from ensemble averages during the simulation while the former requires knowledge of the concentration dependence of  $U_{CG}$  which is usually not available "on the fly". From Fig. S2, we estimate the uncertainty in  $\partial U_{CG}/\partial \Gamma$  by comparing these data to smoothed curves.

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