

Supplemental material for
“Anomalous zeta potential in foam films”

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I. SIMULATION DETAILS

The simulations were performed using LAMMPS [1]. The initial configurations were prepared using Packmol [2], and the configuration files formatted for LAMMPS using the VMD [3] Topotool plugin. The system was maintained at a temperature $T = 300$ K using a Nosé-Hoover thermostat, with damping time 200 fs, applied only to the directions perpendicular to the flow. Long-range Coulombic interactions were computed using the particle-particle particle-mesh (PPPM) method, and water molecules were held rigid using the SHAKE algorithm. The equations of motion were solved using the velocity Verlet algorithm with a timestep of 2 fs. After equilibration, on a relaxation time of 1 to 2 ns consistent with Ref. [4], production runs lasted typically 10 ns.

II. IMPROVED MODEL FOR ZETA POTENTIAL

Here we show that an *ad hoc* but very simple modification of the zeta potential model used in the main text brings the prediction in near quantitative agreement with simulation results.

The expression used in the main text is

$$\zeta = \zeta_{\text{slip}} + \zeta_{\text{no-slip}} = \frac{\Sigma b}{\varepsilon} + V(z_s). \quad (1)$$

$V(z)$ is the exact solution of the Poisson-Boltzmann (PB) equation for a single wall, and is

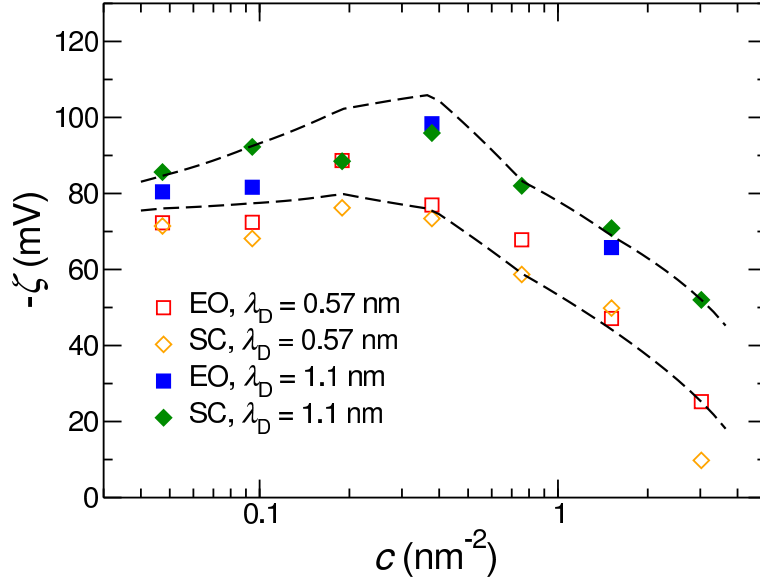


FIG. 1: Prediction of the improved model for the zeta potential (lines) compared to simulation results (points).

given by

$$\tanh\left(\frac{\phi(z)}{4}\right) = \tanh\left(\frac{\phi(0)}{4}\right) e^{-\kappa z}, \quad (2)$$

$$\phi(0) = 2 \operatorname{asinh}(2\pi l_B \lambda_D \Sigma / e), \quad (3)$$

where $\phi = eV/k_B T$ is the dimensionless potential, l_B and λ_D are the Bjerrum and Debye lengths respectively.

In the main text, we use for z_s the simulation result z_s^{sim} . Here we introduce the arbitrary assumption that $z_s = z_s^{sim} + z_s^*$, with z_s^* a free parameter. Taking $z_s^* = 0.3$ nm actually brings the predicted ζ in near quantitative agreement with simulation data, as shown in Fig. 1.

The introduction of z_s^* is *ad hoc* and lacks a straightforward physical meaning. However, we should point out that our continuum description is drastically simplified compared to the real (simulated) system. The PB equation neglects correlations, the finite-size of ions [18], and consider water as medium with a given dielectric constant. Not only may dielectric properties be non-uniform within the film, but according to the work of Refs. [5, 6] on the SDS-water films, the strongly polarized water molecules behaves very differently from an ordinary dielectric. The PB equation further assumes invariance along the lateral plane, neglecting the discrete nature of the charges, and in the present case, the possible formation of surfactant clusters. Given the very idealized continuum description, it might be necessary

to introduce some arbitrary assumption to get quantitative results. The fact that only one parameter is needed to fit the data suggests that the model, though simplified, captures the main physical effects at play.

III. ION-BINDING

To determine the fraction of bound ions θ , we rely on the fact that bound Na^+ ions are very close to the S and O atoms of the surfactant heads, and form a well separated peak in the Na-S and Na-O radial distribution functions. Therefore, we apply a simple geometric criterion on the distance between ions and S or O atoms of the surfactant heads being smaller than 0.44 nm or 0.32 nm respectively, to determine if an ion is bound. The two criterions on the Na-S and Na-O distance provide identical results within a fraction of a percent.

Among the several simulations studies that specifically consider the SDS-water system [5, 7–13], several have mentioned the high fraction of bound ions, but none have focused on the $\theta(c)$ dependence over a large range of surfactant coverage. Existing models for ion-binding (see for instance Ref. [14] and references therein) introduce several parameters, which may be difficult to justify or measure in the simulated system. Here we aim only at a phenomenological description, and we treat the binding as a simple chemical reaction. For simplicity of notations, the binding reaction $\text{Na}^+ + \text{DS}^- \rightleftharpoons \text{NaDS}$ is rewritten as $\text{I} + \text{A} \rightleftharpoons \text{B}$, where I and B refers to free and bound ions, and A to adsorption sites. The reaction constant is expressed from the activities as $K = a_B/(a_I a_A)$.

Approximating the activities by the concentration, i.e. taking an activity coefficient equal to unity, we have: $a_B = c\theta$, by definition of θ ; $a_A = c(1 - \theta)$, where each DS^- ion is assumed to be one adsorbing site for one Na^+ ion; and finally, denoting c_s the salt concentration, $a_I = c_s e^{-\phi(0)}$, since this is the concentration of Na^+ ions at the surface. Altogether this yields

$$\frac{\theta}{1 - \theta} = K c_s e^{-\phi(0)}, \quad (4)$$

where the surface potential $\phi(0)$ is

$$\phi(0) = -2 \operatorname{asinh} [2\pi l_B \lambda_D c(1 - \theta)],$$

that is Eq. (3) with $\Sigma/e = -c(1 - \theta)$. Solving the equation numerically and fitting the simulation data in log-linear scale gives a rather poor fit (not shown).

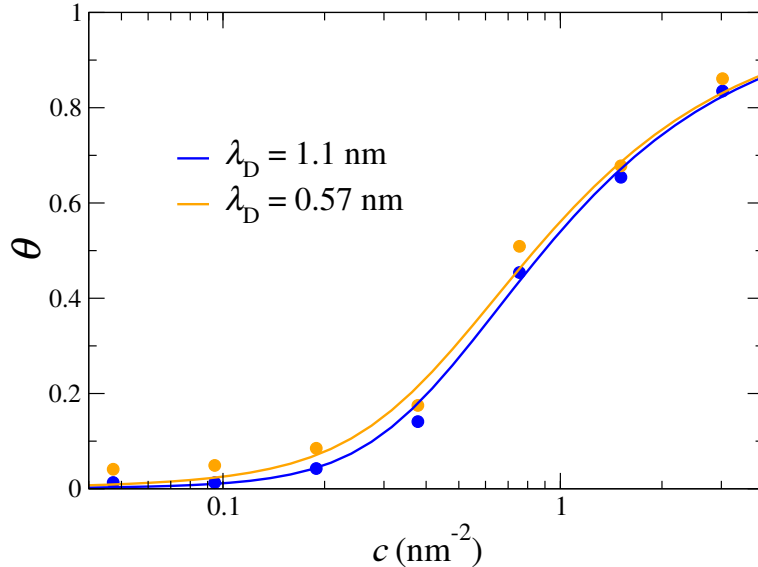


FIG. 2: Fraction of bound ions θ as function of surfactant coverage c . Points are simulation data. See text for fit.

The model above assumes that each DS^- head is an adsorption site. However, there are several hints that adsorption sites for Na^+ may actually involve more than one surfactant head. Reference [15], which simulates a whole SDS micelle, points out that a significant amount (23%) of sodium ions are “bridging”, that is, in contact with two heads groups. Reference [16], which examines MD simulations of a CTAB monolayers, concludes that the “counter-ions are shared by the head-groups”. Finally, from visual inspection of configurations, it appears plausible that an adsorption site is not a single, isolated, head, but the space between two neighboring heads, with the ion bridging between the two. One may then assume that, at low enough concentration, the total number of adsorption sites is proportional to c^2 , rather than to c [19]. Assuming further that one of the head should be unoccupied –that is empty, with no ion adsorbed already– leads to

$$a_A = (1 - \theta)c^2/c_1, \quad (5)$$

where c_1 is a constant that can be absorbed in the reaction constant K . As shown in Fig. 2, the $\theta(c)$ dependence is now well captured, with the same reaction constant $K = 1.00$ for both Debye lengths. The second model thus provides a satisfactory description of the ion-binding fraction, while introducing only one free parameter.

IV. SHIFT OF THE SHEAR PLANE

As discussed in the main text, the evolution of the slip length with the surfactant coverage, $b \propto c^{-1}$, can be rationalized with a simple argument. Can we understand in a similar way the shift in shear plane position z_s ?

For the sake of simplicity [20], the surfactant heads are modeled as an array of cylindrical pillars with height h and number density c (per unit area). Working with the average velocity profile $v(z)$, the total viscous dissipation per unit surface \mathcal{D} is given by

$$\frac{\mathcal{D}}{\eta} = \int_0^\infty dz [v'(z)]^2 + c \int_0^h dz \xi v^2(z), \quad (6)$$

where ξ is a dimensionless friction coefficient quantifying dissipation due to one pillar. Now, for a square array of infinite cylindrical pillars, ξ is given by [17]

$$\frac{4\pi}{\xi(\phi)} = -\frac{1}{2} \log \phi - 0.738 + \phi - 0.887 \phi^2 + 2.039 \phi^3 + O(\phi^4). \quad (7)$$

Here, $\phi = c/c_{max}$ is the surface fraction covered by the pillars (i.e., the surfactants). This expression is reasonable for $\phi \lesssim 0.3$. While Eq. (7) is valid for a flow invariant in the z -direction, we have assumed, for lack of a better approximation, that it holds locally in each layer of thickness dz . Now, minimizing the dissipation yields

$$z \geq h, \quad v_2''(z) = 0, \quad (8)$$

$$z \leq h, \quad v_1''(z) + \frac{v_1(z)}{\lambda^2} = 0, \quad \lambda^2 = \frac{1}{c\xi}. \quad (9)$$

Using the boundary conditions

$$\begin{aligned} v_1'(0) = 0, \quad v_1'(h) = v_2'(h), \quad v_2'(\infty) = \dot{\gamma}, \\ v_1(h) = v_2(h), \end{aligned} \quad (10)$$

one obtains

$$v_1(z) = \lambda \dot{\gamma} \frac{\cosh(z/\lambda)}{\sinh(h/\lambda)}, \quad (11)$$

$$v_2(z) = \dot{\gamma}(z-h) + \frac{\lambda \dot{\gamma}}{\tanh(h/\lambda)}. \quad (12)$$

Since the slip velocity is $v_s = v_1(0)$, the slip length $b = v_s/\dot{\gamma}$ is

$$b = \frac{1}{h c \xi(c)}. \quad (13)$$

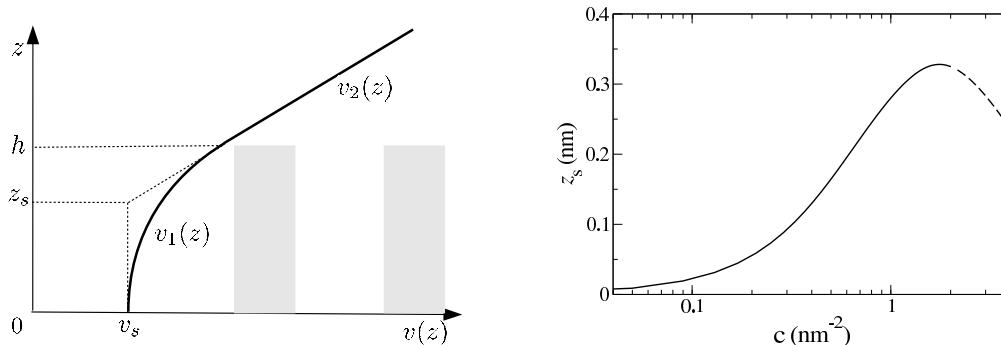


FIG. 3: (Left) Schematic of the velocity profile $v(z)$. (Right) Shear plane position z_s as a function of surfactant density c . The decrease at high c is due to the breakdown of Eq. (7).

So at lowest order, this approach would predict logarithmic correction to the $b \propto c^{-1}$ behavior.

Now, what is the shear plane position z_s ? Defining z_s through $v_1(0) = v_2(z_s)$ as in Fig. 3 yields

$$\frac{z_s}{h} = g(u), \quad g(u) = 1 - \frac{\text{cotanh}(u) - \text{csch}(u)}{u}, \quad u = h\sqrt{c\xi}. \quad (14)$$

Upon increasing u (or the coverage c), the function $g(u)$ increases steadily from $1/2$ to 1 , with most of the change taking place for u in the interval $[1, 20]$. Now, taking $c_{max} = 4 \text{ nm}^{-2}$ and $h = 0.8 \text{ nm}$ [21], one finds that in the range of interest $c \in [0.05, 1] \text{ nm}^{-2}$, u covers the interval $[1, 10]$. We can therefore expect significant variation in the function $z_s(c)$, which is plotted in Fig. 3, taking the origin at the middle height of the pillars. It turns out that i) z_s is located at half-height at low concentration. ii) z_s shifts by a few Å's upon increasing c from 0.1 to 1. Both predictions of the simple model are in qualitative agreement with simulation data.

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- [18] Ions are assumed point-like, whereas their radius is around 0.1 nm, which is comparable to the shift in shear plane position.
- [19] Here we assume that the surfactant heads are placed at random, so at low enough concentration, the number of pairs of neighboring heads roughly grows as c^2 .
- [20] Whereas for the slip dependence, surfactant heads were modeled as half-spheres, here they are considered as cylindrical pillars. In both cases, we chose the simplest geometry that provides a qualitative understanding.
- [21] The width at half-height of surfactant distribution.