

Supplementary Materials

Method

In studies on aqueous films, the thin film balance (TFB) of Scheludko [1, 2] is widely applied for a detailed study of film stability (e.g. lifetime, film thickness) and disjoining pressure. The experiment usually consists of a Scheludko cell for producing foam films with a gas-tight micro syringe pump. A representation of the experimental microinterferometric setup and the part that the MD simulation tries to reproduce are shown in Figure S1.

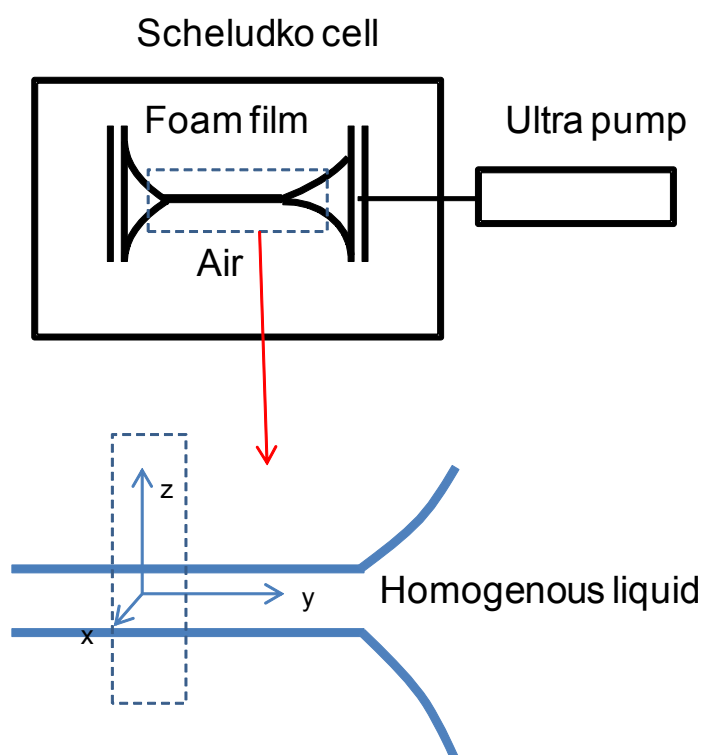


Figure S1 Schematic of the experimental setup for thin aqueous film experiments and the molecular simulation part; the homogenous part was not included in MD.

The MD simulations in this work cover only the film as indicated by the dotted box and arrows; the meniscus is not included in the simulation. The disjoining pressure is the pressure difference between the homogenous liquid and normal pressure of the thin film. The thin liquid film is surrounded by vapor and the liquid/vapor interface is perpendicular to the z -axis. When the thickness increases to a large enough value, e.g. around 5 nm, it is regarded as a thick film (solution with interfaces).

Within the liquid film, the change in the Gibbs free energy of the film is expressed as [3]:

$$d(F^f + P^\beta V^f) = -S^f dT + Ah dP^\beta + 2\sigma_f dA - \Pi A dh + \sum_i \mu_i dN_i^f \quad (1)$$

where F^f is the Helmholtz free energy of the film, P^β is the pressure of the phase surrounding the film, $V^f = Ah$ = volume of the film, A is the cross sectional area of the film, h is the film thickness, S^f is entropy of the film, σ_f is the surface tension of the film, μ_i is the chemical potential of the i^{th} component and N_i^f is mole number of component i . From the above equation, an equation within the film is derived [3-5] as:

$$\gamma_f = 2\sigma_\infty + \int_h^\infty \Pi dh' + \Pi h \quad (2)$$

where γ_f is thin film tension, which is related to surface tension of the film and disjoining pressure shown in equation (3), σ_∞ is surface tension for an infinitely thick film, Π is the disjoining pressure, and h is the film thickness.

From the above equation (2), Π still cannot be obtained, since we cannot determine the film tension and the term $\int_h^\infty \Pi dh'$ shown in equation (2) by MD. So another equation [3-6] was applied as:

$$\gamma_f = 2\sigma_f + \Pi h \quad (3)$$

where σ_f is the surface tension of the thin film. From equations (2) and (3) we can see:

$$\gamma_f = 2\sigma_\infty + \int_h^\infty \Pi dh' + \Pi h = 2\sigma_f + \Pi h \quad (4)$$

From equation (4) we can obtain

$$\int_h^\infty \Pi dh' = 2\sigma_f - 2\sigma_\infty \quad (5)$$

$$\Pi = -\frac{\int_h^\infty \Pi dh'}{dh} = -\left(\frac{2\sigma_f - 2\sigma_\infty}{dh}\right) = -(2\sigma_f - 2\sigma_\infty)'_h = -(2\sigma_f)'_h \quad (6)$$

To clearly show the surface force relationship between equations 3 and 4, an illustration of force balance exerted on the film is plotted in Figure S2. The surface tension of the film cannot be measured experimentally, but the film tension and the surface tension of the solution can be measured experimentally, so it is feasible to study a surfactant stabilized film by determining the film tension and Π . However, for water films (surfactant-free films with and without electrolyte), it is not possible to measure the film tension and Π with ease as the surfactant-free films are unstable and have low elasticity. This makes experimental measurements difficult.

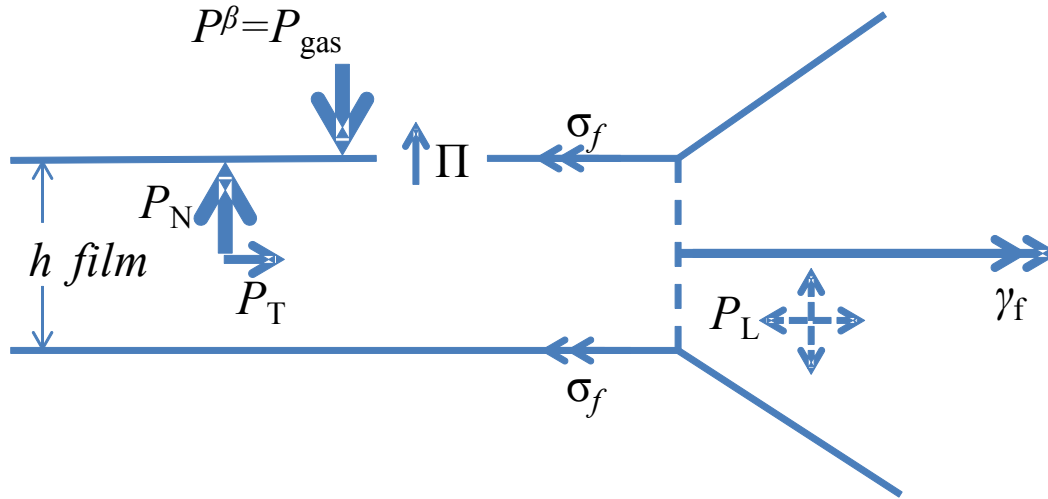


Figure S2 The force balance with of free thin film, showing the corresponding terms in equations 2-6. P_L is pressure in homogeneous liquid. P_N and P_T are the normal and tangential pressure tensors, respectively.

Equation (5) is equal to the interaction energy of a film, which is a significant and valuable property in colloid and surface science [3-5], from which Π - h can be derived.

A slab geometry was employed for thin films. The size of the box was set to $L_x = L_y$ and $L_z = 3 L_x$ with the film lateral dimension ($L_x = L_y$) being the reported box size. The film was centered on the box's z -dimension with the two surfaces perpendicular to the z -axis. In order to obtain the initial configuration of the salt film,

isothermal-isobaric (NPT) ensemble was first performed on bulk to give the correct density. At the density obtained from the NPT ensemble, a bulk NVT (canonical ensemble) simulation was carried out. After running NVT in the bulk, two boxes were added to form interfaces. NVT simulations were then executed to simulate the aqueous-vapor thin NaCl films. A diagram in Figure S3 is shown for illustration. Surface tension is calculated using the pressure tensor approach [7-9] within GROMACS software package 4.5.3 by

$$\sigma_f = \frac{1}{2} L_z \left[\langle P_{zz} \rangle - \frac{1}{2} (\langle P_{xx} \rangle + \langle P_{yy} \rangle) \right] \quad (7)$$

where L_z is the length of the simulation cell and $P_{\alpha\alpha}$ ($\alpha = x, y, z$) are the diagonal components of the pressure tensor. The factor 0.5 outside the squared brackets takes into account as the system has two interfaces, it was checked that the average values of P_{xx} and P_{yy} were the same within the simulation error.

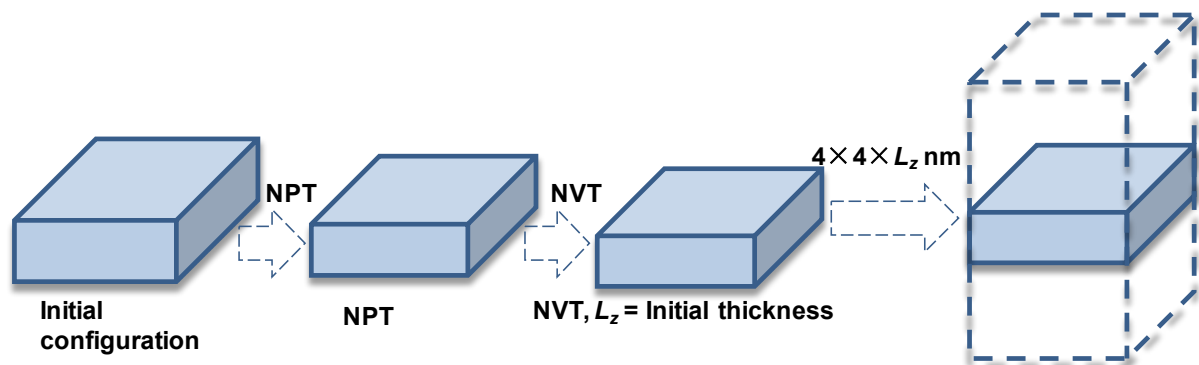


Figure S3 Procedures to build the film configuration, the thickness is initial thickness in the NVT stage.

The number of ion and water molecules, as well as σ_f in each thickness are listed in Table S1 (1.98M NaCl) and Table S2 (0.66M NaCl).

Table S1 σ_f (mN/m) in 1.98 M at different thicknesses and temperatures. Blank cells indicate no stable film at that thickness and temperature. 3 repeats were applied at each thickness.

Water	Ion pairs	Thickness (nm)	σ_f 300 K	σ_f 379 K	σ_f 479 K
988	38	1.286	64.69 \pm 0.10		
1014	39	1.320	64.67 \pm 0.06		
1040	40	1.354	64.58 \pm 0.23		
1066	41	1.388	64.54 \pm 0.18	51.62 \pm 0.11	
1092	42	1.421	64.41 \pm 0.13	51.61 \pm 0.09	28.16 \pm 0.36
1118	43	1.455	64.26 \pm 0.11	51.53 \pm 0.09	31.83 \pm 0.62
1144	44	1.489	64.20 \pm 0.10	51.52 \pm 0.10	32.64 \pm 0.13
1196	46	1.557	64.10 \pm 0.16	51.41 \pm 0.14	33.13 \pm 0.03
1300	50	1.692	63.98 \pm 0.05	51.17 \pm 0.06	33.09 \pm 0.07
1378	53	1.794	63.72 \pm 0.12	50.94 \pm 0.10	32.76 \pm 0.07
1482	57	1.929	63.48 \pm 0.09	50.74 \pm 0.09	32.50 \pm 0.12
1742	67	2.267	63.04 \pm 0.23	50.49 \pm 0.06	32.18 \pm 0.07
2002	77	2.606	62.78 \pm 0.20	50.14 \pm 0.23	31.83 \pm 0.14
2262	87	2.944	62.63 \pm 0.33	50.09 \pm 0.15	31.57 \pm 0.17

Table S2 σ_f in 0.66M at different temperatures, at least 4 repeats were applied at each thickness.

Water	Ion pairs	Thickness (nm)	σ_f 300 K	σ_f 379 K	σ_f 479 K
1148	14	1.430	61.15 \pm 0.18	48.40 \pm 0.09	28.30 \pm 0.39
1230	15	1.532	61.04 \pm 0.04	48.28 \pm 0.06	29.57 \pm 0.03
1312	16	1.635	61.01 \pm 0.16	48.30 \pm 0.09	29.68 \pm 0.12
1394	17	1.737	60.96 \pm 0.18	48.27 \pm 0.10	29.59 \pm 0.10
1476	18	1.839	60.92 \pm 0.18	48.20 \pm 0.12	29.59 \pm 0.06
1558	19	1.941	60.86 \pm 0.12	48.18 \pm 0.20	29.51 \pm 0.12
1640	20	2.043	60.84 \pm 0.13	48.02 \pm 0.13	29.42 \pm 0.04
1722	21	2.145	60.82 \pm 0.21	48.08 \pm 0.07	29.40 \pm 0.11
1804	22	2.248	60.74 \pm 0.15	47.98 \pm 0.12	29.43 \pm 0.08
1968	24	2.452	60.71 \pm 0.07	47.94 \pm 0.07	29.20 \pm 0.08
2132	26	2.656	60.68 \pm 0.30	47.88 \pm 0.10	29.14 \pm 0.05
2378	29	2.963	60.67 \pm 0.11	47.84 \pm 0.19	28.97 \pm 0.07

1. Scheludko, A. and D. Exerowa, *Über den elektrostatischen Druck in Schaumfilmen aus wässrigen Elektrolytlösungen*. Kolloid-Zeitschrift, 1959. **165**(2): p. 148-151.
2. Mysels, K.J., *Soap Films and Some Problems in Surface and Colloid Chemistry*. Christenson, H. K., 1964. **68**(12): p. 3441-3448.

3. Eriksson, J.C. and B.V. Toshev, *Disjoining pressure in soap film thermodynamics*. Colloids and Surfaces, 1982. **5**(3): p. 241-264.
4. Ivanov, I., *Thin liquid films*. Vol. 29. 1988: CRC Press.
5. Ivanov, I. and B. Toshev, *Thermodynamics of thin liquid films*. Colloid And Polymer Science, 1975. **253**(7): p. 593-599.
6. Wang, L., *Surface forces in foam films*. 2006, Virginia Polytechnic Institute and State University.
7. Brown, D. and S. Neyertz, *A general pressure tensor calculation for molecular dynamics simulations*. Molecular Physics, 1995. **84**(3): p. 577-595.
8. LÓPez-Lemus, J. and J. Alejandre, *Thermodynamic and transport properties of simple fluids using lattice sums: bulk phases and liquid-vapour interface*. Molecular Physics, 2002. **100**(18): p. 2983-2992.
9. WANG, J. and X.C. ZENG, *COMPUTER SIMULATION OF LIQUID-VAPOR INTERFACIAL TENSION: LENNARD-JONES FLUID AND WATER REVISITED*. Journal of Theoretical and Computational Chemistry, 2009. **08**(04): p. 733-763.