Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Materials for Can Bulk Nanobubbles be Stabilized by Electrostatic Interaction

Derivation of Equation (2), applicable conditions and its other forms

We use the notations and models in the main text. We consider a spherical bubble with radius R suspended in aqueous gas solution, whose center is located at the origin O. Some charges are adsorbed at gas/water interface, with a uniform surface density of σ. The concentration of the electrolyte (A^+B^-) in the bulk solution is c_0. We will calculate the diffusive part contribution to the pressure, as the first term in Equation (2).

The ion distribution in the diffusive layer is governed by the Boltzmann distribution,

$$c^+(r) = c_0 exp[-\frac{e\phi(r)}{k_B T}]$$

$$c^-(r) = c_0 exp[\frac{e\phi(r)}{k_B T}] \quad \text{(s1)}$$

The electrical potential near the bubble is given by the Poisson Boltzmann Equation,

$$\nabla^2\phi(r) = \frac{2Fc_0}{\epsilon_0\epsilon_r} sinh[\frac{e\phi(r)}{k_B T}] \quad \text{(s2)}$$

The pressure field in the solution is governed by the hydrostatic equation,

$$\nabla P = -\nabla\phi(r)(c^+ - c^-)F \quad \text{(s3)}$$

where the term on the right-hand side of the above equation is the body force due to the electrostatic interaction. Integration of Equation (s3) gives,

$$\Pi_1 = \int_R^{+\infty} dr\, \nabla\phi c_0 \{\exp\left[-\frac{e\phi(r)}{k_B T}\right] - exp[\frac{e\phi(r)}{k_B T}]\}F \quad \text{(s4)}$$

By substitution the variable r to ϕ, we get,

$$\Pi_1 = 2k_B T c_0 N_a [\cosh\left(\frac{e\phi_0}{k_B T}\right) - 1] \quad \text{(s5)}$$

Where ϕ_0 is the potential at the bubble surface.

Note that Equation (s5) is valid for any curved surface, as long as the Poisson Boltzmann Equation is valid.

We can further rewrite Equation (s5) as,

$$\Pi_1 = N_a k_B T[\left(c^+(R) - c_0\right) + (c^-(R) - c_0)] \quad \text{(s6)}$$

Equation (s6) is also known as contact value theorem: the pressure caused by the double-layer is determined by the ion concentration at the surface under equilibrium condition, which can be extended to the case of the presence of multiple electrolytes in the solution.