

Surface Pressure of Liquid Interfaces Laden with Micron-Sized Particles Electronic Supplementary Information

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THEORY

Surface pressure: derivation in canonical ensemble

In the main text, we obtained an expression for the surface pressure Π , in two dimensions, via an analogy with the osmotic pressure of a suspension in three dimensions. Here, we derive an expression for the surface pressure of a particle-laden interface in the canonical ensemble, starting from the (canonical) free energy F of the particle-laden interface.

In analogy with the derivation for the surface tension of surfactant solutions [1], we start with the following expression for particles at liquid interfaces:

$$F(A, T, N) = Af(T, N) , \quad (1)$$

where F is the (canonical) free energy of the interface, A the area of the interface available to the particles, T the temperature and N the number of interfacial particles. Note that $f(T, N)$ is a free-energy density, i.e. free energy per unit area, so it is counter-intuitive that it depends on the total number of interfacial particles N . This inconsistency stems from N being an extensive variable, whereas T and the chemical potential μ (the variables of the free-energy density in the grand-canonical ensemble) are both intensive variables. An intensive variable related to N is the particle number density:

$$\rho = \frac{N}{A} , \quad (2)$$

so we suggest:

$$F(A, T, N) = Af(T, \rho) . \quad (3)$$

For the full differential of the canonical free energy, we can write [1, 2]:

$$dF = \gamma dA - SdT + \mu dN . \quad (4)$$

From equation (3), we obtain:

$$\begin{aligned} dF &= f dA + A df \\ &= f dA + A \left(\frac{\partial f}{\partial T} \right)_{A, \rho} dT + \\ &+ A \left(\frac{\partial f}{\partial \rho} \right)_{A, T} d\rho . \end{aligned} \quad (5)$$

To compare terms in equations (4) and (5) like for like, we have to write $d\rho$ in terms of dN and dA :

$$\begin{aligned} d\rho &= \left(\frac{\partial \rho}{\partial N} \right)_{A, T} dN + \left(\frac{\partial \rho}{\partial A} \right)_{N, T} dA \\ &= \frac{dN}{A} - \frac{\rho dA}{A} . \end{aligned} \quad (6)$$

Substituting equation (6) into equation (5), we get:

$$\begin{aligned} dF &= f dA + A \left(\frac{\partial f}{\partial T} \right)_{A, \rho} dT \\ &+ A \left(\frac{\partial f}{\partial \rho} \right)_{A, T} \left(\frac{dN}{A} - \frac{\rho dA}{A} \right) \\ &= \left(f - \rho \left(\frac{\partial f}{\partial \rho} \right)_{A, T} \right) dA + A \left(\frac{\partial f}{\partial T} \right)_{A, \rho} dT \\ &+ \left(\frac{\partial f}{\partial \rho} \right)_{A, T} dN . \end{aligned} \quad (7)$$

Now, we can compare terms like for like between equations (4) and (7), resulting in:

$$\begin{aligned} \left(\frac{\partial f}{\partial T} \right)_{A, \rho} &= -\frac{S}{A} \\ \left(\frac{\partial f}{\partial \rho} \right)_{A, T} &= \mu = \left(\frac{\partial F}{\partial N} \right)_{A, T} \\ \gamma &= f - \rho \left(\frac{\partial f}{\partial \rho} \right)_{A, T} , \end{aligned} \quad (8)$$

where the right-hand side of the second row employs the definition of chemical potential in the canonical ensemble [2]. Combining rows 2 and 3 of equation (8), we get an expression for the effective interfacial tension γ of a colloid-laden interface in the canonical ensemble:

$$\gamma = f - \rho \mu . \quad (9)$$

Typically, we are interested in the surface pressure of the colloid-laden interface, which in the canonical ensemble is then:

$$\Pi = \gamma_0 - \gamma = \gamma_0 - f + \rho \mu . \quad (10)$$

Note that equation (10) here is equivalent to equation (5) in the main text.

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- [1] M. Doi, in *Soft Matter Physics* (Oxford University Press, Oxford, 2015) Chap. 4, pp. 51 – 73.
- [2] C. Kittel and H. Kroemer, *Thermal Physics* (W. H. Freeman and Company, New York, 1999).