1 Area Compressibility

In thermodynamics, the volume compressibility is defined via its inverse, the volume susceptibility, by

$$\chi_V \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{1}$$

where $\chi_V = 1/K_V$. Analogously, one may define the area compressibility modulus via

$$\chi_A \equiv \frac{1}{A}\left(\frac{\partial A}{\partial \gamma}\right)_T, \tag{2}$$

where $\chi_A = 1/K_A$. There is no negative sign in this definition because positive surface tension means the system is being pulled, which is opposite of how pressure is conceived; positive pressure means the system is compressed. Inverting the above equation, we get

$$K_A = A\left(\frac{\partial \gamma}{\partial A}\right)_T = \left(\frac{\partial \gamma}{\partial (\ln A)}\right)_T. \tag{3}$$

When K_A is considered to be a spring constant in a harmonic potential, one can postulate the free energy, $F(A)$, to be

$$F(A) = \frac{1}{2}K_A\frac{(A-A_0)^2}{A_0}, \tag{4}$$

where A_0 is the free energy minimum. The denominator in the above equation is to have the right dimension. The surface tension, γ, can be defined as

$$\gamma \equiv \left(\frac{\partial F}{\partial A}\right)_T. \tag{5}$$

From Eq. and Eq. , $\gamma = K_A(A-A_0)/A_0$ and one arrives at

$$K_A = A_0\left(\frac{\partial \gamma}{\partial A}\right)_T, \tag{6}$$

which is the definition of K_A that has been used by many literatures. When one attempts to obtain K_A from MD simulations, there is an ambiguity in the value of A_0: whether the experimentally measured value should be used or the

value from MD simulations. If latter, how does one determine A_0 is another question since often electron density profile from MD simulation does not agree with the experimentally determined one. If surface tension is applied to achieve a good match between the experimental and simulation form factors, one could consider using that value as A_0. Including the experimentally determined value, then, one has three choices.

The thermodynamically motivated definition of K_A does not come with the above described issue. It seems that when deviation from the free energy minimum is large, this definition of K_A is more appropriate: the harmonic potential approximation would fail away from the minimum.