Surface Tension

1. *Capillary forces:* Thermodynamic properties of the interface between two phases are described by a state function called the surface tension $\mathcal{S}$. It is defined in terms of the work required to increase the surface area by an amount dA through $dW = \mathcal{S}dA$.

(a) By considering the work done against surface tension in an infinitesimal change in radius, show that the pressure inside a spherical drop of water of radius R is larger than atmospheric pressure by $2\mathcal{S}/R$. What is the air pressure inside a soap bubble of radius R?

(b) A water droplet condenses on a solid surface. There are three surface tensions involved $\mathcal{S}_{aw}$, $\mathcal{S}_{sw}$, and $\mathcal{S}_{sa}$, where a, s, and w refer to air, solid and water respectively. Calculate the angle of contact, and find the condition for the appearance of a water film (complete wetting).

(c) In the realm of "large" bodies gravity is the dominant force, while at "small" distances surface tension effects are all important. At room temperature, the surface tension of water is $\mathcal{S}_o \approx 7 \times 10^{-2} Nm^{-1}$. Estimate the typical length-scale that separates "large" and "small" behaviors. Give a couple of examples for where this length-scale is important.

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2. *Surfactants:* Surfactant molecules such as those in soap or shampoo prefer to spread on the air-water surface rather than dissolve in water. To see this, float a hair on the surface of water and gently touch the water in its vicinity with a piece of soap. (This is also why a piece of soap can power a toy paper boat.)

(a) The air-water surface tension $\mathcal{S}_o$ (assumed to be temperature independent) is reduced roughly by Nk_BT/A, where N is the number of surfactant particles, and A is the area. Explain this result qualitatively.

(b) Place a drop of water on a clean surface. Observe what happens to the air-water-surface contact angle as you gently touch the droplet surface with a small piece of soap, and explain the observation.

(c) More careful observations show that at higher surfactant densities

$$\frac{\partial \mathcal{S}}{\partial A}\bigg|_T = \frac{Nk_BT}{(A - Nb)^2} - \frac{2a}{A}\left(\frac{N}{A}\right)^2 \quad, \quad \text{and} \quad \frac{\partial T}{\partial \mathcal{S}}\bigg|_A = -\frac{A - Nb}{Nk_B};$$

where a and b are constants. Obtain the expression for $\mathcal{S}(A, T)$ and explain qualitatively the origin of the corrections described by a and b.

(d) (Optional) Find an expression for $C_{\mathcal{S}} - C_A$ in terms of $\frac{\partial E}{\partial A}\big|_T$, $\mathcal{S}$, $\frac{\partial \mathcal{S}}{\partial A}\big|_T$, and $\frac{\partial T}{\partial \mathcal{S}}\big|_A$.

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Suggested Reading: Landau & Lifshitz, Chapter XV; Huang, Chapter 2.