Master φCS 2017-2018

SOFT MATTER

PRACTICES 4

Thermal fluctuations of surfaces and membranes

Equilibrium configuration of a two-dimensional bubble

For a bubble with low surface energy, thermal fluctuations can alter the bubble shape, as sketched in Fig. 1. For simplicity, we will consider a "two-dimensional" bubble; this may correspond to a bubble squeezed between two parallel plates. The surrounding gas is at constant pressure P_0 and constant temperature T. We assume that the inside gas and the outside gas are the same. We note 2γ the surface tension of the liquid film (the prefactor 2 takes the two liquid-gas interfaces into account), and h the height between the two parallel plates. We use a coarse-grained description in

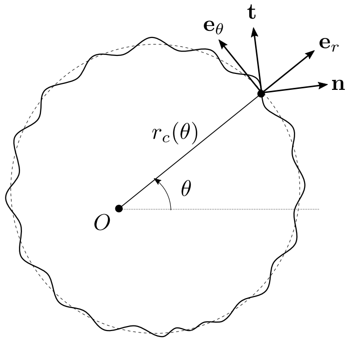

Figure 1: Thermal fluctuations of a small two-dimensional bubble.

which every microstate L of the bubble corresponds to a given contour $\mathbf{r}(s)$ of the bubble, where s represents the curvilinear coordinate along the contour: $L \equiv (T, P_0, \{\mathbf{r}(s)\})$. We define the partial free enthalpy (or partial Gibbs free energy) of the bubble G_L through:

$$e^{-\beta G_L} = \sum_{\{\lambda | \mathbf{r}_\lambda(s) = \mathbf{r}(s)\}} e^{-\beta(E_\lambda + P_0 h A_\lambda)},$$

where the sum is carried over all the fine-grained microstates λ that are compatible with the given contour of the bubble (in a classic description, λ may correspond to the position and momentum of all the molecules of the encapsulated gas and those of the liquid film). E_λ and A_λ are the corresponding energy and surface area of the bubble.

In the following, we want to derive a tractable expression for G_L. We suppose that fluctuations are slow enough so that γ is constant, and the inside gas is always at equilibrium, and we note P_L the uniform pressure inside the bubble in microstate L.

1. Justify that G_L does not explicitly depend on the details of the bubble contour, but only on the bubble surface area A and perimeter $\mathcal{L}$.
2. We note $G_L^{(f)}(T, P_0; \mathcal{L})$ and $G_L^{(g)}(T, P_0; A)$ the partial free enthalpy of the liquid film and of the inside gas, respectively: $G_L = G_L^{(f)} + G_L^{(g)}$, with $G_L^{(f)} = 2\gamma h \mathcal{L}$. Show that

$$P_L - P_0 = -\frac{1}{h}\left(\frac{\partial G_L^{(g)}}{\partial A}\right)_{T,P_0}.$$

3. Let A_0 be the area that the encapsulated gas would occupy for its pressure to be equal to the surrounding pressure P_0. Show that for small values of $P_L - P_0$, G_L can then be expanded as:
$$G_L \simeq G_0 + 2\gamma h\mathcal{L} + \frac{B(T,P_0)h}{2}\frac{(A-A_0)^2}{A_0}, \tag{1}$$
and give the physical interpretation of G_0.

4. Calculate $P_L - P_0$. What is the physical meaning of $B(T,P_0)$?

We now want to determine the average bubble configuration.

5. Justify that the average bubble configuration is obtained by looking for the contour that minimizes the partial free enthalpy [Eq. (1)].

6. To describe the bubble contour, we use the polar parametrization $\theta \mapsto r_c(\theta)$, as shown in Fig. 1. The origin O can be any point within the bubble. Does this parametrization allow to consider all possible configurations of the contour ?

7. Let $\mathrm{d}s$ be the length of an elementary piece of the contour. Express $\mathrm{d}s/\mathrm{d}\theta$ in terms of $r_c(\theta)$ and its derivative $\dot{r}_c(\theta)$.

8. Deduce the integral expression for the partial free enthalpy of the liquid film $G_L^{(f)} = 2\gamma h\mathcal{L}$.

9. We admit that the area of the bubble is $A = \oint r_c^2(\theta)\mathrm{d}\theta/2$. Show that the change of partial free enthalpy [Eq. (1)] associated with the elementary change of contour $r_c(\theta) \to r_c(\theta) + \delta r_c(\theta)$ can be written:
$$\delta G = \oint f(r_c,\dot{r}_c)\delta r_c(\theta)\mathrm{d}\theta + \oint g(r_c,\dot{r}_c)\delta\dot{r}_c(\theta)\mathrm{d}\theta, \tag{2}$$
where functions f and g have to be expressed.

10. What is the relation between $\delta r_c(\theta)$ and $\delta\dot{r}_c(\theta)$? Using integration by parts on the second integral, finally show that the contour that extremizes the partial free enthalpy is given by:
$$2\gamma\left[\frac{1}{(r_c^2+\dot{r}_c^2)^{1/2}} - \frac{1}{r_c}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\dot{r}_c(r_c^2+\dot{r}_c^2)^{-1/2}\right)\right] + B\frac{A-A_0}{A_0} = 0. \tag{3}$$

11. To interpret this equation, it is useful to introduce the local curvature $\kappa(\theta)$ of the contour, defined through:
$$\frac{\mathrm{d}\mathbf{t}}{\mathrm{d}s} = -\kappa(\theta)\mathbf{n},$$
where $\mathbf{t} = \frac{\mathrm{d}\mathbf{r}}{\mathrm{d}s}$ and $\mathbf{n}$ are the unit vectors locally tangent and normal to the contour respectively, as depicted in Fig. 1. Express the components of $\mathbf{t}$, $\frac{\mathrm{d}\mathbf{t}}{\mathrm{d}s}$ and $\mathbf{n}$ on the polar vector basis $(\mathbf{e}_r, \mathbf{e}_\theta)$, and show that the local curvature is given:
$$\kappa(\theta) = (r_c^2+\dot{r}_c^2)^{-1/2} - \frac{1}{r_c}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\dot{r}_c(r_c^2+\dot{r}_c^2)^{-1/2}\right).$$

12. Rewrite Eq. (3) by introducing $\kappa(\theta)$. How is called the obtained relation ? What is the average shape of the bubble ?

13. Without doing all the calculations, what would have changed in Eq. (3) if, instead of taking the contribution of the compressive term into account in the partial free enthalpy, we would have consider that the inside gas was incompressible (*i.e.* A = constant) ?