Advanced Statistical Physics – CORRECTION OF THE JANUARY 2024 EXAM

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2 Wetting transition

The substrate is at $z = 0$ and the fluid with density $n(z)$ above. The grand potential is

$$g_f[n(z)] = \int_0^\infty \mathrm{d}z \left[\frac{1}{2} B \left[\partial_z n(z) \right]^2 + W(n(z)) \right] , \tag{1}$$

Additionally there is a surface term (interaction between the substrate and the fluid) :

$$g_s(n_s) = a_0 - a_1 \frac{n_s}{n_l - n_v} + \frac{1}{2} a_2 \frac{n_s^2}{(n_l - n_v)^2} + \dots \tag{2}$$

where $n_s = n(z = 0)$ is the density of the fluid at the solid surface.

1/ The form (1) is a Ginzburg-Landau functional and (2) is a Landau expansion.

2/ Field equation is

$$\frac{\delta g_f}{\delta n(z)} = -B\, n''(z) + W'(n(z)) = 0 \tag{3}$$

We denote $n_*(z)$ its solution.

3/ We identify a conserved quantity :

$$\mathcal{E} = \frac{B}{2} \left[n_*'(z) \right]^2 - W(n_*(z)) \tag{4}$$

(independent of z). At infinity the density is that of the vapor, $n_*(z \to \infty) = n_v$, hence $\mathcal{E} = -W(n_v) = 0$. As a result, the solution satisfies $n_*'(z) = \pm\sqrt{2\, W(n_*(z))/B}$. Note that the vapor density is the lowest, hence $n_*(z)$ decreases with z.

4/ We deduce

$$g_f[n_*] = B \int_0^\infty \mathrm{d}z \left[n_*'(z) \right]^2 = -B \int_0^\infty \mathrm{d}z\, \frac{\mathrm{d}n_*(z)}{\mathrm{d}z} \sqrt{\frac{2}{B} W(n_*(z))} = \sqrt{2B} \int_{n_v}^{n_s} \mathrm{d}n \sqrt{W(n)} \tag{5}$$

A. Thin-film profile.— We choose the simple form $W(n) = c\,(n - n_v)^2 (n - n_l)^2$ for $n_v < n_s < n_l$.

5/ The field equation leads to the

$$n'(z) = -\sqrt{\frac{2c}{B}}\, (n_l - n)(n - n_v) \tag{6}$$

6/ Integration is easy. We write

$$\frac{\mathrm{d}n}{(n_l-n)(n-n_v)} = -\sqrt{\frac{2c}{B}}\,\mathrm{d}z \qquad \text{i.e.} \qquad \int_{n_s}^{n_*(z)} \mathrm{d}z\left(\frac{1}{n_l-n}+\frac{1}{n-n_v}\right) = -z/\xi \tag{7}$$

where $\xi = \sqrt{\frac{B}{2c}}(n_l-n_v)^{-1}$. We get

$$\frac{n_*(z)-n_v}{n_l-n_*(z)} = \underbrace{\frac{n_s-n_v}{n_l-n_s}}_{=\Delta}\ \mathrm{e}^{-z/\xi} \tag{8}$$

i.e

$$n_*(z) = \frac{n_v+n_l\,\Delta\,\mathrm{e}^{-z/\xi}}{1+\Delta\,\mathrm{e}^{-z/\xi}} \tag{9}$$

We check that it decreases from $n_*(0)=n_s$ to $n_*(z\to\infty)=n_v$.

7/ If $n_s \gg n_v$, then $n_*(z) \simeq n_l\left[1+e^{(z-z_0)/\xi}\right]^{-1}$ where $z_0 = \xi\log\left(\frac{n_s}{n_l-n_s}\right)$. It is a step function where the drop of the density occurs around z_0, on a scale ξ. Hence z_0 can be interpreted as the height of the liquid/gas interface (this makes sense for $z_0 \gg \xi$).

B. Wetting transitions

8/ Consider a liquid/gas interface where the density varies from n_l to n_v. The vapor-liquid interfacial energy is

$$\begin{aligned}\gamma = g_f[n_*] &= \sqrt{2B}\int_{n_v}^{n_l}\mathrm{d}n\sqrt{W(n)} = \sqrt{2Bc}\int_{n_v}^{n_l}\mathrm{d}n\,(n_l-n)(n-n_v)\\ &= \sqrt{2Bc}\int_0^{n_l-n_v}\mathrm{d}x\,(n_l-n_v-x)\,x = \sqrt{2\,B\,c}\,(n_l-n_v)^3\left(\frac{1}{2}-\frac{1}{3}\right) = \frac{\sqrt{2\,B\,c}}{6}\,(n_l-n_v)^3\end{aligned}$$

9/ In the general case where $n_s \neq n_l$,

$$g_f[n_*(z)] = \sqrt{2B}\int_{n_v}^{n_s}\mathrm{d}n\sqrt{W(n)} = \sqrt{2\,B\,c}\,(n_l-n_v)^3\left[\frac{1}{2}\left(\frac{n_s-n_v}{n_l-n_v}\right)^2-\frac{1}{3}\left(\frac{n_s-n_v}{n_l-n_v}\right)^3\right] \tag{10}$$

10/ We set $\psi = \frac{n_l-n_s}{n_l-n_v}$. For $n_s\in[n_v,n_l]$ we have $\psi\in[0,1]$ ($\psi=1$ for the vapor and $\psi=0$ for the liquid). We write

$$\frac{n_s-n_v}{n_l-n_v} = 1-\psi \tag{11}$$

hence

$$g_f[n_*] = \gamma\left(1-3\psi^2+2\psi^3\right)\ . \tag{12}$$

11/ We write the surface contribution in terms of the new parameter

$$g_s(n_s) = g_s(n_l) + \left(a_1 - a_2\frac{n_l}{n_l-n_v}\right)\psi + \tfrac{1}{2}\,a_2\,\psi^2\,. \tag{13}$$

As a result, the total grand potential is

$$g_{tot}(n_s) = \gamma + g_s(n_l) + \left(a_1 - a_2\frac{n_l}{n_l-n_v}\right)\psi + \left(\frac{1}{2}a_2 - 3\gamma\right)\psi^2 + 2\gamma\,\psi^3 \tag{14}$$

which has the form of a Landau expansion, in terms of the order parameter $\psi\in[0,1]$.

12/ We introduce $\epsilon = (n_l - n_s)/n_s$. We find

$$\frac{1}{\psi} = \left(1 - \frac{n_v}{n_l}\right)\left(1 + \frac{1}{\epsilon}\right) \tag{15}$$

Above, we have introduced $e^{z_0/\xi} = \Delta = -1 + 1/\psi$. Hence there is a mapping between the order parameter ψ and the position of the interface z_0. In the liquid phase $\psi \to 0$ and the position of the interface diverges (wetting). In the vapor phase (no wetting) $\psi \lesssim 1$ and the position of the interface is $z_0 \lesssim 0$, density is low at the interface.

For $\psi \ll 1$ we have $\epsilon \simeq \psi \simeq e^{-z_0/\xi}$.

13/ Because $\epsilon \simeq \psi$ we find a similar expansion

$$g_{tot} = \gamma + g_s(n_l) + \alpha\,\epsilon + \beta\,\epsilon^2 + \theta\,\epsilon^3 + \ldots \tag{16}$$

(no need to compute the coefficients).

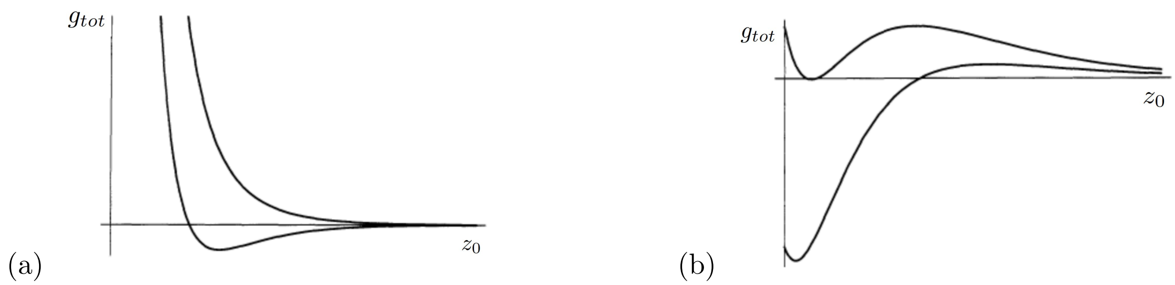

Figure 1: Plot of the system grand potential g_{tot} as a function of the parameter z_0 for two different temperatures for a given set of microscopic coefficients. (a) $\beta > 0$. (b) with another set of parameters with $\beta < 0$

14/ The figure shows the grand potential as a function of z_0 (instead of ϵ or ψ). In the figure (a), the top curve has a minimum for $z_0 = \infty$ (liquid, $n_s = n_l$) and the other curve has a minimumu for z_0 finite ($n_s < n_l$). This describes the transition between a wet substrate and non-wet substrate.

15/ Figure (a) : the transition looks second order as we go continuously from one situation to the other.

Figure (b) : clearly the minimum jumps discontinuously when one goes from one curve to the other. The transition is first order.

Apparently, wetting transition is more likely first order (coefficients corresponding to second scenario).