

Advanced Statistical Physics – Exam

Tuesday 9 January 2024

Duration : 3h

Lecture notes are allowed (nothing else, no cell phone, no calculator,...)

⚠ Write Exercices 1 & 2 on separate sheets (with your name on both!) ⚠

1 XXX

...

2 Wetting transition

Introduction.— We study a fluid in either liquid or vapor phase, on the top of a substrate. Complete wetting is characterized by a macroscopic liquid film in between the solid substrate and the vapor. Partial wetting is characterized by the solid substrate covered by a wedge or finite drop of the fluid. In the macroscopic picture, the remainder of the solid contacts the vapor. However, interactions with the solid can result in a local density of molecules near the substrate that is quite different from the density of either the liquid or the vapor. We consider the following cases: (i) The interaction with the solid substrate is repulsive, favoring a low density of molecules on the substrate - i.e., a gas. In this case, there is solid-vapor equilibrium and one would not expect small contact angle wetting of the substrate by the liquid. (ii) The interaction with the substrate is attractive, favoring a high density of the fluid. In this case, there is the possibility for solid-fluid-vapor equilibrium, with a layer of fluid on the substrate whose density is larger than that of the vapor, but may not equal that of the bulk fluid phase. When this intervening fluid layer is macroscopically thick, one has complete wetting. When this intervening fluid layer is not macroscopically thick, it can coexist with a macroscopic liquid phase.

Equilibrium equations.— We consider a vapor-liquid system in contact with a solid substrate, where the total grand potential per unit area, $g_{tot} = g_f[n(z)] + g_s(n_s)$, consists of the sum of g_f , the liquid/vapor grand potential, with the fluid/substrate interfacial contribution g_s . For simplicity, we consider a situation translation invariant in two directions : the plane substrate is normal to the z direction, and assume that the layer density only depends on z . For the fluid above the substrate ($z > 0$), we consider the free energy

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

where $n(z)$ is the density of the fluid-vapor above the solid ($z > 0$). The contribution $W(n)$ includes the chemical potential and also subtracts off the grand potential of the uniform bulk phase. The interfacial grand potential is assumed to be given with a Virial expansion

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

where $n_s = n(z = 0)$ is the density of the fluid at the solid surface, while n_l and n_v are the bulk, equilibrium liquid and vapor densities respectively. The first term in this expression is a

constant term, the second represents an attraction (when $a_1 > 0$) of the molecules to the surface (recall that if the molecules are repelled from the surface it is highly unlikely for a fluid-like layer to exist near the surface of the substrate), and the third term represents an "excluded-volume" type of interaction (which can be repulsive or attractive) of the molecules adsorbed on the surface. For simplicity, we consider the case where this interaction is repulsive ($a_2 > 0$) so the added complication of a liquid-gas phase separation by the adsorbed molecules is absent. We consider the case where the substrate is uniformly covered by a layer of "fluid", but that this layer is not necessarily at the equilibrium fluid density.

1/ Comment on the form of the grand potentials (1) and (2).

Strategy.— We consider the total grand potential is thus a function of spatially varying density, $n(z)$, and by the value of the density on the surface, $n_s = n(z = 0)$. We first minimize g_{tot} with respect to the $n(z)$ with a fixed value of the surface density, n_s to find the profile for arbitrary surface densities. Afterward, one uses this solution for $n(z)$ to minimize g_{tot} again to find the local surface density, including the contributions from both g_s and g_f , both of which depend on n_s .

2/ Derive the equation on $n(z)$ resulting from the minimization of $g_f[n]$ with respect to the density profile $n(z)$, in terms of $\partial^2 n / \partial z^2$ and $\partial W / \partial n$.

3/ Assuming the boundary condition $W = 0$ in the liquid or vapor phase far away from the substrate, show that the solution for $n_*(z)$ satisfies

$$\frac{1}{2}B \left(\frac{\partial n_*}{\partial z} \right)^2 = W(n_*(z)). \quad (3)$$

4/ Using the latter equation and assuming $n(z \rightarrow \infty) = n_v$, show that the fluid grand potential is merely

$$g_f[n_*] = \int_{n_v}^{n_s} dn \sqrt{2BW(n)}. \quad (4)$$

A. Thin-film profile.— In the following, we consider the simplified form

$$W(n) = c(n - n_v)^2(n - n_l)^2, \quad (5)$$

and clearly we have $n_v < n_s < n_l$.

5/ Write the corresponding equilibrium equation for $\partial n / \partial z$.

6/ Show that its solution such that $n_*(z \rightarrow \infty) = n_v$ is

$$n_*(z) = \frac{(n_v - n_l) + n_l(1 + \Delta e^{-z/\xi})}{1 + \Delta e^{-z/\xi}}, \quad (6)$$

where $\Delta = \frac{n_s - n_v}{n_l - n_s} > 0$ and $\xi = \sqrt{\frac{B}{2c}}(n_l - n_v)^{-1}$.

If $n_s \gg n_v$, then $n_*(z) \simeq n_l [1 + e^{(z-z_0)/\xi}]^{-1}$ where $z_0 = \xi \log \left(\frac{n_s}{n_l - n_s} \right)$.

7/ Plot the density profile $n_*(z)$, and comment on the meaning of z_0 .

One can observe an increase in the thickness of the film z_0 by changing temperature. We consider the case where n_s is relatively insensitive to the temperature, but, as is usual for the liquid-gas transition, the liquid density, $n_l(T)$, decreases as one approaches the bulk transition temperature for the phase separation. One then expects a finite thickness film of size z_0 at low temperatures where $n_l \gg n_s$, and a transition to an infinitely thick layer at some higher temperature, T_w , when $n_l(T_w) = n_s$. As the temperature approaches the wetting transition temperature T_w , $n_l(T) \rightarrow n_s$, and the thickness of the film diverges; there is a macroscopically thick fluid layer in between the solid and liquid, i.e. a transition to complete wetting.

B. Wetting transitions.— We define the vapor-liquid interfacial energy $\gamma = \int_{n_v}^{n_l} dn \sqrt{2BW(n)}$.

8/ Show that

$$\gamma = \frac{1}{6} \sqrt{2Bc} (n_l - n_v)^3. \quad (7)$$

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

$$g_f[n_*(z)] = \sqrt{2Bc} (n_l - n_v)^3 \left[\frac{1}{2} \left(\frac{n_s - n_v}{n_l - n_v} \right)^2 - \frac{1}{3} \left(\frac{n_s - n_v}{n_l - n_v} \right)^3 \right] \quad (8)$$

10/ We set $\psi = \frac{n_l - n_s}{n_l - n_v}$. What is the range for ψ ? Show that

$$g_f[n_*] = \gamma (1 - 3\psi^2 + 2\psi^3). \quad (9)$$

11/ Show that the fluid/substrate interaction can be expressed as

$$g_s(n_s) = g_s(n_l) + \left(a_1 - a_2 \frac{n_l}{n_l - n_v} \right) \psi + \frac{1}{2} a_2 \psi^2. \quad (10)$$

Eventually, we consider the case of thick wetting films where $n_l \simeq n_s$, so that we can assume $\psi \ll 1$. We also define $\epsilon = \frac{(n_l - n_s)}{n_s}$. To simplify our calculations, we assume $n_v \ll n_l$.

12/ Relate ϵ to z_0 .

13/ Find the expansion

$$g_{tot} = \gamma + g_s(n_l) + \alpha \epsilon + \beta \epsilon^2 + \theta \epsilon^3 + \dots \quad (11)$$

With this result in hand, together with the relationship between ϵ and z_0 , one can then plot g_{tot} as a function of z_0 (instead of ϵ or ψ). Depending on the type of interaction between the substrate and the fluid, but also on the temperature, we can typically find the following figures for g_{tot} , each for a given set of parameters, but for different temperatures, see Fig. 1.(a) and (b).

14/ Comment on the behavior of the system, and on a possible transition.

15/ Comment on the order of the transition for the thickness of the film.

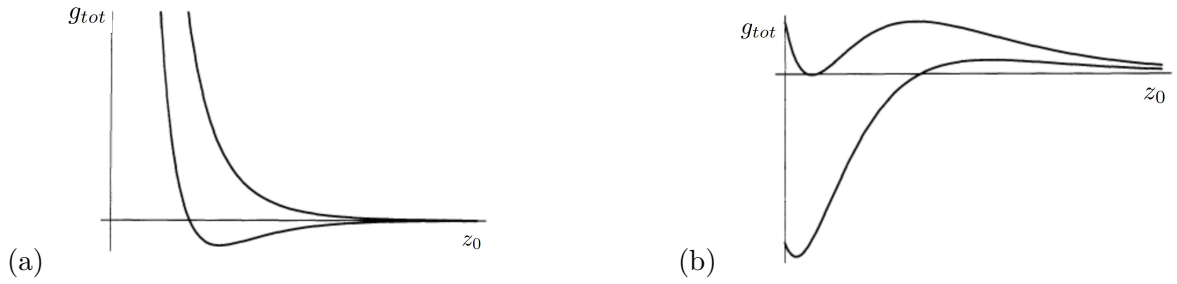


Figure 1: Plot of the system grand potential g_{tot} as a function of the parameter z_0 for two different temperatures for a given set of microscopic coefficients. (a) $\beta > 0$. (b) with another set of parameters with $\beta < 0$