

ÉCOLE NORMALE SUPÉRIEURE

DÉPARTEMENT DE PHYSIQUE

M1 ICFP

Lectures Notes on Soft Matter and interfaces

BY LYDÉRIC BOCQUET

NOTES TRANSCRIBED BY MARTIN CAELEN, ENS

Introduction

In these lectures, our goal is to describe in a microscopic way the behaviour of what we can study in soft matter physics. Soft matter physics is a field of physics interested in the understanding of phenomena with a typical energy of the order of magnitude of kT (where k is the Boltzmann constant and T the temperature): thermal fluctuation and entropy will play a huge role in the description of such phenomena. As a consequence, noise is a key feature in the understanding of soft matter physics. In addition, the systems described here will be very dense, so we will have to take into account a huge number of components in our system. Thus, the introduction of the tools of statistical physics is necessary to obtain an understandable description of the collective behaviour of these very dense systems.

Contents

Introduction	2
1 Interactions	5
1.1 Dipolar interactions and Van der Waals	5
1.1.1 Quick reminder on dipoles	5
1.1.2 Electric susceptibility of a permanent dipole	5
1.1.3 Qualitative understanding of $V \sim -1/r^6$ in Van der Waals interactions	6
1.2 Van der Waals interaction between surfaces	7
1.3 Electrostatic interactions	7
1.3.1 What is the surface charge ?	7
1.3.2 Electrostatic lengths	8
1.3.3 Poisson-Boltzmann (PB) theory	9
1.3.4 Boundary conditions	9
1.3.5 Debye-Hückel theory	9
1.3.6 Full 1D solution of PB equation	10
1.3.7 Interaction between charged surfaces	11
1.4 DLVO (Derjaguin Landau Verwey Overbeek) theory	12
2 From capillarity to Density Functional Theory (DFT)	14
2.1 Quick reminder	14
2.2 Capillarity induced phase transitions	14
2.2.1 Liquid-vapour phase transition	14
2.2.2 Effect of capillarity	14
2.3 Density Functional Theory	17
2.3.1 Thermodynamics	17
2.3.2 Introducing the heterogeneity	18
2.4 Cahn-Hilliard theory of wetting transition	19
2.4.1 Experimental results and introduction of some concepts	19
2.4.2 Thermodynamics	20
2.4.3 Graphical solution for a Van der Waals fluid	21
2.5 Dynamics: Time-Dependent Density Functional Theory (TD-DFT)	23
2.5.1 Phenomenological laws	24
2.5.2 Application to the DFT theory	24
3 Fluctuations and entropic interactions	26
3.1 Fluctuation of liquid-vapour interfaces	26
3.1.1 Introduction	26
3.1.2 Fourier analysis	27
3.2 Fluctuation of membranes	28
3.2.1 Introduction	28
3.2.2 Fourier analysis	28
3.3 Density fluctuations	29
3.4 Entropic forces	30

3.4.1	Osmosis	30
3.4.2	Depletion interactions	32
3.4.3	Helfrich interactions	33
4	Noise, brownian motion and dynamics	36
4.1	Langevin theory	36
4.1.1	Introduction and hypotheses	36
4.1.2	Diffusive motion	37
4.1.3	Velocity correlations	37
4.1.4	Fluctuation-dissipation theorem	38
4.2	Diffusion and Smoluchowski	38
4.3	Generalization	40
4.4	Barrier crossing	40
4.5	Application: nucleation theory	42

Chapter 1

Interactions

In this chapter, we propose a description of the interactions between particles (e.g. colloids) in an electrolyte (e.g. Na^+ , Cl^- in water). At the microscopic scale, the interactions are dominated by electromagnetism and quantum effects.

In water, we have three main types of interaction (where V is the potential of interaction between the particles, and r is the distance which separates them):

1. Van der Waals interactions: attractive interactions between fluctuating dipoles: $V \sim -1/r^6$.
2. direct electrostatic interactions, which directly follow Coulomb's law: $V \sim qq'/r$.
3. hydrogen bonding: direct attractive interaction between oxygen and hydrogen in water, which tends to "align" molecules of water in the solvent (in competition with entropy). This is the interaction which gives their tetrahedral structure to water crystals (ice).

In this chapter, we will focus on the first two interactions: Van der Waals and electrostatic interactions.

1.1 Dipolar interactions and Van der Waals

1.1.1 Quick reminder on dipoles

A globally neutral cloud of charges may be described by its *electric dipole* $\mathbf{p} = \sum_j q_j \mathbf{r}_j$ where q_j and \mathbf{r}_j are the charges and positions of the punctual charges. If two clouds which are globally neutral (i.e. $\sum_j q_j = 0$ for each of them) interact, then the potential of interaction between them is dominated by the contribution of their dipoles, following:

$$V(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{1}{r^3} \left(\mathbf{p}_1 \cdot \mathbf{p}_2 - \frac{3(\mathbf{p}_1 \cdot \mathbf{r})(\mathbf{p}_2 \cdot \mathbf{r})}{r^2} \right)$$

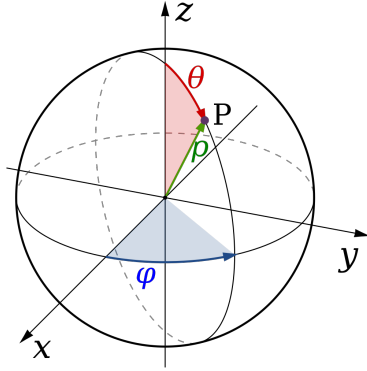
And the energy of interaction between an electric dipole and an electric field is given by $\mathcal{E} = -\mathbf{p} \cdot \mathbf{E}$.

Very often, electric dipoles may be induced by their surrounding electric field \mathbf{E} . For a linear response ($\|\mathbf{E}\| \rightarrow 0$), we define the *electric susceptibility* α so that: $\langle \mathbf{p} \rangle = \alpha \mathbf{E}$.

Let us compute this susceptibility for a permanent dipole.

1.1.2 Electric susceptibility of a permanent dipole

We will here compute the value of the susceptibility for an electric dipole freely rotating in the presence of a given electric field. The length of the electric dipole is fixed to $\|\mathbf{p}\| = p$.



Let choose our basis vectors so that \mathbf{E} is aligned to the z axis. We will call θ the angle between \mathbf{E} and \mathbf{p} . In the spherical coordinates, θ is then the polar angle, and the description of \mathbf{p} is completed with its fixes length p and its azimuthal angle φ .

By symmetry of rotation around the vertical axis, we have immediately that $\langle p_x \rangle = \langle p_y \rangle = 0$. As a consequence, we are just interested here in $\langle p_z \rangle$. To compute $\langle p_z \rangle$, we will use a Boltzmann-weighted distribution (where each configuration is weighted by $\exp\left(-\frac{\mathcal{E}(\text{config.})}{k_B T}\right)$). Means are then obtained by integrating among all possible configurations of the system). Each configuration is given here by (θ, φ) or equivalently by the solid angle $\Omega(\theta, \varphi)$. Integrating over all Ω possible gives:

$$\langle p_z \rangle = \langle p \cos \theta \rangle = \frac{\int d\Omega p \cos \theta \exp\left(\frac{Ep \cos \theta}{kT}\right)}{\int d\Omega \exp\left(\frac{Ep \cos \theta}{kT}\right)}$$

where $d\Omega = \sin \theta d\theta d\varphi$.

Integrating over φ in both members of the fraction gives geometric terms that simplify (since nothing depends on φ in the integral). Then, calling $z = -\frac{Ep}{kT}$ and changing variables in the integral ($u = \cos \theta$) yields:

$$\langle p_z \rangle = p \frac{\int_{-1}^1 du u \exp(-zu)}{\int_{-1}^1 du \exp(-zu)} = p \times \left(-\frac{\partial}{\partial z} \log \left(\int_{-1}^1 du \exp(-zu) \right) \right) = p \times \left(-\frac{\partial}{\partial z} \log \left(\frac{2 \sinh z}{z} \right) \right)$$

The susceptibility is defined for a small electric field, so for $z \rightarrow 0$. Then: $\log(\sinh z/z) \approx \log(1 + z^2/6 + \dots) \approx z^2/6$. As a consequence:

$$\langle p_z \rangle = -p \times \frac{2}{6} z = \frac{p^2}{3kT} E = \alpha E$$

We finally obtain:

$$\alpha = \frac{p^2}{3kT}$$

Remark. A cloud of punctual charges may not have a permanent dipole. But, in presence of an external electric field, the creation of an electric dipole may be induced. This induced permanent dipole has a quantum origin (it is caused by the perturbation of the orbitals of particles by an external electric field), and the electric susceptibility of such a dipole is $\alpha = 4\pi\epsilon_0 a_0^3$ where a_0 is the characteristic size of an atom.

1.1.3 Qualitative understanding of $V \sim -1/r^6$ in Van der Waals interactions

Let us consider two dipoles, and let us discuss the interaction between them. The first dipole creates the following electric field:

$$\mathbf{E}_1(\mathbf{r}) = \frac{1}{4\pi\epsilon_0} \frac{1}{r^3} \left(\frac{3(\mathbf{p}_1 \cdot \mathbf{r})\mathbf{r}}{r^2} - \mathbf{p}_1 \right)$$

And it can be approximated by $\mathbf{E}_1(\mathbf{r}) \sim -\mathbf{p}_1/r^3$.

Using this external electric field to compute $\langle \mathbf{p}_2 \rangle$, we obtain: $\langle \mathbf{p}_2 \rangle \sim -\alpha_2 \mathbf{p}_1/r^3$. This electric dipole creates in return an electric field, the value of which being: $\mathbf{E}_2 \sim -\mathbf{p}_2/r^3 \sim \alpha_2 \mathbf{p}_1/r^6$.

Finally, the Van der Waals interaction potential between the two dipoles is:

$$V_{dW} = -\langle \mathbf{p}_1 \cdot \mathbf{E}_2 \rangle \sim -\alpha_2 \langle \|\mathbf{p}_1\|^2 \rangle / r^6 \sim {}^1 - \alpha_1 \alpha_2 / r^6$$

¹ $\alpha = \frac{p^2}{3kT}$

Remark.

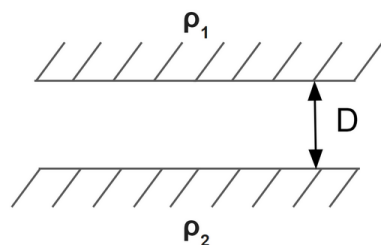
1. This Van der Waals interaction, and especially its exponent 6 in $-1/r^6$ are universal. They do not depend on the kind of particles considered, nor of the solvent.
2. This interaction is attractive. But it can be made repulsive if the surrounding medium is well chosen and one of the dipoles is induced. Indeed, the true expression of α for an induced dipole depends on the relative permittivities of the particles and of the solvent: $\alpha = 4\pi a_0^3 \bar{\epsilon} \frac{\epsilon - \bar{\epsilon}}{\epsilon + 2\bar{\epsilon}}$ where $\bar{\epsilon}$ is the permittivity of the solvent, and ϵ is the permittivity of the particles. It can be experimentally interesting to finely tune the permittivity of the solvent in order to destroy the Van der Waals interaction.
3. There are retarded Van der Waals interactions, which are caused by the delay induced by the finite speed of propagation of electromagnetic waves. But it is very long-distance effect, and we will always neglect it. For a retarded Van der Waals interaction, the potential is $V \sim -1/r^7$.

1.2 Van der Waals interaction between surfaces

We've just quantitatively explained Van der Waals interactions. These interactions are attractive and may lead to interaction between surfaces. The understanding of this phenomenon is crucial to us, who want to study soft matter physics, which is often interested in surfaces. In fact, because of Van der Waals interaction, two surfaces tend to attract each other. The calculation of the effect of Van der Waals interaction on two surfaces is left as an exercise to the reader, but the main steps of it are:

1. Start from one atom in front of a surface, and integrate over all the interactions between it and each atom of the other surface.
2. Sum for all the atoms of the surface the interaction potential obtained before for just one atom.

The result is:



$$W(D) = -\frac{A}{12\pi D^2}$$

where D is the distance between the two surfaces, and A is called the Hamaker constant and depends on the geometries and electric properties of the two surfaces. In particular: $A \propto \alpha_1 \alpha_2 \rho_1 \rho_2$ where ρ_1 and ρ_2 are the densities of the two surfaces.

Remark.

1. Order of magnitude: $A \sim 10^{-21} - 10^{-20}$ J. In particular, for two quartz surfaces separated by water: $A = 6.3 \times 10^{-21}$ J.
2. There exists an exact computation of the Hamaker constant, which has been proposed by Lifschitz. If two surfaces of permittivities ϵ_1 and ϵ_2 are separated by a medium of permittivity ϵ_3 , we can obtain: $A \approx \frac{3}{4} kT \left(\frac{\epsilon_1 - \epsilon_3}{\epsilon_1 + \epsilon_3} \right) \left(\frac{\epsilon_2 - \epsilon_3}{\epsilon_2 + \epsilon_3} \right) + \frac{3h}{4\pi} \int_{\nu_1}^{\infty} d\nu \left(\frac{\epsilon_1(i\nu) - \epsilon_3(i\nu)}{\epsilon_1(i\nu) + \epsilon_3(i\nu)} \right) \left(\frac{\epsilon_2(i\nu) - \epsilon_3(i\nu)}{\epsilon_2(i\nu) + \epsilon_3(i\nu)} \right)$ where $\nu_1 = 2\pi kT/h$.

1.3 Electrostatic interactions

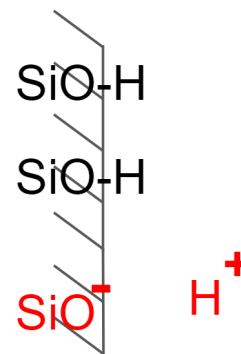
As we've just seen, because of Van der Waals interactions, two surfaces are attracted one towards the other. This is a huge issue for anyone who wants to prepare a suspension of particles (e.g. of colloids), because these particles will aggregate because of Van der Waals interactions. "Hopefully", another kind of interaction may be repulsive enough to maintain the suspension non-aggregated: the electrostatic interaction, and what we call the *double layer phenomenon*. This section is devoted to the understanding of this phenomenon.

1.3.1 What is the surface charge ?

An *electrolyte* is by definition a conductive phase. Here, electrolytes will be conductive liquids, and may be ionic solutions (e.g. Na^+ , Cl^- in water) or ionic liquids (e.g. salts in fusion). Here, we will focus on ionic solutions, and more specifically on salts dissolved in water.

When a solid plate is submerged in an electrolyte, it may become charged on its surface. Indeed, the ions in the electrolyte (and also water itself) have the ability to stabilize charges, and any charge-creating dissociation of the molecule constituting the plate can be favoured by entropic forces. For example, in SiO_2 plates, the molecules of SiOH in contact with water will leave their proton and become SiO^- and H^+ , H^+ being stabilized by anions and by water itself (this huge stabilization of ions by water solutions is included in the value of the relative electric permittivity in water, which is equal to 80).

As a consequence, solid plates may become charged on surface. We will call σ their surface charge (i.e. their charge by unit area). As an order of magnitude, for SiO_2 in water: $\sigma \sim 10 - 50 \text{ mC/m}^2$.



1.3.2 Electrostatic lengths

As we will see later, many typical lengths may arise when studying electrostatics. Let us give some of them, that we will encounter later in our calculations.

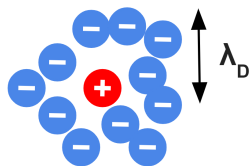
Bjerrum length

This length is obtained by equating the interaction potential between two unitary charges and the thermal energy kT :

$$l_B = \frac{e^2}{4\pi\epsilon kT}$$

In water at room temperature: $l_B = 7\text{\AA}$.

Debye length



In an electrolyte, ions may be surrounded by counter-ions (we say that the ions are dressed). The Debye length gives a typical radius to such clouds (or dresses): $N_{\text{counter-ions}} \times \frac{e^2}{4\pi\epsilon\lambda_D} \sim kT$ (which gives the competition between entropy and electrostatic forces that respectively disperse and condense such clouds). $N_{\text{counter-ions}} \sim \rho_s \lambda_D^3$ where ρ_s is the concentration of the salt in the electrolyte.

$$\lambda_D^2 \propto \frac{1}{l_B \rho_s}$$

As an order of magnitude, if $\rho_s \sim 1 \text{ M}$, then $\lambda_D \sim 3\text{\AA}$.

Gouy-Chapman length

$$l_{GC} = \frac{1}{2\pi \frac{\sigma}{e} l_B}$$

Dukhin length

$$l_{Dk} = \frac{\sigma/e}{\rho_s}$$

Remark. There are many other lengthscales. The existence of that many lengthscales makes the study of electrostatic interactions in electrolytes very challenging, and the first to really construct a good stable and basic understanding of this subject are Verwey and Overbeck in the 1940's.

1.3.3 Poisson-Boltzmann (PB) theory

The PB theory aims to describe the distribution of charges (and therefore the electric potential) in a (mono-valent) ionic solution with an infinitely large charge plate of charge surface σ .

The PB theory is mainly the coupling between two equations:

Poisson equation

$$\Delta V = -\frac{e}{\epsilon}(\rho_+ - \rho_-)$$

where ρ_+ and ρ_- are the concentrations of the cations and anions.

Boltzmann equilibrium

$$\rho_{\pm} = \rho_s e^{\mp \frac{eV}{kT}}$$

These two equations combined, we have:

$$\Delta V = -\frac{e}{\epsilon} \rho_s (e^{-\frac{eV}{kT}} - e^{+\frac{eV}{kT}})$$

Introducing the dimensionless potential $\phi = \frac{eV}{kT}$ (with $\frac{kT}{e} \sim 25$ mV) and $\kappa_D = 1/\lambda_D$, we obtain the Poisson-Boltzmann equation:

$$\Delta \phi = \kappa_D^2 \sinh \phi$$

Remark. A cleaner way to describe this system is to see it as the neighbourhood of the plate connected to a reservoir of salt concentration ρ_s . Using the equilibrium of the electro-chemical potential (of a perfect gas) in the neighbourhood of the plate and in the reservoir yields the Boltzmann equilibrium:

$$\mu_{\pm} = kT \log(\rho_{\pm} \lambda_T^3) \pm eV = \mu_{\text{reservoir}} = kT \log(\rho_s \lambda_T^3)$$

where λ_T is the thermal de Broglie wavelength.

1.3.4 Boundary conditions

The boundary conditions that have to be used are the Gauss boundary conditions of the electric field: $\frac{\sigma}{\epsilon} = \mathbf{E} \cdot \mathbf{n}|_{\text{surface}}$.

With $\mathbf{E} = -\nabla V$, and calling the axis normal to the surface the z axis: $-\frac{\partial V}{\partial z}|_{\text{surface}} = \frac{\sigma}{\epsilon}$.

And finally:

$$-\frac{\partial \phi}{\partial z}(z=0) = \frac{e\sigma}{\epsilon kT} = 4\pi l_B \frac{\sigma}{e} = \frac{2}{l_{GC}}$$

1.3.5 Debye-Hückel theory

The Debye-Hückel theory is the PB theory which is linearized for $\phi \ll 1$ i.e. for $V \ll \frac{kT}{e} \sim 25$ mV. With addition of the symmetries of the problem giving $\Delta \phi = \frac{\partial^2 \phi}{\partial z^2} = \frac{d^2 \phi}{dz^2}$, the linearized PB equation is:

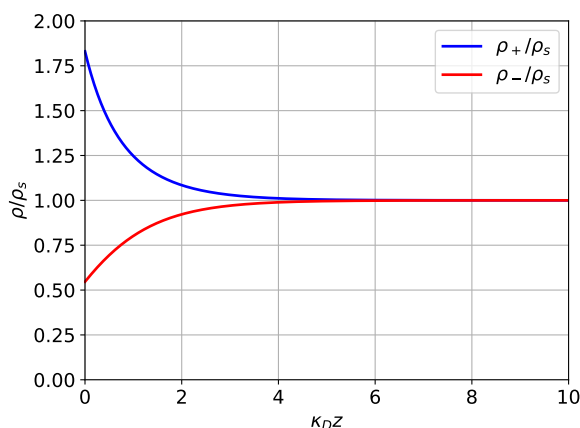
$$\frac{\partial^2 \phi}{\partial z^2} \approx \kappa_D^2 \phi$$

Avoiding divergence of the solution and respecting the boundary conditions, we can integrate:

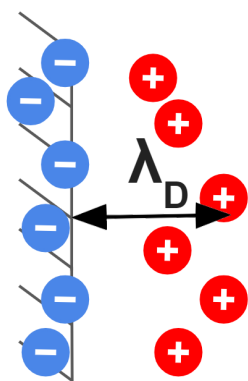
$$V(z) = \frac{\sigma \lambda_D}{\epsilon} e^{-\kappa_D z}$$

And:

$$\rho_{\pm}(z) = \rho_s e^{\mp \frac{eV(z)}{kT}} \approx \rho_s \left(1 \mp \frac{e}{kT} V(z) \right) \approx \rho_s \left(1 \mp \frac{e\sigma}{\epsilon kT} \lambda_D e^{-\kappa_D z} \right) = \rho_s \left(1 \mp \frac{2\lambda_D}{l_{GC}} e^{-\kappa_D z} \right)$$



Surface capacitance



From the boundary conditions on the plate (that we just used to integrate the differential equation), we have found $\sigma = CV_0$ where $C = \epsilon/\lambda_D$. This means that the system near the plate behaves like a capacitance. From this point of view, we can see the system as a charged plate with a layer of counter-charges in front of it at a distance λ_D . We call this the *electric double layer*.

We can develop this description by showing that the free energy per unit area of the system includes a term behaving like the energy of a capacitance ($V_0 d\sigma$ being the contribution of electrostatics in the free energy):

$$d\mathcal{F} = -S dT + \mu_+ dN_+ + \mu_- dN_- + V_0 d\sigma$$

Integrating the electrostatic contribution:

$$\mathcal{F}_{es}(\sigma) = \mathcal{F}_{es}(\sigma = 0) + \frac{\sigma^2}{2C}$$

Remark. $\frac{\sigma^2}{2C}$ looks like the energy of a capacitance but it is here a free energy. This means that all possible contributions are taken into account into this $\frac{\sigma^2}{2C}$, including entropic contributions.

1.3.6 Full 1D solution of PB equation

By arguments of symmetry, we can restrict ourselves to a 1D potential ($V(\mathbf{r}) = V(z)$, z being the axis normal to the charged surface). The PB equation is then:

$$\frac{d^2\phi}{dz^2} = \kappa_D^2 \sinh \phi$$

We take the first integral of this differential equation by multiplying by $\frac{d\phi}{dz}$ and by integrating. Asking for ϕ and $\frac{d\phi}{dz}$ decaying toward 0 at infinity yields:

$$\frac{1}{2} \left(\frac{d\phi}{dz} \right)^2 = \kappa_D^2 (\cosh \phi - 1)$$

Using a separation of variables:

$$\frac{d\phi}{\sqrt{\cosh \phi - 1}} = \sqrt{2} \kappa_D dz$$

Finally, integrating yields:

$$\phi = -2 \log \left[\frac{1 + \gamma e^{-\kappa_D z}}{1 - \gamma e^{-\kappa_D z}} \right]$$

where: $\gamma^2 + 2 \frac{l_{GC}}{\lambda_D} - 1 = 0$.

Remark.

1. For $z \gg \lambda_D$, $\phi \sim -4\gamma e^{-\kappa_D z}$.

2. For a large surface charge ($l_{GC} \ll \lambda_D$), we have $\gamma \sim 1$ and for $z \gg \lambda_D$:

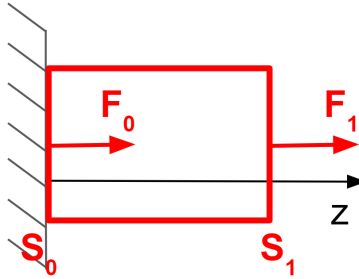
$V \sim -\frac{4kT}{e} e^{-\kappa_D z} \sim (-100 \text{ mV}) e^{-\kappa_D z}$. Thus, the potential induced by a large enough surface charge does not depend on the characteristic of this surface charge.

1.3.7 Interaction between charged surfaces

Now, we will consider two parallel similarly charged surfaces, separated by a distance D . We want to find an expression for the force between the two charged surfaces due to the electrostatics interactions between them. Of course, we will use the result from the previous section.

Action of an electric potential on one plate

We will first consider the action of a given electric potential on one plate. To do so, let us consider the global force balance on a cylinder of fluid of section S and height h , normal to the plate, and touching with one of its surfaces the plate. Let's call the surface of the cylinder in contact with the plate S_0 , and the opposite surface of the cylinder S_1 . \mathbf{F}_0 and \mathbf{F}_1 are the forces acting on S_0 and S_1 , and F_0 and F_1 are their projections on the z axis. We are only interested in the balance of forces along the z axis, so we will forget about the forces acting on the cylinder perpendicularly to the z axis (and we are supposing that the fluid is non-viscous and does not transmit momentum through the lateral walls of the cylinder).



First of all, we have to remark that F_0 is the opposite of the force acting on the plate through the surface S_0 (this is just an application of the third law of Newton (action-reaction)). Then, the balance of our cylinder of fluid along the z axis gives $F_0 + F_1 = 0$. Finally, F_1 is equal to the force acting on the plate through S_0 , and, with the hypotheses made above, this equality does not depend on the position of S_1 along the z axis.

Now, $F_1 = F$ is made of two contributions: the pression (which we will obtain supposing our fluid behaves like a perfect gas) and the electrostatics:

$$\frac{F}{S} = -p(z) + \int dz \rho_c E_z$$

where: $p(z) = (\rho_+(z) + \rho_-(z))kT$, $\rho_c = -\epsilon \frac{d^2 V}{dz^2}$, and $E_z = -\frac{dV}{dz}$.

We have then: $\rho_c E_z = \frac{\epsilon}{2} \frac{d}{dz} \left[\left(\frac{dV}{dz} \right)^2 \right]$. And:

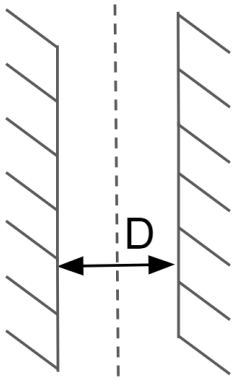
$$\frac{F(z)}{S} = -p(z) + \int_0^z dz \frac{\epsilon}{2} \frac{d}{dz} \left[\left(\frac{dV}{dz} \right)^2 \right] = -p(z) + \frac{\epsilon}{2} \left(\frac{dV}{dz} \right)^2$$

We call the *Maxwell stress tensor* $\Pi(z) = -\frac{F(z)}{S}$.²

This tensor is in fact constant along the z axis: $\frac{d\Pi}{dz} = 0 \iff -\frac{dp}{dz} + \rho_c E = 0 \iff \Delta\Phi = \kappa_D^2 \sinh \phi$, which is of course true here, since we are considering a solution of PB equation.

Interaction between the two plates

We consider now the two plates, but we still use our reasoning with the balance of forces on the left-most plate. The action of the second plate will be contained in the calculation of the Maxwell stress tensor: the force per unit area exercised by the second plate on the first is equal to $-\Pi$. Since Π is constant along the z axis, we will compute its value on a particular point: $z = D/2$ which is on the plane of symmetry of our system. The symmetry of our problem states that $V(z - D/2)$ is an even function. As a consequence, $\frac{dV}{dz}$ is odd and vanishes at $z = D/2$. Then:



$$\frac{F}{S} = -\Pi = -p(z) + \frac{\epsilon}{2} \left(\frac{dV}{dz} \right)^2 = -p(z) = -kT(\rho_+ + \rho_-)(z = D/2)$$

Now, we need to give $(\rho_+ + \rho_-)(z = D/2)$, but it is not that easy. The PB equation is non linear and therefore it is not trivial to obtain the solution for ϕ when there are two plates.

Here, we will then make an approximation: we will suppose that we can act as if the PB equation was linear (for that, we suppose that ϕ is small enough). We say with this approximation that the solution of PB for two plates is the sum of the solution of PB for each plate.

As a consequence, here, with $D/2 \gg \lambda_D$: $\phi \sim -8\pi\gamma e^{-\kappa_D D/2}$.

And, finally:

$$\frac{F}{S} = -2kT\rho_s \cosh \phi = -P_0 - 64kT\rho_s\gamma^2 e^{-\kappa_D D}$$

for $\phi \ll 1$, where $P_0 = 2kT\rho_s$ is the osmotic pressure due to the bulk concentration.

Remark.

1. $F_{es} = -64kT\rho_s\gamma^2 e^{-\kappa_D D} < 0$: the interaction between the two plates due to the electrostatic interactions is a repulsive interaction.
2. The contribution of $kT\rho_s$ is a perfect gas contribution, and highlights the fact that this repulsion is due to the entropic repulsion of the particles between the two plates.
3. For weak charged surfaces, $\gamma \propto \sigma$ and then $F_{es} \propto \sigma^2$.

1.4 DLVO (Derjaguin Landau Verwey Overbeek) theory

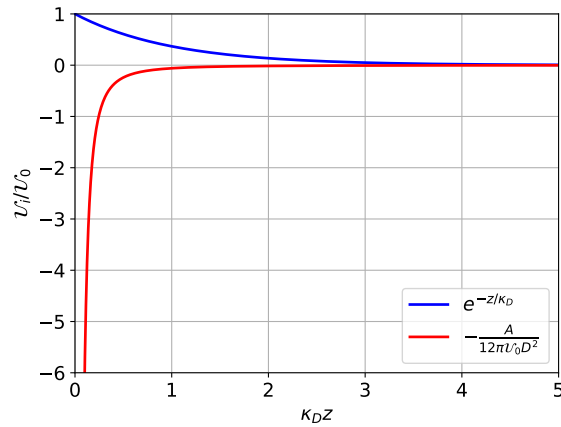
The DLVO theory explains the aggregation of dispersions in electrolytes. By combining the effects of the Van der Waals attraction and the electrostatic repulsion due to the electric double layer effect, one can understand how particles in an electrolyte aggregate or not, depending on the electrolyte's and particles' characteristics.

The interaction between two particles can be locally understood as the interaction between two surfaces. From the previous part, we now have the dependence of the interaction between the particles on their distance from each other. The total free energy in that case is:

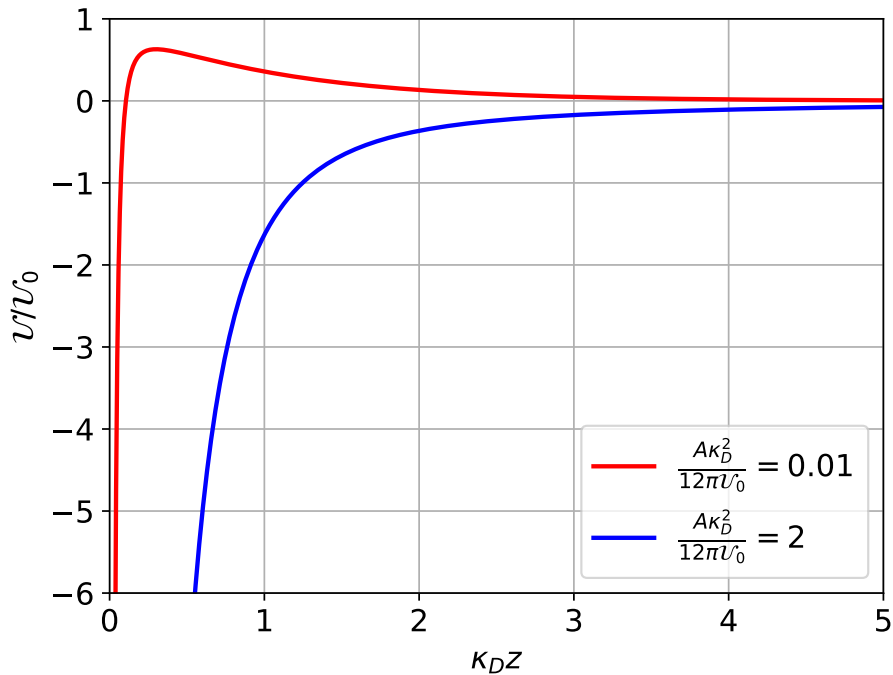
$$\mathcal{U}(D) = -\frac{A}{12\pi D^2} + \mathcal{U}_0 e^{-\kappa_D D}$$

A stable state for the system has to minimize of free energy. From this, we can distinguish two main cases:

²Read the book of Jackson on electromagnetism to learn more about this tensor



1. The Van der Waals attraction is dominant for all D . This corresponds to $\kappa_D > (\frac{U_0}{A})^{1/2}$, therefore to a large salt concentration ($\kappa_D \propto \sqrt{\rho_s}$): the salt screens the stabilizing electrostatic repulsion. In this case, \mathcal{U} has no local extremum, and as a consequence, the only stable state for the system is a full collapse ($D \rightarrow 0$). This aggregation is called a *flocculation*.
2. If, in the opposite, κ_D is small enough (small enough salt concentration, or high surface charge), the electrostatic interaction is strong enough to challenge the Van der Waals attraction. This leads to the appearance of a local maximum for \mathcal{U} at D_0 . This creates a free energy barrier that particles have to cross to collide. If this barrier is greater than kT , then particles remain at a distance $D > D_0$ from their neighbours. In this case, the suspension of particles is stabilized. We call this the *electrostatic stabilization*.



Chapter 2

From capillarity to Density Functional Theory (DFT)

2.1 Quick reminder

Creating a surface between two phases has a cost of energy. We call the cost of free energy per unit area the *surface tension* or *surface energy*. We write it γ_{ij} where i and j refer to the two phases in contact at the interface (in general, L for liquid, V for vapour and S for solid).

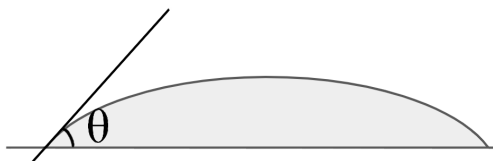
As an order of magnitude: $\gamma_{LV}^{(water)} \sim 70 \text{ mN m}^{-1}$.

As you may have noticed, the unity of γ is the same as for $\frac{\text{Force}}{\text{Length}}$ or for Pressure \times Length.

This is a good way to remember that one effect of surface tension is to create forces on lines of interface, normal to the line and parallel to the interface, which are equal to γl where l is the length of the line of interface considered. Another effect of surface tension is to create a discontinuity of pressure across curved interfaces: $p_{ext} - p_{int} = \gamma \mathcal{C}$, where \mathcal{C} is the curvature of the interface. This is called the *Laplace pressure*.

Finally, the contact angle of a liquid drop on a solid in a gas atmosphere is given by the *Young angle* θ :

$$\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$$



2.2 Capillarity induced phase transitions

2.2.1 Liquid-vapour phase transition

There is an equilibrium between the liquid and the gas phases where the chemical potentials of both phases are equal. This leads to an equation ($\mu_{liquid}(T, P) = \mu_{gas}(T, P) = \mu_{sat}(T)$), which, when solved, gives a relation between the temperature T and the pressure P . With this relation, one can build a phase transition diagram, where a line $P = P_{sat}(T)$ gives the equilibrium of the two phases.

2.2.2 Effect of capillarity

Now we consider a more complex situation. We take a vapour phase, with T and P so that $\mu(T, P) \neq \mu_{sat}(T, P)$. In such a system, we put a porous material, whose pores have a typical diameter H . We want to know the state of the fluid inside the pores depending on H . Will it stay gaseous or will it become liquid?

Qualitative description

The vapour is more stable in the bulk (this is our hypothesis), therefore, the free energy of the vapour is lower than the liquid's: $f_V \times V < f_l \times V$ where f_i is the free energy of the phase i by unit volume.

But if the surface are wetting ($\gamma_{SV} > \gamma_{SL}$), the free energy due to the interface is $\gamma_{SL} \times \text{Area} < \gamma_{SV} \times \text{Area}$.

There is a competition between a bulk effect and a surface effect. Thus, a typical length scale H_c will emerge from the proper calculation of the free energy. From what we've already said, when $H > H_c$, the bulk effect will dominate and there will be vapour in the pores. On the contrary, if $H < H_c$, the surface effect will dominate and the pores will be filled by liquid: it is the *capillary condensation*.

Proper thermodynamics

We will work in the grand canonical ensemble (the thermodynamical variables are then μ , V and T). The system that we will work on is the porous material, which can exchange particles with the bulk, that we will see as a reservoir of particles with fixed μ and T .

The grand potential of such system is:

$$\Omega = F - \mu N = -pV + \gamma A$$

where V is the volume of the pores in the porous material, and A their area.

To simplify the calculation, we will now only consider one pore, which is a gap between two parallel surfaces of area A . Here, the surface of the pore is $2A$.

We have to compare two situations: the pore is either filled with vapour (with its grand potential written as Ω_V), either filled with liquid (Ω_l): $\Omega_i = -p_i V + 2\gamma_{Si} A$.

We have then:

$$\Delta\Omega = \Omega_l - \Omega_V = -(p_L - p_V)HA + 2(\gamma_{SL} - \gamma_{SV})A = A(\Delta p H - 2\gamma_{LV} \cos \theta)$$

where θ is given by Young law.

If $\Delta\Omega > 0$, then the vapour is favoured, else it is the liquid that is favoured. And H_c is obtained for $\Delta\Omega(H_c) = 0$. We have then:

$$H_c = \frac{2\gamma_{LV} \cos \theta}{p_V - p_L}$$

which is called the *Kelvin length*.

Kelvin length expressed in RH (Relative Humidity)

We define RH as: $\text{RH}(T) = \frac{p_V^{(\text{water})}}{p_{\text{sat}}(T)}$, and we want to express H_c as a function of RH.

First, we want to express RH as a function of $\Delta\mu = \mu_{\text{sat}} - \mu$. We write $\mu = \mu_L = \mu_V$ since in both cases the liquid of gaseous phase is in equilibrium with the reservoir at fixed chemical potential μ .

As we assimilate our vapour to a perfect gas, we have: $\mu_V = \mu = kT \log(\rho_V \lambda_T^3) = kT \log\left(\frac{p_V}{kT} \lambda_T^3\right)$ (where λ_T is the thermal de Broglie wavelength).

As a consequence:

$$\Delta\mu = \mu_{\text{sat}} - \mu = kT \log \frac{p_{\text{sat}}}{p_V} = kT \log(\text{RH}^{-1})$$

Now, we want to express $p_V - p_L$ as a function of $\Delta\mu$. To do so, we use the *Gibbs-Duheim relationship*:

$$N d\mu = V dp - S dT$$

Considering that the liquid we may obtain is incompressible: $\rho_L = N/V$ is constant (and independent of p_L), with Gibbs-Duheim at fixed T ($dT = 0$): $dp = \rho_L d\mu$. Integrating yields: $p_L - p_{\text{sat}} = -\rho_L \Delta\mu$.

Finally, considering that $p_i - p_{\text{sat}} \propto \rho_i$ and $\rho_V \ll \rho_L$, we have: $p_V \ll p_L$, and finally:

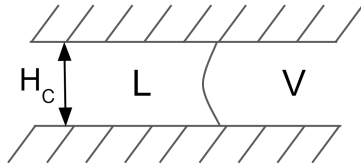
$$p_V - p_L \approx -p_L = \rho_L \Delta\mu$$

Finally:

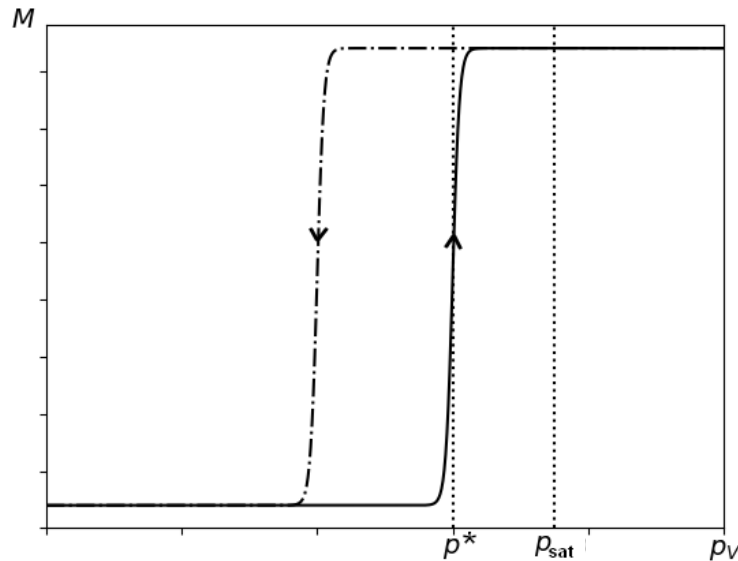
$$H_c = \frac{2\gamma_{LV} \cos \theta}{\rho_L \Delta\mu} = \frac{2\gamma_{LV} \cos \theta}{\rho_L kT \log(RH^{-1})}$$

Remark.

1. If $H < H_c$, we can have a phase transition even though $\mu < \mu_{sat}$: here, confinement has induced a shift of transition.
2. The value of H_c could have also been computed by considering a system where both liquid and gaseous phases are in equilibrium and form a meniscus. This situation only occurs when $H = H_c$, when both phases have the same free energy. With the expression of the Laplace pressure at the meniscus, the value of H_c can easily be found.



If we weigh such a porous medium in a reservoir of gas, we would obtain a very sharp sigmoid-like $masse = f(pression)$ curve. The point of inflexion of this curve is then p^* such that $p^* = p_{sat} - \frac{2\gamma \cos \theta}{H}$, where H is the size of the pores in the porous material. If there is a distribution of pore sizes in the material, then the curve $masse = f(pression)$ will be a superposition of the curve obtained for a unique pore size. Such a curve can then be a way to measure experimentally the distribution of pore sizes in a given porous material.



Remark. The hysteresis that can be seen in the curve is due to the nature of the transition induced by capillary condensation. Even though the system might be in a less favorable state than its minimum of energy, there is an energy barrier that has to be crossed to go to the favored state. This energy barrier delays the transition and is the cause of the hysteresis that can be observed.

Orders of magnitude

The Kelvin length for water in our atmosphere is about 1 nm. Typically:

$$H_c \sim \frac{1 \text{ nm}}{\log \text{RH}^{-1}}$$

And, if we compute the Δp induced by the *capillary bridge* (the filling of pores by liquid), we obtain: $\Delta p \sim 1 \times 10^3$ bar which is very huge. That's why such even small in size objects may have a macroscopic effect.

An effect of capillary condensation: adhesion

The capillary bridges that may be created by capillary condensation act like a glue. In fact, they change the Amontons-Coulomb law by adding an additional force in the slip threshold:

$$F_T \leq (F_N + F_{cap})$$

And for a porous medium, F_{cap} may depend on the "age" of the medium. Indeed, the filling of pores in the material may take some time, and the longer we wait before pushing the material, the more it has been filled by water, and the larger F_{cap} will be. The growth of F_{cap} is generally logarithmic with respect to the time of wait, because of the large distribution of pore sizes.

2.3 Density Functional Theory

Now, we will try to better describe an interface between liquid and vapour.

2.3.1 Thermodynamics

We could write an hamiltonian for the system, derive from it the partition function:

$$Z_N = \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \exp\left(-\frac{1}{kT} H(\{\mathbf{r}_i\}, \{\mathbf{p}_i\})\right)$$

and then obtain the free energy $F(N, V, T) = -kT \log Z_N$ in the canonical ensemble.

But, most of times, we work with fixed density $\rho = N/V$ and then the thermodynamic variables are related, which is a problem. In fact, the grand canonical ensemble (μ, V, T) is better suited to describe systems with fixed densities. (Furthermore, free energy is not the best to describe equivalence between different phases).

We can then introduce the grand potential $\Omega(\mu, V, T) = F - \mu N = -p(\mu, T)V$. We will also introduce the intensive $\omega = \Omega/V$: $\omega(\rho; \mu, T) = f(\rho, T) - \mu\rho$ where $f = F/V$. In $\omega(\rho; \mu, T)$, ρ is not a thermodynamic variable, it has to be seen as a constraint, whose value at equilibrium minimizes ω ($\partial_\rho \omega(\rho_{eq}) = 0$). This is a way to say $\partial_\rho f(\rho_{eq}) = \mu$: the chemical potential of the system is equal at equilibrium to the one of the reservoir.

First example with a perfect gas

$$Z_N = \frac{1}{N!} \frac{V^N}{\lambda_T^{3N}}$$

$$\text{with } \lambda_T = \sqrt{\frac{h^2}{2\pi m k T}}.$$

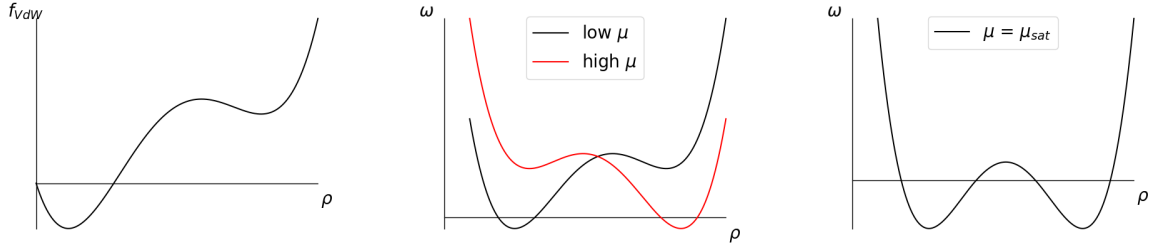
$$f = \frac{F}{V} = kT [\rho \log(\rho \lambda_T^3) - \rho]$$

And then:

$$\omega(\rho) = kT [\rho \log(\rho \lambda_T^3) - \rho] - \mu \rho$$

And the equilibrium finally gives:

$$\mu = kT \log(\rho \lambda_T^3)$$



And now with a Van der Waals fluid

The Van der Waals model takes into account two main things:

1. The fluid's molecules interact via Van der Waals attraction.
2. There is a hard core repulsion at short distance.

With such a model, the contribution to the free energy per unit volume of the interactions between particles is given by $-\frac{1}{2}a(T)\rho^2$. The free energy per unit volume is then:

$$f = kT \left[\rho \log \left(\frac{\rho \lambda_T^3}{1 - b\rho} \right) - \rho \right] - \frac{1}{2}a(T)\rho^2$$

A good model close to critical point is then:

$$\Delta\omega = \omega - \omega_{sat} = A(\rho - \rho_L)^2(\rho - \rho_V)^2$$

2.3.2 Introducing the heterogeneity

Now, the fluid density may vary with space. As a consequence, $\Omega(\{\rho\})$ is a functional of $\rho(\mathbf{r})$. If we suppose that the variations of ρ are small (the gradients are negligible), we can write Ω as an expansion of ρ and its derivatives.

If we make the *local density approximation* (LDA), we totally neglect the gradients, and write:

$$\Omega(\{\rho\}) = \int d\mathbf{r} \omega(\rho(\mathbf{r}))$$

But here, we want to take into account the cost in energy of density gradients. To do so, we add the first term compatible with the symmetries of our system (isotropy, etc...), which is $|\nabla\rho|^2$.¹ We then have:

$$\Omega(\{\rho\}) = \int d\mathbf{r} \omega(\rho(\mathbf{r})) + \frac{1}{2}m|\nabla\rho|^2$$

We orientate our x axis so that $\rho(-\infty) = \rho_L$ and $\rho(+\infty) = \rho_V$. The minimization through the Euler-Lagrange equation yields (in a 1D system):

$$-m \frac{d^2\rho}{dx^2} + \frac{d\omega}{d\rho} = 0$$

¹For a deeper description of symmetry arguments, see Chaikin & Lubensky.

Taking the first integral:

$$-\frac{1}{2}m \left(\frac{d\rho}{dx} \right)^2 + \Delta\omega = cst$$

With the boundary conditions ($\Delta\omega = 0$ and $\frac{d\rho}{dx} = 0$ at $\pm\infty$), we have $cst = 0$ and then, asking for ρ to be decreasing:

$$\frac{d\rho}{dx} = -\sqrt{\frac{2}{m}\Delta\omega(\rho)}$$

A separation of variables gives:

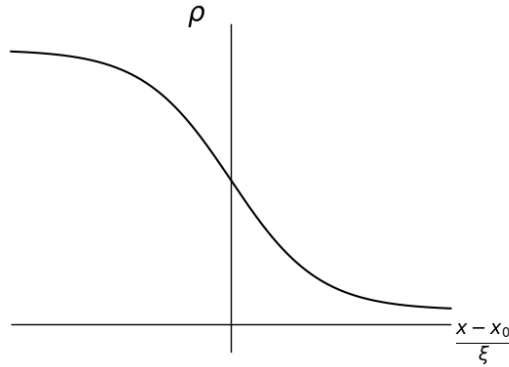
$$\int \frac{d\rho}{\frac{2}{m}\Delta\omega(\rho)} = -x + cst$$

And finally, using $\Delta\omega = A(\rho - \rho_L)^2(\rho - \rho_V)^2$ and $\rho_V < \rho < \rho_L$, we obtain:

$$\rho(x) = \frac{\rho_V + \rho_L e^{-\frac{x-x_0}{\xi}}}{1 + e^{-\frac{x-x_0}{\xi}}}$$

where $\xi = \frac{1}{\sqrt{\frac{2A}{m}\Delta\rho}}$.

Remark. When $T \rightarrow T_c$, $\rho_L \rightarrow \rho_v$ and $\xi \rightarrow \infty$: the characteristic length of the interface diverges when approaching criticality.



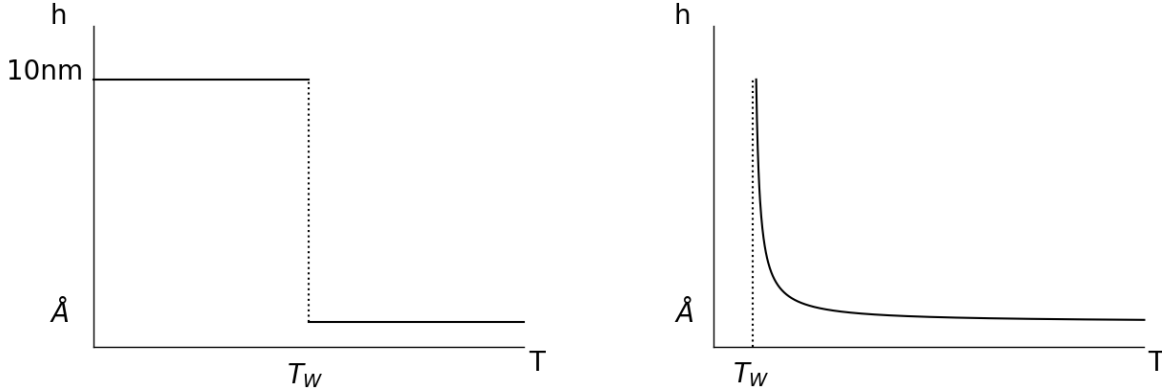
2.4 Cahn-Hilliard theory of wetting transition

2.4.1 Experimental results and introduction of some concepts

The wetting properties of a liquid on a substrate depend on its temperature. Indeed, many experiments have shown a transition from a partial wetting (characterized by its Young's angle) to a total wetting (when a drop of the liquid entirely spreads when deposited on the solid substrate). To characterize this wetting property, one can look at the thin wetting film at the vicinity of a drop of liquid initially partially wetting on a solid substrate. When varying the temperature of the system, a transition occurs and the initially very thin film of liquid (of a molecular size) becomes huge ($\sim 10 - 100$ nm).

The experiments have exhibited two types of behaviour:

1. A first order one, when the transition is discontinuous, and when the the thcikness of the film remains finite.
2. A second order one, when the transition from a thin to a thick film of liquid is continuous. When $T \rightarrow T_W$, the thickness of the film diverges.



Our goal is to describe and to distinguish these two types of transition. We will again use a square gradient theory (*i.e.* a theory where $|\nabla\rho|^2$ appears in the free energy (in the following, we will call Ω the free energy, even though this is in fact the grand potential. $\Omega = F - \mu N$).

Finally, as we want to describe the wetting of a liquid on a substrate, we will have to consider the *spreading parameter*: $S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$. If $S > 0$, then $\gamma_{SV} > (\gamma_{SL} + \gamma_{LV})$ and the existence of layer of liquid between the solid and the vapour is favoured: the system is wetting. Inversely, if $S < 0$, the system is just partially wetting: the liquid forms a drop whose contact angle is determined by Young's law.

2.4.2 Thermodynamics

The total free energy of the system is given by the free energy of the fluid (liquid or gas), that we have described in the previous part, and the free energy of the solid. Calling ρ_S the density of the fluid directly in contact with the solid substrate, we can make a Taylor expansion of the free energy per unit area of the solid substrate with respect to ρ_S : $\Delta\Omega_S/\mathcal{A} = \gamma_S^{(0)} - \gamma_S^{(1)}\rho_S + \frac{1}{2}\gamma_S^{(2)}\rho_S^2$, where the second order has been kept to ensure a saturation of ρ_S when minimizing the free energy, and where $\gamma_S^{(i)} > 0$.

Then, the total free energy per unit area is (with z being the axis normal to the surface of the solid substrate):

$$\frac{\Delta\Omega^{TOT}(\{\rho\}, \rho_S)}{\mathcal{A}} = \gamma_S^{(0)} - \gamma_S^{(1)}\rho_S + \frac{1}{2}\gamma_S^{(2)}\rho_S^2 + \int dz \left[\frac{1}{2}m|\nabla\rho|^2 + \Delta\omega(\rho) \right]$$

Minimizing with respect to $\{\rho\}$ yields the same equations as in the previous part (in 1D):

$$-m\frac{d^2\rho}{dz^2} + \frac{d\omega}{d\rho} = 0$$

And the first integral gives:

$$d\rho = -dz \sqrt{\frac{2}{m}\Delta\omega(\rho)}$$

In 1D, we then have:

$$\frac{1}{2}m|\nabla\rho|^2 + \Delta\omega(\rho) = \frac{m}{2} \times \frac{2}{m} \Delta\omega(\rho) + \Delta\omega(\rho) = 2\Delta\omega(\rho)$$

And finally, changing variables in the integral yields:

$$\int dz \left[\frac{1}{2}m|\nabla\rho|^2 + \Delta\omega(\rho) \right] = \int d\rho \sqrt{2m\Delta\omega(\rho)}$$

We can now write the total free energy per unit area with ρ_S and $\rho_{bulk} = \lim_{z \rightarrow \infty} \rho(z)$:

$$\frac{\Delta\Omega^{TOT}}{\mathcal{A}} = \gamma_S^{(0)} - \gamma_S^{(1)}\rho_S + \frac{1}{2}\gamma_S^{(2)}\rho_S^2 + \int_{\rho_{bulk}}^{\rho_S} d\rho \sqrt{2m\Delta\omega(\rho)}$$

Minimizing with respect to ρ_S finally yields:

$$\sqrt{2m\Delta\omega(\rho_S)} = \gamma_S^{(1)} - \gamma_S^{(2)}\rho_S$$

2.4.3 Graphical solution for a Van der Waals fluid

Let's recall the simple equation we used in the previous section for $\Delta\omega$:

$$\Delta\omega = A(\rho - \rho_V)^2(\rho - \rho_L)^2$$

With such a model, the equation for ρ_S is given by:

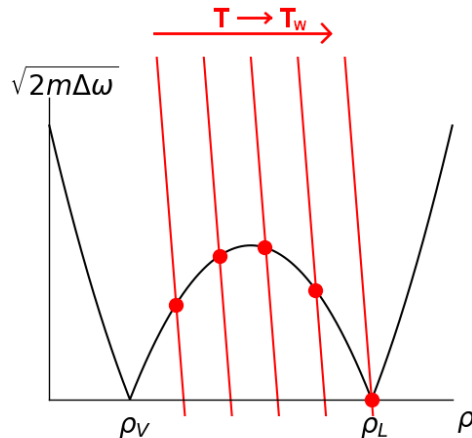
$$\sqrt{2mA}|\rho_S - \rho_V||\rho_S - \rho_L| = \gamma_S^{(1)} - \gamma_S^{(2)}\rho_S$$

Put graphically, this means that ρ_S is found by looking for the intersection between a straight line and a juxtaposition of parabolas.

Now we have to distinguish two cases: is the slope $\gamma_S^{(2)}$ high enough for the straight line to cross more than once the parabolas? We are interested in the region where $\rho_S \approx \rho_L$ (the region of the transition from a thin layer of liquid to a thick one), so we want to compare $\gamma_S^{(2)}$ to $\sqrt{2mA}(\rho_L - \rho_V)$.

In the following, we will consider that $\gamma_S^{(2)}$ is fixed (it represents the hard-core repulsion of particles which does not really depend on temperature) and that $\gamma_S^{(1)}$ increases when T decreases (when the entropy decreases, the attraction effect increases).

First case: $\gamma_S^{(2)} > \sqrt{2mA}\Delta\rho$

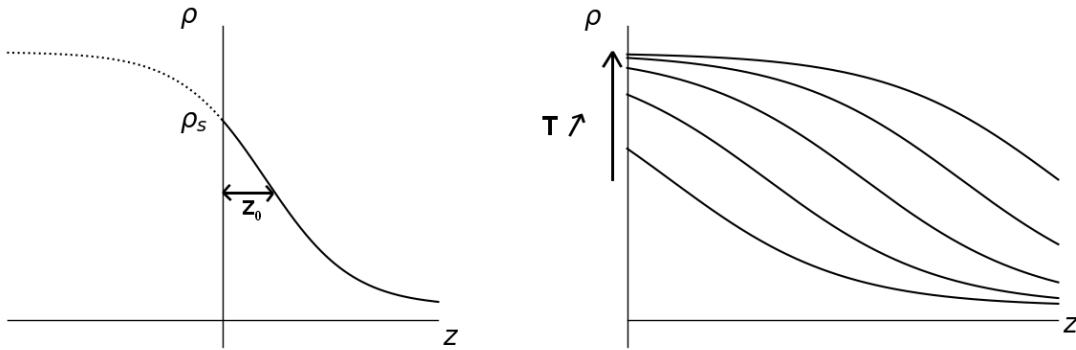


Close to ρ_L , the straight line will intersect only at one point the parabolas. There is no choice for the system: only one solution is possible for ρ_S . When T decreases, the straight line is translated to the higher densities, and $\rho_S \rightarrow \rho_L$. We define T_W the temperature of wetting so that $\rho_S(T_W) = \rho_L$.

This case corresponds to the second order transition: the change of ρ_S is continuous, there is absolutely no discontinuity in this transition. Now, to understand the divergence of the thickness of the layer of liquid in contact to the substrate, one has to recall the expression of $\rho(z)$ obtained in the previous section:

$$\rho(z) = \frac{\rho_V + \rho_L e^{-\frac{z-z_0}{\xi}}}{1 + e^{-\frac{z-z_0}{\xi}}}$$

Here, $\xi = \frac{1}{\sqrt{\frac{2A}{m}\Delta\rho}}$ and is rather constant: T is varying close to T_W in our description, and is far enough from criticality so that $\Delta\rho(T) \approx cst$.



In our expression for $\rho(z)$, there is still one parameter that has to be fixed: z_0 . To fix it one has to recall that we impose a density ρ_S on the contact with the solid substrate, at $z = 0$. In that case, z_0 is fixed so that $\rho(z = 0) = \rho_S$. Thus, varying ρ_S is just shifting our density profile sigmoid so that $\rho(z = 0) = \rho_S$. We have:

$$z_0 = \xi \log \left(\frac{\rho_S - \rho_V}{\rho_L - \rho_S} \right) \approx \frac{1}{\sqrt{\frac{2A}{m}\Delta\rho}} \log \left(\frac{\Delta\rho}{\rho_L - \rho_S} \right)$$

and z_0 is in fact the typical thickness of the layer of liquid. We recover as shown by the experiments the divergence of the thickness:

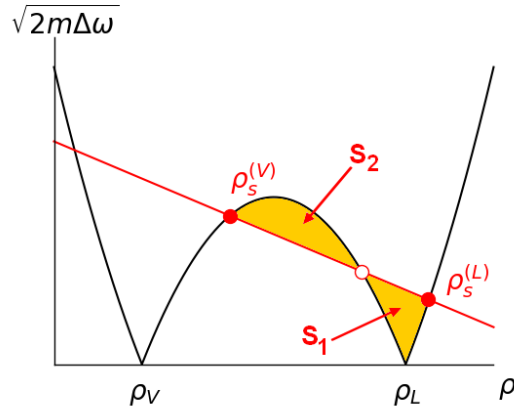
$$\lim_{\rho_S \rightarrow \rho_L} z_0 = +\infty$$

Second case: $\gamma_S^{(2)} < \sqrt{2m\bar{A}\Delta\rho}$

Here, the slope of the straight line is low enough for it to intersect three times the parabolas. In that case, there are two stable solutions for ρ_S . The system has to choose between these two values of ρ_S : $\rho_S^{(V)}$ being close to ρ_V and $\rho_S^{(L)}$ being close to ρ_L (with $\rho_S^{(L)} > \rho_L$).

Remark. The solution $\rho(z) = \frac{\rho_V + \rho_L e^{-\frac{z-z_0}{\xi}}}{1 + e^{-\frac{z-z_0}{\xi}}}$ has been obtained for $\rho_V < \rho < \rho_L$. When $\rho > \rho_L$, one has to redo the calculation with: $\int \frac{d\rho}{\frac{2}{m}\Delta\omega(\rho)} = -x + cst$ and $\sqrt{\Delta\omega} = \sqrt{\bar{A}(\rho - \rho_L)(\rho - \rho_V)}$.

This choice of value for ρ_S will depend one what is the more favoured between a solid-liquid-vapour and a solid-vapour interfaces. It will then depend on the value of the spreading parameter $S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV})$.



To compute it, we first need to obtain the equations giving γ_{ij} . For that, one has to recall the definition of the surface tension being the free energy per unit area caused by interfaces. We've already written it, without calling it the surface tension:

$$\begin{aligned}\gamma_{LV} &= \int_{\rho_V}^{\rho_L} d\rho \sqrt{2m\Delta\omega} \\ \gamma_{SV} &= \int_{\rho_V}^{\rho_S^{(V)}} d\rho \sqrt{2m\Delta\omega} - \int_{\rho_0}^{\rho_S^{(V)}} d\rho \left(\gamma_S^{(1)} - \gamma_S^{(2)} \rho \right) \\ \gamma_{SL} &= \int_{\rho_L}^{\rho_S^{(L)}} d\rho \sqrt{2m\Delta\omega} - \int_{\rho_0}^{\rho_S^{(L)}} d\rho \left(\gamma_S^{(1)} - \gamma_S^{(2)} \rho \right)\end{aligned}$$

where ρ_0 is chosen so that: $\int_{\rho_0}^{\rho_S^{(L)}} d\rho \left(\gamma_S^{(1)} - \gamma_S^{(2)} \rho \right) = \gamma_S^{(0)} - \gamma_S^{(1)} \rho_S + \frac{1}{2} \gamma_S^{(2)} \rho_S^2$.

Finally:

$$S = \gamma_{SV} - (\gamma_{SL} + \gamma_{LV}) = \int_{\rho_S^{(V)}}^{\rho_S^{(L)}} d\rho \left(\gamma_S^{(1)} - \gamma_S^{(2)} \rho - \sqrt{2m\Delta\omega(\rho)} \right)$$

Graphically, this corresponds to saying that $S = S_1 - S_2$ where the areas S_1 and S_2 are defined in the previous figure

Here, T_W is defined differently: for $T = T_W$, $S_1 = S_2$. If we still assume that $\gamma_S^{(1)}$ increases when T decreases, we can see graphically, that:

- If $T > T_W$, $S_1 < S_2$ and then $S < 0$: a thick liquid film is not favoured and the system is partially wetting. We also have $\rho_S = \rho_S^{(V)}$.
- If $T < T_W$, $S_1 > S_2$ and then $S > 0$: a thick liquid film is favoured and the system is totally wetting. We also have $\rho_S = \rho_S^{(L)}$.

In this case, when T crosses T_W , the system jumps instantaneously from a partially wetting to a totally wetting state. ρ_S is a discontinuous function of T . This transition is a first order transition.

2.5 Dynamics: Time-Dependent Density Functional Theory (TD-DFT)

For the moment, we have only described the equilibrium state of a given system. But, here, we want to discuss the dynamics of its trajectory towards its equilibrium. If we perturb the system, how will it go back to its equilibrium?

Again, we will not do a microscopic description of our system (it is far too difficult), but we will use a coarse-grain (or mesoscopic) description.

2.5.1 Phenomenological laws

Supported by experiments, phenomenological laws have been proposed to describe such dynamics. The following laws will focus on the density dynamics.

Non-conserved dynamics

$$\frac{\partial \rho}{\partial t} = -\Gamma \frac{\delta \Omega}{\delta \rho}$$

This is just a way to minimize Ω with respect to ρ by the steepest descent. This is very similar to the proportionality between the velocity and the viscous friction in mechanics.

These dynamics are called “non-conserved” because the total number of particles $\int d\mathbf{r} \rho$ is not conserved with such dynamics.

Conserved dynamics

$$\frac{\partial \rho}{\partial t} = \lambda \nabla^2 \frac{\delta \Omega}{\delta \rho}$$

To derive this law, we take the conservation law: $\frac{\partial \rho}{\partial t} = -\nabla \cdot \mathbf{J}$ where \mathbf{J} is a current of particles given by the phenomenological law: $\mathbf{J} = -\lambda \nabla \mu$ where $\mu = \frac{\delta \Omega}{\delta \rho}$ is the chemical potential of the system.

2.5.2 Application to the DFT theory

We have in the DFT theory including square gradients:

$$\Omega(\{\rho\}) = \int d\mathbf{r} \left[\frac{1}{2} m |\nabla \rho|^2 + \omega(\rho(\mathbf{r})) \right]$$

We then have:

$$\frac{\delta \Omega}{\delta \rho} = -m \nabla^2 \rho + \frac{d\omega}{d\rho}$$

For conserved dynamics:

$$\frac{\partial \rho}{\partial t} = \lambda \nabla^2 \left[-m \nabla^2 \rho + \frac{d\omega}{d\rho} \right]$$

Now, we want to study the relaxation of fluctuations around the equilibrium. We then write ρ as $\rho = \rho_0 + \delta \rho$ where ρ_0 is the homogeneous equilibrium density for the system.

The previous equation becomes now, linearized with $\delta \rho \ll \rho_0$:

$$\frac{\partial \delta \rho}{\partial t} = \lambda \nabla^2 \left[-m \nabla^2 \delta \rho + \omega''(\rho_0) \delta \rho \right]$$

Remark. $\omega''(\rho_0)$ is related to the compressibility of the fluid. If $\chi_T = -\frac{1}{V} \frac{\partial V}{\partial P}|_T$, then: $\omega''(\rho_0) = \frac{1}{\rho_0^3 \chi_T}$ (obtained thanks to the Gibbs Duheim relation $\rho d\mu = dp$ and to $\omega'' = \frac{d\mu}{d\rho}$). The thermodynamic stability implies that $\chi_T \geq 0$, then ω is a complex function of ρ .

To study this equation on $\delta \rho$, we go in Fourier space, with the conventions:

$$\begin{aligned} \delta \hat{\rho}(\mathbf{q}, t) &= \int d\mathbf{r} \delta \rho(\mathbf{r}, t) e^{i\mathbf{q} \cdot \mathbf{r}} \\ \delta \rho(\mathbf{r}, t) &= \int \frac{d\mathbf{q}}{(2\pi)^3} \delta \hat{\rho}(\mathbf{q}, t) e^{-i\mathbf{q} \cdot \mathbf{r}} \end{aligned}$$

In Fourier space, the differentiation equation on $\delta\rho$ becomes:

$$\frac{\partial \delta \hat{\rho}}{\partial t} = -\lambda [mq^4 + \omega''(\rho_0)q^2] \delta \hat{\rho}$$

Integrating this yields, with $\nu(q) = \lambda [mq^4 + \omega''(\rho_0)q^2]$:

$$\delta \hat{\rho}(\mathbf{q}, t) = \delta \hat{\rho}(\mathbf{q}, t=0) e^{-\nu(q)t}$$

We recover from this that for ρ to be stable, we need $\omega''(\rho) > 0$.

From this, we can, if we want to, recover $\rho(\mathbf{r}, t)$ in real space.

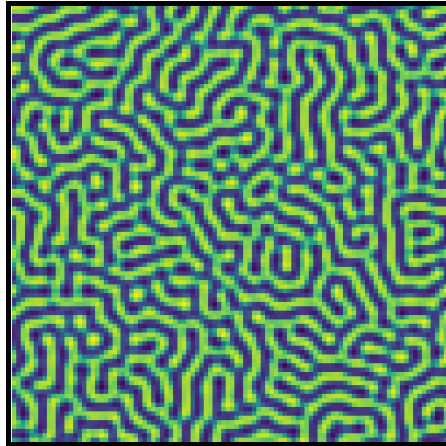
Application: spinodal decomposition

Spinodal decomposition is a mechanism for the rapid unmixing of a mixture of two phases. Our Fourier description of the dynamics of $\delta\rho$ gives us to have a qualitative understanding on how these two phases unmix.

To illustrate the process, let's imagine that we first have a system at a temperature such that $\omega''(\rho_0) > 0$. For the moment, for all \mathbf{q} , $\nu(q) > 0$ and all modes are stable for the system.

Now we modify the temperature so that $\omega''(\rho_0) < 0$. Now, $\nu q = \lambda [mq^4 + \omega''(\rho_0)q^2]$ will be negative for small values of q . In particular, $\nu(q)$ has a minimum at $q^* = \sqrt{-\frac{\omega''(\rho_0)}{2m}}$ which corresponds to the most unstable mode of the system.

The consequence of this is the exponential growth of the unstable modes, which is the fastest for the mode q^* . In this spinodal decomposition, we will see the appearance of two domains corresponding to the two phases unmixing, the unmixing having a typical lengthscale $\lambda^* \sim 1/q^*$.



Chapter 3

Fluctuations and entropic interactions

In the following we will study the statistical aspects of the parameters describing the interfaces developed in the previous chapters. As before, we will denote $\langle X \rangle$ the mean value of a random variable X .

As a consequence to the central limit theorem, we will encounter many times the normal probability distribution:

$$\mathcal{P}(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2}\right)$$

which yields $\langle x \rangle = 0$ and $\langle x^2 \rangle = \sigma^2$.

In physics, this normal distribution is very often given by the Boltzmann weight. For a given configuration $\{X_i\}$ of the system:

$$\mathcal{P}(\{X_i\}) \propto \exp\left(-\frac{H(\{X_i\})}{kT}\right)$$

where H is the hamiltonian of the considered system.

A general property of such a Boltzmann distribution is the equipartition theorem. This theorem essentially states:

$$\frac{1}{2}\alpha\langle X^2 \rangle = \frac{1}{2}kT$$

if X is described by a Boltzmann distribution and $\frac{1}{2}\alpha\langle X^2 \rangle$ is an independent contribution in the hamiltonian of the system ($H = H_0 + \frac{1}{2}\alpha\langle X^2 \rangle$ where H_0 does not depend on X).

This result is obtained by integrating by part the expression of $\langle X^2 \rangle$ (the contribution of H_0 simplifies itself by being factorized out of the integrals on dx):

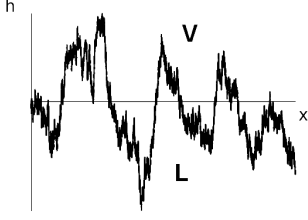
$$\langle X^2 \rangle = \frac{\int dx x^2 \exp\left(-\frac{1}{2}\frac{\alpha x^2}{kT}\right)}{\int dx \exp\left(-\frac{1}{2}\frac{\alpha x^2}{kT}\right)} = \frac{\left[-\frac{kT}{\alpha} x \exp\left(-\frac{1}{2}\frac{\alpha x^2}{kT}\right)\right]_{-\infty}^{+\infty} + \frac{kT}{\alpha} \int dx \exp\left(-\frac{1}{2}\frac{\alpha x^2}{kT}\right)}{\int dx \exp\left(-\frac{1}{2}\frac{\alpha x^2}{kT}\right)} = \frac{kT}{\alpha}$$

As a consequence of this equipartition theorem, for each quadratic degree of freedom $\frac{1}{2}\alpha X^2$ in the hamiltonian of a system, there is a contribution of $\frac{1}{2}kT$ in the mean energy of this system.

3.1 Fluctuation of liquid-vapour interfaces

3.1.1 Introduction

We want to study the amplitude of the fluctuations of a liquid-vapour interface. Thus, we consider a system composed of vapour and of liquid, divided along the $z = 0$ plane by an interface given by its height $h(x, y, t)$. To study this system, the strategy is first to obtain its free energy. Then, the probability of a given interface configuration $\{h\}$ will be: $\mathcal{P}(\{h\}) \propto \exp\left(-\frac{\mathcal{F}(\{h\})}{kT}\right)$.



Here, we suppose that $\mu_L = \mu_V$: the two phases coexist at equilibrium. Therefore, there is no bulk cost to the overall quantities of liquid or vapour: the only cost comes from the interface. As a consequence, by definition of the surface tension, we immediately obtain: $\mathcal{F} = \gamma_{LV} \times Area$. And the area is given by: $Area = \int dx dy \sqrt{1 + |\nabla h|^2}$.

Taking a reference \mathcal{F}_0 for $h = cst$ and supposing $|\nabla h|^2 \ll 1$, we finally have:

$$\Delta\mathcal{F} = \mathcal{F} - \mathcal{F}_0 = \frac{1}{2}\gamma_{LV} \int dx dy |\nabla h|^2$$

We will also add the effect of gravity on the interface. To do so, we will neglect the density of the vapour, and call ρ the density of the liquid. With this, we now have:

$$\Delta\mathcal{F} = \int dx dy \left[\frac{1}{2}\gamma_{LV} |\nabla h|^2 + \frac{1}{2}\rho g h^2 \right]$$

With \mathcal{F} we will be able to compute $\langle h^2 \rangle(x, y)$. We will then compute $(\Delta h)^2 = \frac{1}{L^2} \int dx dy \langle h^2 \rangle(x, y)$, which is the mean fluctuation of h averaged on the whole surface.

3.1.2 Fourier analysis

We decompose h on its Fourier modes as: $h_{\mathbf{q}} = \int d\mathbf{r} h(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}}$. We obtain thanks to the Parseval theorem:

$$\Delta\mathcal{F} = \int \frac{d\mathbf{q}}{(2\pi)^2} \frac{1}{2} (\gamma_{LV} q^2 + \rho g) |h_{\mathbf{q}}|^2$$

If the box containing our system is of size L , then \mathbf{q} is discretized as $\mathbf{q} = \frac{2\pi}{L}(n\hat{\mathbf{e}}_x + m\hat{\mathbf{e}}_y)$ where $(n, m) \in \mathbb{Z}^2$. This trick allows us to see $\Delta\mathcal{F}$ as a sum of independent quadratic terms:

$$\Delta\mathcal{F} = \frac{1}{L^2} \sum_{\mathbf{q}} \frac{1}{2} (\gamma_{LV} q^2 + \rho g) |h_{\mathbf{q}}|^2$$

Thanks to the equipartition theorem, for each \mathbf{q} , we have:

$$\langle |h_{\mathbf{q}}|^2 \rangle = \frac{kTL^2}{\gamma_{LV} q^2 + \rho g}$$

We have, thanks again to Parseval's theorem:

$$(\Delta h)^2 = \frac{1}{L^2} \int dx dy \langle h^2 \rangle(x, y) = \frac{1}{L^2} \int \frac{d\mathbf{q}}{(2\pi)^2} \langle |h_{\mathbf{q}}|^2 \rangle$$

Injecting the value obtained for $\langle |h_{\mathbf{q}}|^2 \rangle$:

$$(\Delta h)^2 = \frac{1}{L^2} \int \frac{d\mathbf{q}}{(2\pi)^2} \frac{kTL^2}{\gamma_{LV} q^2 + \rho g} = \frac{kT}{(2\pi)^2 \rho g} \int \frac{2\pi q dq}{1 + (l_c q)^2}$$

with $l_c = \sqrt{\frac{\gamma_{LV}}{\rho g}}$. Then, with the changing of variables $u = (l_c q)^2$:

$$(\Delta h)^2 = \frac{kT}{4\pi \rho g} \frac{1}{l_c^2} \int \frac{du}{1 + u} = \frac{kT}{4\pi \gamma_{LV}} [\log(1 + u)]_0^{u_{max}}$$

u_{max} is a natural cut-off that occurs because q is limited by $q_{max} = \frac{2\pi}{a}$ where a is a characteristic microscopic lengthscale. This is a way to take into account *a posteriori* the microscopic degrees of freedom. Finally, we have:

$$(\Delta h)^2 = \frac{kT}{4\pi \gamma_{LV}} \log \left(1 + \left(2\pi \frac{l_c}{a} \right)^2 \right)$$

Remark.

1. If $g \rightarrow 0$, $l_c \rightarrow +\infty$, and $u_{max} = l_c q_{max} \rightarrow +\infty$ is no longer a good cut-off and the cut-off is now given by the size L of the box.
2. Close to the critical point, we have $\gamma_{LV} \rightarrow 0$ as $\gamma_{LV} \propto (\rho_L - \rho_V)^3$:

$$\gamma_{LV} = \int_{\rho_V}^{\rho_L} d\rho \sqrt{2m\Delta\omega} = \sqrt{2m\bar{A}} \int_{\rho_V}^{\rho_L} d\rho (\rho_L - \rho)(\rho - \rho_V) = \sqrt{2m\bar{A}}(\rho_L - \rho_V)^3 \int_0^1 dx x(1-x)$$

Close to T_c , we then have $(\Delta h)^2 \propto (\rho_L - \rho_V)^{-3}$: the interface becomes huge, until it reaches the size of the box.

3.2 Fluctuation of membranes

3.2.1 Introduction

Unlike for interfaces, membranes are a continuous material, so there are free energy costs to what corresponds to the undulations and deformations of the membrane¹:

- for the stretching of the membrane: $\Delta\mathcal{F}_{stretching} = \frac{1}{2}\kappa \left(\frac{\mathcal{A}-\mathcal{A}_0}{\mathcal{A}_0}\right)^2 \mathcal{A}_0$. But, here, we will consider that κ is so large that $\mathcal{A} \approx \mathcal{A}_0$.
- for the bending of the membrane: $\Delta\mathcal{F}_{bending} = \int d\mathbf{r} \left(\frac{1}{2}\frac{B}{\mathcal{R}^2} + \frac{1}{2}\frac{B_G}{\mathcal{R}_1\mathcal{R}_2}\right)$. Where $\frac{1}{\mathcal{R}} = \frac{1}{\mathcal{R}_1} + \frac{1}{\mathcal{R}_2}$ is the local curvature of the membrane, and $\frac{1}{\mathcal{R}_1\mathcal{R}_2}$ its gaussian curvature. The gaussian curvature can be non-negligible, but we will nonetheless forget it, in order not to be disturbed by non-linearities. For graphene, $B \sim 1$ eV.

With our simplifications, we have:

$$\Delta\mathcal{F} = \int d\mathbf{r} \frac{1}{2} \frac{B}{\mathcal{R}^2}$$

\mathcal{R} is the local radius of curvature of h . For a small enough curvature, we can write h in a parabolic approximation: $h(x, y) = h_0 + \frac{1}{2}\frac{x^2+y^2}{\mathcal{R}}$. In this approximation, we have: $\frac{1}{\mathcal{R}} = \nabla^2 h$.

And finally:

$$\Delta\mathcal{F} = \int d\mathbf{r} \frac{1}{2} B (\nabla^2 h)^2$$

3.2.2 Fourier analysis

We conduct our Fourier analysis just as before. With Parseval's theorem:

$$\mathcal{P}(\{h\}) \propto \exp\left(-\frac{1}{kT} \int d\mathbf{r} \frac{1}{2} B (\nabla^2 h)^2\right) = \exp\left(-\frac{1}{kT} \int \frac{d\mathbf{q}}{(2\pi)^2} \frac{1}{2} B q^4 |h_{\mathbf{q}}|^2\right)$$

Then, we invoke the finitude of the system (it is in a box of size L) to discretize \mathbf{q} :

$$\mathcal{P}(\{h\}) \propto \prod_{\mathbf{q}} \exp\left(-\frac{Bq^4}{2L^2kT} |h_{\mathbf{q}}|^2\right)$$

Then the equipartition theorem gives:

¹see Helfrich for a detailed description of the elasticity of cell membranes.

$$\langle |h_{\mathbf{q}}|^2 \rangle = \frac{kTL^2}{Bq^4}$$

Finally, with Parseval's theorem again:

$$(\Delta h)^2 = \frac{1}{L^2} \int dx dy \langle h^2 \rangle(x, y) = \frac{1}{L^2} \int \frac{d\mathbf{q}}{(2\pi)^2} \langle |h_{\mathbf{q}}|^2 \rangle = \frac{kT}{2\pi B} \int \frac{q dq}{q^4} = \frac{kT}{4\pi B} \left[\frac{1}{q^2} \right]_{q_{min}}^{+\infty}$$

Choosing the natural cut-off $q_{min} = \frac{2\pi}{L}$:

$$(\Delta h)^2 = \frac{kT}{16\pi^3 B} L^2$$

Remark. $\Delta h \propto L$ means that the fluctuations scale like the size of the system. One cannot neglect such fluctuations by choosing a bigger system, unlike with the fluctuations of the liquid-vapour interface.

As a numerical application, let's consider a graphene membrane, for which $B \sim 1\text{eV}$ at ambient temperature ($kT \sim \frac{1}{40}eV$): $\Delta h/L \sim 10^{-2}$. This is not that small: the fluctuations of the membranes are a phenomenon that can easily be seen.

3.3 Density fluctuations

In the DFT, we have looked at a thermodynamical potential (the grand potential or the free energy, depending on the considered ensemble). Here, we will call this thermodynamical potential the free energy and write it \mathcal{F} , but keep in mind that if we work in the grand canonical ensemble, \mathcal{F} is in fact the grand potential.

Previously, in Chapter 2, we were just looking for the equilibrium density, defined as $\frac{\delta\mathcal{F}}{\delta\rho} = 0$. Now, we want to study the fluctuations around the equilibrium homogeneous density ρ_0 , and to do so, we will use exactly the same approach as in the previous sections. We write our fluctuations as $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$, and we suppose them small before ρ_0 . Finally, we will also $f(\rho) \equiv \mathcal{F}/V$.

In the square gradient description, we have then:

$$\mathcal{F}(\{\rho\}) = \int d\mathbf{r} \left[\frac{1}{2}m|\nabla\rho|^2 + f(\rho) \right]$$

Recalling that ρ_0 is a minimum for $f(\rho)$, we can approximate $f(\rho)$ around ρ_0 : $f(\rho) \approx f_0 + f''(\rho_0)\delta\rho$. Hence:

$$\Delta\mathcal{F}(\{\rho\}) = \mathcal{F} - \mathcal{F}_0 = \int d\mathbf{r} \left[\frac{1}{2}m|\nabla\delta\rho|^2 + f''(\rho_0)\delta\rho \right]$$

As before, we use the Parseval's theorem and the Fourier transform of $\delta\rho$, and with the equipartition theorem, we obtain:

$$\langle |\delta\hat{\rho}_{\mathbf{k}}|^2 \rangle = \frac{kTV}{mk^2 + f''(\rho_0)}$$

Usually, people define here the structure factor: $S(\mathbf{k}) = \frac{1}{N} \langle |\delta\hat{\rho}_{\mathbf{k}}|^2 \rangle$.

Remark. *Be carefully, the expression obtained here is only true for small k . Indeed, the gradient approximation only holds for big length scales (hence for small k). We can not use our results to study the structure of our system at a molecular scale.*

In our expression for $\langle |\delta\hat{\rho}_{\mathbf{k}}|^2 \rangle$, a natural lengthscale appears, which is $\zeta^2 = m/f''(\rho_0)$. Recalling that $\frac{d^2f}{d\rho^2} = \frac{d\mu}{d\rho} = \frac{1}{\rho} \frac{dp}{d\rho}$ (thanks to Gibbs-Duheim's relation) and that $\chi_T = \frac{1}{\rho} \frac{dp}{d\mu}$, we have:

$$\zeta^2 = m\rho_0^2 \chi_T$$

This yields an important result: at critical point, since we have $\frac{dp}{d\rho} \rightarrow 0$ and then $\chi_T \rightarrow +\infty$:

$$\lim_{T \rightarrow T_c} \zeta^2 = +\infty$$

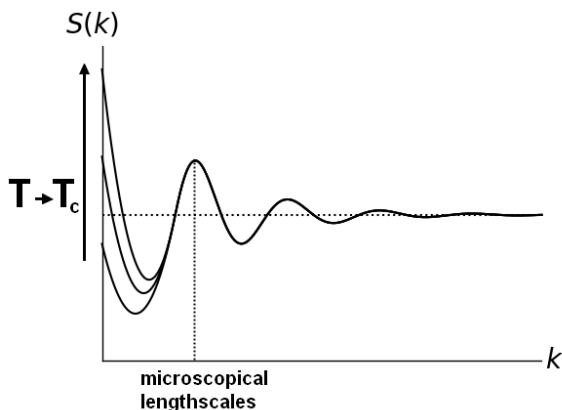
This is the cause of the milky aspect that has any solution near critical point: as soon as ζ is close to the wavelength of visible light, the solution becomes strongly diffusing.

Finally, to compute the typical size of the fluctuations of the number of particles $\langle \Delta N^2 \rangle$, one has to remember that $\Delta N = \int \mathbf{r} \delta \rho(\mathbf{r})$, which is exactly the value of $\delta \hat{\rho}_0 = \int \mathbf{r} \delta \rho(\mathbf{r}) \exp(i\mathbf{0} \cdot \mathbf{r})$.

Finally, recalling that $\rho_0 = N/V$:

$$\langle \Delta N^2 \rangle = \frac{VkT}{f''(\rho_0)} = NkT\rho_0\chi_T$$

Hence, we recover the law of large numbers: $\langle \Delta N^2 \rangle \propto N$. And we have: $\lim_{T \rightarrow T_c} \langle \Delta N^2 \rangle = +\infty$.



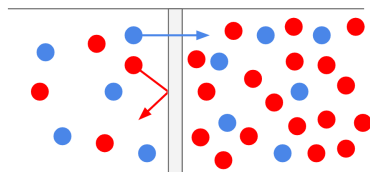
Typical $S(\mathbf{k})$.

3.4 Entropic forces

As said in the introduction, kT is the central characteristic energy in the system we consider. Hence, the entropy is a key feature of soft matter.

When we constrain a system, we reduce the accessible volume in its phase space: the entropy is therefore lower in a constrained system than in a system at equilibrium. As a consequence, the system will act against the constraint in order to reach equilibrium. In many such cases, the effect of entropy is then a conversion of entropic terms into mechanical forces.

3.4.1 Osmosis



Osmosis is an example where a difference of concentrations drives a flow across a semipermeable membrane. Let's consider a system which is a mixture of two species: the solute and the solvent. The recipient containing this mixture is separated by a semipermeable membrane, letting the solvent going through it, but not the solute. Finally, we write C_1 and C_2 the concentrations of the solute at each side of the membrane. We suppose $C_2 > C_1$ at equilibrium for the system.

Qualitative understanding

Qualitatively, the system is “unhappy” with such a situation: in the more concentrated part of the system, the solute would like to be dilute. It can be done by taking a bit of solvent from the less concentrated part of the system, which needs less solvent to be happy. But, the solvent is already at its prefer density in each part of the system (thanks to the permeable membrane that let it go towards its density equilibrium) and it does not want to flow through the membrane to “help” the solute. This unwillingness of the solvent to flow manifests as a pressure opposing the unwanted flow.

Of course, this was very qualitative, and the compromise found in satisfying both solvent and solute is given by the equality:

$$\mu_{solvent}^{(1)}(C_1, p_1) = \mu_{solvent}^{(2)}(C_2, p_2)$$

By solving it, we can obtain the Van’t Hoff law:

$$\Delta\Pi = kT\Delta C$$

where $\Delta\Pi = p_2 - p_1$ and $\Delta C = C_2 - C_1$.

Alternative calculation

Another way to obtain the Van’t Hoff law is to see the membrane as an energy barrier for the solute, creating a potential $\mathcal{U}(x)$ with $\mathcal{U}_{max} \gg kT$. Hence, the concentration of the solute at each side (1 or 2) of the membrane is at thermal equilibrium:

$$C_i(x) = C_i^\infty e^{-\frac{\mathcal{U}(x)}{kT}}$$

where C_1^∞ and C_2^∞ are the concentration given far from the membrane, and that we simply called C_1 and C_2 .

Now, the force of the membrane on the particle in a given side of the membrane is given by the derivative of its potential:

$$F_{\text{membrane} \rightarrow \text{solute particles}} = \sum_{\text{each solute particle}} (-\partial_x \mathcal{U})(\mathbf{r}_{\text{solute particle}})$$

Hence, taking a continuous limit of this sum and forgetting the subscripts, we obtain:

$$F_i = \int dx dy dz \left(C_i e^{-\frac{\mathcal{U}(x)}{kT}} \right) \times (-\partial_x \mathcal{U}) = \mathcal{A} kT C_i \left[e^{-\frac{\mathcal{U}(x=\pm\infty)}{kT}} - e^{-\frac{\mathcal{U}(x=0)}{kT}} \right]$$

$$\frac{F_i}{\mathcal{A}} = -kT C_i$$

And finally, the difference of pressure exerted by the fluid on the membrane is equal to:

$$\Delta\Pi = -\frac{F_2 - F_1}{\mathcal{A}} = kT\Delta C$$

Remark.

1. *The osmosis pressure results of a conversion of a chemical potential into a mechanical work, thanks to the effect of entropy.*
2. *The osmosis pressure is a huge pressure! For instance, a difference of concentration of 2 molars results in a difference of pressure of 50 bars: this is the pressure 500 m below sea level.*
3. *Such differences of pressure can be used in order to harvest energy (which is sometimes called blue energy). For a river like the Amazon river (with a water flux $Q = 200\,000 \text{ m}^3/\text{s}$) reaching the sea, the osmotic energy is $1 \text{ kWh}/\text{m}^3$ and then the total power that we could obtain is about 1 TW, which corresponds to the combined power of a thousand nuclear reactors.*

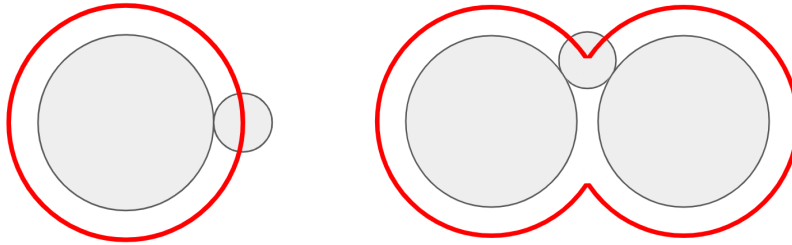
3.4.2 Depletion interactions

The depletion interactions results from the finite size of particles. Indeed, if particles have a non-zero radius, their presence in a mixture will reduce the available volume in the phase space of the other particles. As we will see, bringing closer two particles can increase the available volume in the phase space. Hence, entropic forces will tend to bring closer particles in order to maximize the available volume. In real experiments, the large and small particles can be for instance colloids with polymers, or soap films with surfactants.

Calculation of the excluded volume

Let's call σ the diameter of the small particles, and D the diameter of the large ones. When there is only 1 large particle in the mixture, small particles can go everywhere as long as they do not penetrate the large particle. Therefore, the minimal distance between the center of a small particle and the center of a large one is equal to $\frac{D+\sigma}{2}$. In this simple case, the excluded volume is just:

$$\mathcal{V} = \frac{4}{3}\pi \left(\frac{D+\sigma}{2}\right)^3 = \frac{\pi}{6}(D+\sigma)^3$$



When there are 2 large particles, the situation is less simple to describe, since the two excluded volumes of the large particles can interpenetrate themselves, and thus reduce the true excluded volume for the small particles. If r is the distance between the two centers of the large particles, this situation happens when $r < D + \sigma$.

In that case, a bit of geometry is needed to show that:

$$\mathcal{V} = \frac{\pi}{6}(D+\sigma)^3 \left[1 + \frac{3}{2} \frac{r}{D+\sigma} - \frac{1}{2} \left(\frac{r}{D+\sigma}\right)^3 \right]$$

From this, we can apply statistical mechanics to the bath of small particles, cohabiting with 2 large particles, of fixed position, separated by a distance r . The partition function of these small particles is, assuming a dilute regime (we neglect the interactions between these particles):

$$Z = \frac{1}{N!} \left(\frac{V_{free}}{\lambda_T^3} \right)^N$$

where, as usual, λ_T is the de Broglie wavelength, and where $V_{free} = V - \mathcal{V}$.

From this, we can derive the free energy:

$$\mathcal{F}(r) = -kT \log(Z) = -kT \log \left(\frac{1}{N!} \left(\frac{V_{free}(r)}{\lambda_T^3} \right)^N \right) \approx \mathcal{F}_{ideal\ gas} + NkT \frac{\mathcal{V}(r)}{V}$$

From this free energy, we can obtain the force of the small particles acting on the large ones:

$$F = -\frac{\partial \mathcal{F}}{\partial r} = \rho kT \times \left(-\frac{\partial \mathcal{V}}{\partial r} \right)$$

where ρ is the density of the small particles.

\mathcal{V} being an increasing function of r , the force is negative and tends to bring closer the two large particles: we have obtained an entropic attractive force between the large particles.

Remark.

1. *The same result can be obtained by integrating the osmotic pressure ρkT of the small particles over the accessible area around the large particles.*
2. *A liquid-vapour transition can be observed in solutions of polymers and colloids as a consequence of this entropic attractive force.*

3.4.3 Helfrich interactions

These interactions are due to the fluctuations we have studied in the previous sections. The Helfrich interactions are the soft matter analogous of the Casimir attractive forces that are due to the vacuum electromagnetic fluctuations².

The Helfrich interactions are some interactions that occur between fluctuating membranes. As we have shown before, elastic membranes of size L with a bending modulus B have fluctuations of height h , with:

$$h^2 \sim \frac{kT}{B} L^2$$

If two such membranes are close enough one from the other, their fluctuations are limited, since some configurations may be forbidden (these membranes cannot interpenetrate). This constraint limits the possible configurations, and, as before, this will create a force tending to remove the constraints.

We want to show, the free energy per unit area will behave like $\sim \frac{(kT)^2}{Bd^2}$, where d is the size of the confinement induced by the proximity of the membranes (which corresponds to a repulsive force, acting to increase d).

Simple derivation

The first way to derive this power law is by counting the number of Fourier modes authorized for a membrane close to a rigid wall by a distance d . For $h > d$, the membrane would penetrate the wall. Such a configuration is forbidden, therefore h has to be smaller than d . Recalling that $h^2 \sim \frac{kT}{B} L^2$, a maximum length L_{max} arises so that: $L_{max}^2 \sim \frac{Bd^2}{kT}$.

Any Fourier mode associated to a length above L_{max} is forbidden. As a consequence, the number of authorized modes scales as $1/L_{max}^2$ (L_{max} is to the power of 2 because the Fourier modes are in a 2D space discretized by $2\pi/L_{max}$).

Thanks to the equipartition theorem, we can say that each acceptable Fourier mode contributes by $\frac{kT}{2}$ to the free energy. Finally, the free energy per unit area is:

$$\frac{\mathcal{F}}{L^2} \sim \frac{kT}{L_{max}^2} \sim \frac{(kT)^2}{Bd^2}$$

Derivation from statistical mechanics

The calculation that we will conduct in this section can be seen as a case example for the study of fluctuation-induced interactions in statistical mechanics.

To begin, we will just consider a membrane confined in a harmonic potential such that:

$$V(\{h\}) = \int d\mathbf{r} \frac{1}{2} \kappa h(\mathbf{r})^2$$

The role of V is to mimic the membrane-membrane confinement: later, we will choose κ so that the mean value of h^2 calculated with this potential is equal to d^2 .

(i) *First step: calculation of $\langle h^2 \rangle$.*

²There are also Casimir interactions in a fluid at critical point, that can be either attractive or repulsive. This phenomenon had been proposed by De Gennes and Fischer in 1978, and has been first measured in 2007.

$$\mathcal{F}(\{h\}) = \int d\mathbf{r} \left[\frac{1}{2} B (\nabla^2 h)^2 + \frac{1}{2} \kappa h(\mathbf{r})^2 \right]$$

Going to the Fourier space, with Parseval's theorem:

$$\mathcal{F}(\{h\}) = \int \frac{d\mathbf{q}}{(2\pi)^2} \frac{1}{2} [Bq^4 + \kappa] |h_{\mathbf{q}}|^2 = \frac{1}{L^2} \sum_{\mathbf{q}} \frac{1}{2} [Bq^4 + \kappa] |h_{\mathbf{q}}|^2$$

With the theorem of equipartition:

$$\langle |h_{\mathbf{q}}|^2 \rangle = \frac{kTL^2}{Bq^4 + \kappa}$$

Finally, thanks again to Parseval's theorem, we have:

$$\langle h^2 \rangle = \frac{kT}{(2\pi)^2} \int_0^{+\infty} \frac{2\pi q dq}{Bq^4 + \kappa}$$

With the successive changes of variable $u = q^2$ and $v^2 = \frac{B}{\kappa} u^2$, we obtain:

$$\langle h^2 \rangle = \frac{kT}{4\pi} \int_0^{+\infty} \frac{du}{Bu^2 + \kappa} = \frac{kT}{4\pi\kappa} \sqrt{\frac{\kappa}{B}} \int_0^{+\infty} \frac{dv}{1 + v^2}$$

Finally, with $\int_0^{+\infty} \frac{dv}{1+v^2} = \pi/2$, we have:

$$\langle h^2 \rangle = \frac{kT}{8\sqrt{\kappa B}}$$

Remark. $\lim_{\kappa \rightarrow 0} \langle h^2 \rangle = +\infty$: indeed, without confinement, the fluctuations diverge until they reach the cut-off $\langle h^2 \rangle \sim L^2$.

We want the potential of confinement to mimic the confinement induced by two walls unclosing the membrane and separated by a distance d . As a consequence, we want $\langle h^2 \rangle = d^2$, whence:

$$\kappa = \left(\frac{kT}{8d^2} \right)^2 \frac{1}{B}$$

(ii) *Second step: derivation of the free energy induced by a confinement.*

To obtain the free energy induced by a confinement of the membrane, we want to compare a situation with no confinement ($\kappa = 0$) and with a confinement at a distance d ($\kappa = \left(\frac{kT}{8d^2}\right)^2 \frac{1}{B}$).

We can write the partition function of the system as:

$$Z = \sum_{\{h\}} \exp\left(-\frac{\mathcal{F}(\{h\})}{kT}\right)$$

Indeed, this is just a way to rewrite the sum of the partition function:

$$Z = \sum_{\text{all microstates}} \exp(-\beta E_s) = \sum_{\{h\}} \sum_{\text{all microstates with } \{h\}} \exp(-\beta E_s) = \sum_{\{h\}} \exp\left(-\frac{\mathcal{F}(\{h\})}{kT}\right)$$

with $\sum_{\text{all microstates with } \{h\}} \exp(-\beta E_s) = \exp\left(-\frac{\mathcal{F}(\{h\})}{kT}\right)$.

We can also write the partition function as:

$$Z = \sum_{\{h_{\mathbf{q}}\}} \exp\left(-\frac{\mathcal{F}(\{h_{\mathbf{q}}\})}{kT}\right) = \int dh_{\mathbf{q}_1} \dots dh_{\mathbf{q}_N} \exp\left(-\frac{\mathcal{F}(h_{\mathbf{q}_1}, \dots, h_{\mathbf{q}_N})}{kT}\right)$$

Remark. *Be careful, this way of writing the partition function implies that we only consider independent $h_{\mathbf{q}_i}$. Therefore, since h is a real function, we cannot use all $h_{\mathbf{q}_i}$, because $h_{-\mathbf{q}_i} = h_{\mathbf{q}_i}^*$. As a consequence, we will only use half of all \mathbf{q} vectors.*

As a consequence:

$$Z = \prod_{\mathbf{q}} \int dh_{\mathbf{q}} \exp\left(-\frac{L^2}{2kT}(Bq^4 + \kappa)|h_{\mathbf{q}}|^2\right)$$

Again with the equipartition theorem:

$$Z = \prod_{\mathbf{q}} \frac{2\pi kT}{L^2(Bq^4 + \kappa)}$$

The total free energy is then:

$$\mathcal{F} = -kT \log(Z) = -kT \sum_{\mathbf{q}} \log\left(\frac{2\pi kT}{L^2(Bq^4 + \kappa)}\right)$$

And, finally, we have $\Delta\mathcal{F}$, the free energy induced by the confinement:

$$\Delta\mathcal{F} = \mathcal{F}(\kappa) - \mathcal{F}(\kappa = 0) = -kT \sum_{\mathbf{q}} \log\left(\frac{Bq^4}{Bq^4 + \kappa}\right) = \frac{kT}{2} \int \frac{d\mathbf{q}}{(2\pi/L)^2} \log\left(1 + \frac{\kappa}{Bq^4}\right) \propto kTL^2 \sqrt{\frac{\kappa}{B}}$$

And, recalling that $\kappa = \left(\frac{kT}{8d^2}\right)^2 \frac{1}{B}$, we obtain:

$$\frac{\Delta\mathcal{F}}{L^2} \propto \frac{(kT)^2}{Bd^2}$$

which is the free energy of an entropic repulsion.

Chapter 4

Noise, brownian motion and dynamics

4.1 Langevin theory

4.1.1 Introduction and hypotheses

Langevin theory is the study of the Langevin equation, which describes the motion of a big particle in a bath of small particles, the whole system being at thermal equilibrium. The collisions of the small particles with the big one has two effects: the mean effect of these collisions is a fluid friction force that slows down the big particle, and in addition to this mean effect, there is a random force, whose mean value is equal to 0, that takes into account the randomness of the collisions.

The Langevin equation is then:

$$M \frac{d\mathbf{V}}{dt} = -\zeta \mathbf{V} + \delta \mathbf{F}(t)$$

where M is the mass of the big particle, \mathbf{V} its velocity, ζ the fluid friction coefficient and $\delta \mathbf{F}(t)$ the random force induced by the collisions.

We have:

$$\langle \delta \mathbf{F}(t) \rangle = 0$$

Furthermore, we suppose from a causality argument that, if $t > t'$:

$$\begin{aligned} \langle \delta F_\alpha(t) R_\beta(t') \rangle &= 0 \\ \langle \delta F_\alpha(t) V_\beta(t') \rangle &= 0 \end{aligned}$$

where \mathbf{R} is the position of the big particle.

Remark. *Be careful, for $t < t'$ this is no longer true.*

The last hypothesis to make is on $\langle \delta F_\alpha(t) \delta F_\beta(0) \rangle$. The time scale τ for the force correlation will be supposed to be very small compared to the macroscopic time scale of the movement of the big particle: $\tau \ll M/\zeta$. As a consequence, for $\tau \rightarrow 0$, and supposing that the force does not correlate orthogonal directions:

$$\langle \delta F_\alpha(t) \delta F_\beta(t') \rangle = R_0 \delta_{\alpha\beta} \delta(t - t')$$

where R_0 is for the moment undetermined: its value will have to be calculated from the thermal equilibrium (this is the Langevin approach).

In the following, we will only consider a 1D trajectory, in order to simplify the notations.

4.1.2 Diffusive motion

We want to calculate $\langle (x(t) - x(0))^2 \rangle$ (we will take $x(0) = 0$), from:

$$M \frac{d^2 x}{dt^2} = -\zeta \frac{dx}{dt} + \delta F_x(t)$$

Multiplying the equation and taking its mean value yields:

$$M \langle x(t) \ddot{x}(t) \rangle = -\zeta \langle x(t) \dot{x}(t) \rangle + \langle x(t) \delta F_x(t) \rangle$$

We make the hypothesis that $\langle x(t) \delta F_x(t) \rangle = 0$ and we recall that $x \dot{x} = \frac{1}{2} \frac{d}{dt} \left(\frac{d(x^2)}{dt} \right) - \dot{x}^2$:

$$M \left[\frac{d^2}{dt^2} \left(\frac{\langle x(t)^2 \rangle}{2} \right) - \langle \dot{x}(t)^2 \rangle \right] = -\zeta \frac{d}{dt} \left(\frac{\langle x(t)^2 \rangle}{2} \right)$$

We call $Y(t) = \frac{d}{dt} \left(\frac{\langle x(t)^2 \rangle}{2} \right)$, and from the equipartition theorem, we have $M \langle \dot{x}(t)^2 \rangle = kT$. Thus:

$$M \frac{dY}{dt} = MkT - \zeta Y$$

For $t \rightarrow +\infty$, we have:

$$Y(t) = \frac{kT}{\zeta}$$

And finally, we obtain a diffusive motion for x :

$$\langle x(t)^2 \rangle \underset{t \rightarrow +\infty}{\sim} 2Dt$$

with $D = \frac{kT}{\zeta}$.

4.1.3 Velocity correlations

We now multiply the Langevin equation by $V_x(0)$ and take its mean value:

$$M \left\langle \frac{dV_x}{dt} V_x(0) \right\rangle = -\zeta \langle V_x(t) V_x(0) \rangle + \langle \delta F_x(t) V_x(0) \rangle$$

and we have $\langle \delta F_x(t) V_x(0) \rangle = 0$ because $t > 0$.

We define the correlation function as:

$$C(t) = \langle V_x(t) V_x(0) \rangle$$

We have:

$$M \frac{dC}{dt} = -\zeta C$$

As a consequence, with $C(0) = \langle V_x(0)^2 \rangle = \frac{kT}{M}$ thanks to the equipartition theorem, we have:

$$C(t) = \frac{kT}{M} \exp\left(-\frac{\zeta t}{M}\right)$$

We can show that the diffusion coefficient D is equal to $\int_0^{+\infty} dt C(t)$. We can verify the consistence of our relations with:

$$D = \int_0^{+\infty} dt \frac{kT}{M} \exp\left(-\frac{\zeta t}{M}\right) = \frac{kT}{\zeta}$$

4.1.4 Fluctuation-dissipation theorem

Now we totally solve the Langevin equation with the method of variation of the constant:

$$V_x(t) = V_x(0) \exp\left(-\frac{\zeta t}{M}\right) + \int_0^t ds \exp\left(-\frac{\zeta(t-s)}{M}\right) \frac{\delta F_x(s)}{M}$$

Now, we have:

$$\begin{aligned} \langle V_x(t)^2 \rangle &= \langle V_x(0)^2 \rangle \exp\left(-2\frac{\zeta t}{M}\right) \\ &+ 2 \exp\left(-\frac{\zeta t}{M}\right) \int_0^t ds \frac{\exp\left(-\frac{\zeta(t-s)}{M}\right)}{M} \langle \delta F_x(s) V_x(0) \rangle \\ &+ \int_0^t ds \int_0^t ds' \exp\left(-\frac{\zeta(t-s)}{M}\right) \exp\left(-\frac{\zeta(t-s')}{M}\right) \frac{\langle \delta F_x(s) \delta F_x(s') \rangle}{M^2} \end{aligned}$$

Recalling that $\langle \delta F_x(s) V_x(0) \rangle = 0$ for $s > 0$, and that $\langle \delta F_x(s) \delta F_x(s') \rangle = R_0 \delta(s - s')$, we obtain:

$$\langle V_x(t)^2 \rangle = \langle V_x(0)^2 \rangle \exp\left(-2\frac{\zeta t}{M}\right) + \int_0^t ds \exp\left(-2\frac{\zeta(t-s)}{M}\right) \times \frac{R_0}{M^2}$$

Whence:

$$\langle V_x(t)^2 \rangle = \langle V_x(0)^2 \rangle \exp\left(-2\frac{\zeta t}{M}\right) + \frac{R_0}{2\zeta M} \left(1 - \exp\left(-2\frac{\zeta t}{M}\right)\right)$$

For $t \rightarrow +\infty$, the particle relaxes towards thermal equilibrium:

$$\lim_{t \rightarrow +\infty} \langle V_x(t)^2 \rangle = \frac{1}{M} \frac{R_0}{2\zeta} = \frac{kT}{M}$$

From this, we obtain the fluctuation-dissipation theorem:

$$R_0 = 2kT\zeta$$

that links the fluctuations of the system (R_0) to its dissipation (ζ).

We can also write this fluctuation-dissipation theorem as the Green-Kubo equation:

$$\zeta = \frac{1}{kT} \int_0^{+\infty} \langle \delta F_x(t) \delta F_x(0) \rangle dt$$

4.2 Diffusion and Smoluchowski

In this section, we want to study the evolution of $\mathcal{P}(\mathbf{R}, t)$, the probability to find the brownian particle at a position \mathbf{R} at a given time t .

Diffusion without an external force

The first equation that we can write is just a conservation law:

$$\frac{\partial \mathcal{P}}{\partial t} = -\nabla \cdot \mathbf{J}$$

where \mathbf{J} is the density of probability current. To complete the equation, we need a relation that is verified by \mathbf{J} , and for that we can use the phenomenological Fick's law:

$$\mathbf{J} = -D\nabla \mathcal{P}$$

A way to grasp the origin of Fick's law, we can consider 1D brownian particles with a diffusive motion as $\sqrt{\langle x^2 \rangle} \sim \sqrt{Dt}$. The current J at a position x_0 is the mean number of brownian particles that cross the plane $x = x_0$ from left to right during a given amount of time, divided by this amount of time:

$$J = J_+ - J_- = \mathcal{P}(x - \Delta x) \frac{\Delta x}{\Delta t} - \mathcal{P}(x + \Delta x) \frac{\Delta x}{\Delta t} \sim -\frac{\Delta x^2}{\Delta t} \partial_x \mathcal{P}(x) = -D \partial_x \mathcal{P}(x)$$

where J_+ (*resp.* J_-) is the exact number of particles going from left to right (*resp.* from right to left) during Δt divided by Δt .

From Fick's law, we now have:

$$\frac{\partial \mathcal{P}}{\partial t} = D \nabla \cdot \mathbf{J}$$

This is a diffusion equation. To obtain its solution, we go through the Fourier space, defining:

$$\mathcal{P}(\mathbf{k}, t) = \int d\mathbf{r} \mathcal{P}(\mathbf{r}, t) e^{i\mathbf{k} \cdot \mathbf{r}}$$

We now have:

$$\frac{\partial \mathcal{P}}{\partial t} = -D k^2 \mathcal{P}$$

Taking the inverse fourier transform of the solution $\mathcal{P}(\mathbf{k}, 0) e^{-Dk^2 t}$:

$$\mathcal{P}(\mathbf{r}, t) = \int d\mathbf{r}' \mathcal{P}(\mathbf{r} - \mathbf{r}', 0) \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{r'^2}{4Dt}\right)$$

Diffusion with an external force

We define the mobility μ so that at equilibrium, when applied an external force, we obtain:

$$\mathbf{V} = \mu \mathbf{F}_{ext}$$

From what we know in hydrodynamics, we can define a convective flux:

$$\mathbf{J}_{conv} = \mathcal{P} \mathbf{V} = \mu \mathcal{P} \mathbf{F}_{ext}$$

We can add this to the Fick's flux in the total flux:

$$\mathbf{J} = -D \nabla \mathcal{P} + \mu \mathcal{P} \mathbf{F}_{ext}$$

From this, we can derive the Smoluchowski's equation:

$$\frac{\partial \mathcal{P}}{\partial t} = -\nabla \cdot [-D \nabla \mathcal{P} + \mu \mathcal{P} \mathbf{F}_{ext}] = -\nabla \cdot [-D \nabla \mathcal{P} + \mu \mathcal{P} \times (-\nabla \mathcal{U}_{ext})]$$

where $\mathbf{F}_{ext} = (-\nabla \mathcal{U}_{ext})$.

At equilibrium, we have $\frac{\partial \mathcal{P}}{\partial t} = 0$, and then $\mathbf{J} = \mathbf{0}$.

$$\mathbf{0} = -D \nabla \mathcal{P} + \mu \mathcal{P} \times (-\nabla \mathcal{U}_{ext})$$

Whence:

$$\nabla (\log \mathcal{P}) = -\frac{\mu}{D} (-\nabla \mathcal{U}_{ext})$$

Finally, we have:

$$\mathcal{P} \propto \exp\left(-\frac{\mu}{D} \mathcal{U}_{ext}\right)$$

In order to recover the Boltzmann's weights $\mathcal{P} \propto \exp\left(-\frac{\mathcal{U}_{ext}}{kT}\right)$, we finally obtain the Einstein relationship:

$$D = \mu kT$$

4.3 Generalization

This study of $\mathcal{P}(\mathbf{R}, t)$ can be generalized to any order parameter $\phi(\mathbf{r}, t)$, whose equilibrium is given by the minimization of a free energy $\Omega(\{\phi\})$.

Non conserved dynamics

We can have the following equation for $\phi(\mathbf{r}, t)$:

$$\frac{\partial \phi}{\partial t} = -\Gamma \frac{\delta \Omega}{\delta \phi} + \delta R(t)$$

where $\delta R(t)$ is a random function and plays the same role as δF in Langevin's equation. With the fluctuation dissipation theorem, we have:

$$\langle \delta R(t) \delta R(t') \rangle = 2kT\Gamma \delta(t - t')$$

Following the same method as before, we can write an equation for $\mathcal{P}(\{\phi\}, t)$:

$$\frac{\partial \mathcal{P}}{\partial t} = -\frac{\partial}{\partial \phi} \left[-D \frac{\partial \mathcal{P}}{\partial \phi} + \Gamma \mathcal{P} \times \left(-\frac{\delta \Omega}{\delta \phi} \right) \right]$$

The equilibrium yields:

$$\mathcal{P} \propto \exp\left(-\frac{\Omega(\{\phi\})}{kT}\right)$$

and we recover an Einstein equation:

$$D = kT\Gamma$$

Conserved dynamics

We can also work with conserved dynamics. The equations in this case are:

$$\frac{\partial \phi}{\partial t} = -\nabla \cdot \mathbf{J} + \delta R(\mathbf{r}, t)$$

with:

$$\mathbf{J} = -\Gamma \nabla \left(\frac{\delta \Omega}{\delta \phi} \right)$$

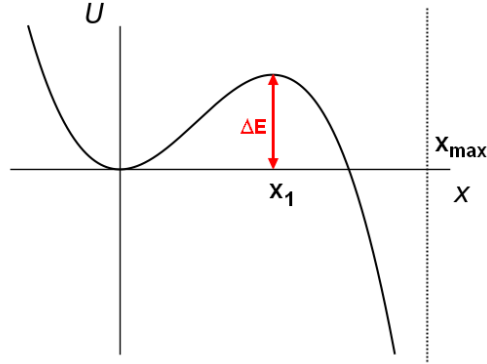
and:

$$\langle \delta R(\mathbf{r}, t) \delta R(\mathbf{r}', t') \rangle = 2kT\Gamma \delta(t - t') \times (-\nabla^2 \delta(\mathbf{r} - \mathbf{r}'))$$

4.4 Barrier crossing

The goal in this section is to describe the dynamics of the crossing of an energy barrier. To model this, we consider a system in a potential $\mathcal{U}(x)$ with the following properties:

1. \mathcal{U} has a local minimum at $x = 0$.
2. \mathcal{U} has a local maximum at $x = x_1$.
3. $\mathcal{U}(x_1) - \mathcal{U}(0) = \Delta E$.
4. $\lim_{x \rightarrow -\infty} \mathcal{U}(x) = +\infty$.
5. $\lim_{x \rightarrow x_{max}} \mathcal{U}(x) = -\infty$.



Using the Smoluchowski equation, we have:

$$\frac{\partial \mathcal{P}}{\partial t} = -\frac{\partial}{\partial x} \left[-D \frac{\partial \mathcal{P}}{\partial x} + \mu \mathcal{P} \times \left(-\frac{\partial U}{\partial x} \right) \right]$$

Using the Einstein relationship $D = \mu kT$ and looking for an equilibrium ($\frac{\partial \mathcal{P}}{\partial t} = 0$):

$$J = cst = -D \frac{\partial \mathcal{P}}{\partial x} + \frac{D}{kT} \mathcal{P} \times \left(-\frac{\partial U}{\partial x} \right)$$

The resolution of this equation yields:

$$\mathcal{P} = A \exp\left(-\frac{U(x)}{kT}\right) - \exp\left(-\frac{U(x)}{kT}\right) \int_0^x \frac{J}{D} \exp\left(+\frac{U(x')}{kT}\right) dx'$$

and imposing $\mathcal{P}(x_{max}) = 0$:

$$\mathcal{P}(x) = \frac{J}{D} \exp\left(-\frac{U(x)}{kT}\right) \int_x^{x_{max}} \exp\left(+\frac{U(x')}{kT}\right) dx'$$

We define the escape rate ν as the frequency at which particles cross the local maximum of U . By definition of J , J is equal to ν times the number of particles that are left to the local minimum (*i.e.* that has not yet crossed it). This number is equal to $\int_{-\infty}^{x_1} dx \mathcal{P}(x)$. We then have:

$$\frac{J}{\nu} = \frac{J}{D} \int_{-\infty}^{x_1} dx \exp\left(-\frac{U(x)}{kT}\right) \int_x^{x_{max}} \exp\left(+\frac{U(x')}{kT}\right) dx'$$

And finally:

$$\nu = \frac{D}{\int_{-\infty}^{x_1} dx \exp\left(-\frac{U(x)}{kT}\right) \int_x^{x_{max}} \exp\left(+\frac{U(x')}{kT}\right) dx'}$$

Simplification

$\int_x^{x_{max}} \exp\left(+\frac{U(x')}{kT}\right) dx'$ is dominated by what happens close to the local maximum. We expand U around x_1 :

$$U(x) \sim \Delta E - \frac{1}{2} \kappa_{max} (x - x_1)^2$$

and $\int_x^{x_{max}} \exp\left(+\frac{U(x')}{kT}\right) dx'$ can be approximated as:

$$\int_x^{x_{max}} \exp\left(+\frac{\mathcal{U}(x')}{kT}\right) dx' \approx \exp\left(+\frac{\Delta E}{kT}\right) \int_{-\infty}^{+\infty} \exp\left(-\frac{1}{2} \frac{\kappa_{max}}{kT} (x - x_1)^2\right) = \exp\left(+\frac{\Delta E}{kT}\right) \sqrt{\frac{2\pi kT}{\kappa_{max}}}$$

The other integral, $\int_{-\infty}^{x_1} dx \exp\left(-\frac{\mathcal{U}(x)}{kT}\right)$, is dominated by what happens close to 0. We expand \mathcal{U} close to 0:

$$\mathcal{U}(x) \sim \frac{1}{2} \kappa_{min} x^2$$

In that case:

$$\int_{-\infty}^{x_1} dx \exp\left(-\frac{\mathcal{U}(x)}{kT}\right) \approx \sqrt{\frac{2\pi kT}{\kappa_{min}}}$$

And finally, we recover the Arrhenius formula:

$$\nu = \frac{D}{2\pi kT} \sqrt{\kappa_{min} \kappa_{max}} \exp\left(-\frac{\Delta E}{kT}\right)$$

4.5 Application: nucleation theory

In the previous chapters we have studied the liquid-vapour phase transition. We have showed that, even when one phase is more favoured than the other, there is a free energy barrier per unit volume $\Delta\omega^+$. This $\Delta\omega^+$, when multiplied by typical volumes becomes very huge, and a homogeneous bulk phase transition would take according to Arrhenius formula far too many time.

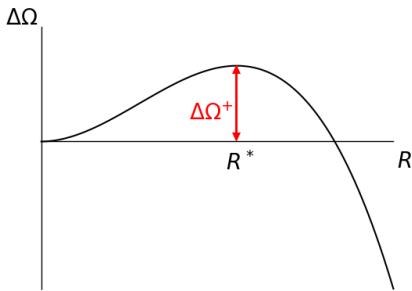
That's why phase transition start with a nucleation process: the transition starts locally to involve gradually the whole volume.

To study nucleation processes, we will consider a situation where the liquid phase is more favourable than the vapour phase. At the beginning of the process, the whole system is in the vapour phase. It wants to transform into a liquid. This process is seen as the growth of a liqui drop which starts at $R = 0$ and that grows until it occupies the whole volume. We want to know the time it takes for this drop to undergo this whole process.

To do so, we write the free energy of such a drop of radius R :

$$\Delta\Omega(R) = -(\rho_L - \rho_V)(\mu - \mu_{sat})\frac{4}{3}\pi R^3 + 4\pi R^2 \gamma_{LV}$$

From this, we want the free energy barrier, in order to use the Arrhenius formula. The local maximum of $\Delta\Omega$ is achieved at R^* so that:



$$\frac{\partial \Delta\Omega}{\partial R}(R^*) = 0 = -(\rho_L - \rho_V)(\mu - \mu_{sat})4\pi R^{*2} + 8\pi R^* \gamma_{LV}$$

We obtain from the Arrhenius formula the time it would take for a drop to grow from $R = 0$ to $R = +\infty$:

$$\tau_{nucleation} = \tau_0 \exp\left(\frac{\Delta\Omega^+}{kT}\right)$$

This timescale does not depend on the global volume and is therefore more achievable than the timescale we would obtain without a nucleation process.