

Soft Matter Exam

Nota Bene

Exam duration : 3H

Lecture notes are not allowed. Electronic devices (including cell phones) are prohibited, at the exception of pocket calculators.

Accepted languages : english, french.

The two parts are independent. **Please use two separate copies for your answers to the two parts.**

1st PART

Several of the questions in this part of the exam are a review of what has been discussed in class. Answer every question in the most detailed yet synthetic way.

1 Structure of a simple/complex liquid.

The key concepts

In this section, we will discuss the tools that we introduced to describe the structure of simple and complex interacting liquids.

- (a) Explain the general difficulties of treating an interacting system in the context of the canonical ensemble. Sketch the possible strategies we have discussed in the course to overcome these limitations.
- (b) Define the distribution functions, $\rho_N^{(n)}(r)$, in the canonical ensemble and discuss what is the advantage in introducing such distribution functions. In particular, discuss $\rho_N^{(1)}(r)$ and $\rho_N^{(2)}(r)$ for an Isotropic and Homogeneous fluid. How are they normalized ?
- (c) This is the key point. For a 2-body isotropic and homogeneous interacting system, the radial distribution function (RDF) is the main function. Discuss its definition and physical interpretation. What is the low density limit of the RDF? Draw qualitatively a RDF and discuss it.
- (d) Show, briefly, how the internal energy U is calculated from the RDF.
- (e) Discuss the relation between the RDF and the static structure factor $S(q)$. Can you say something about the $q \rightarrow 0$ limit of the structure factor ?
- (f) Discuss how scattering can be used to measure the structure of a fluid. In particular how do you measure the shape of a particle ?

The Van der Waals approximation for an interacting system

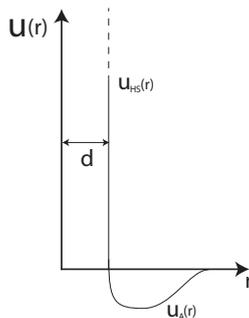


FIGURE 1 – The interaction potential $u(r)$, d is the particle diameter.

Consider, N interacting particles in a volume V at constant temperature T . The particles interact by a 2-body interaction potential given by a hard sphere repulsion and an attractive tail :

$$u(r) = u_{HS} + u_A(r). \quad (1)$$

see Fig.1.

We will use the distribution function to re-derive a classical result of thermodynamics, the Van der Wals equation of state :

$$\left(P + \frac{a}{v^2}\right)(v - b) = k_B T \quad (2)$$

where $v = V/N$ and a and b are two constants we will derive by a mean field approximation.

(a) Following what we did in the course, we will first introduce the counting operator

$$\hat{\rho}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \quad (3)$$

where \mathbf{r}_i is the position of particle i and the sum is on all the N particles. Show that this operator is directly related to density distribution by :

$$\rho^{(1)}(\mathbf{r}) = \rho(\mathbf{r}) = \langle \hat{\rho}(\mathbf{r}) \rangle \quad (4)$$

where $\langle \cdot \rangle$ is the canonical average. Show that for a homogenous system the local density is constant :

$$\rho(\mathbf{r}) = \rho = \frac{N}{V} = cte \quad (5)$$

(b) Show that the partition function is given by :

$$Z_N = \frac{1}{\lambda^3 N!} Q_N \quad (6)$$

where λ is the de Broglie length (irrelevant for this problem), and the configuration integral is given by :

$$Q_N = \int d^3\mathbf{r}_1 \dots d^3\mathbf{r}_N \left(\prod_{i<j} S(|\mathbf{r}_i - \mathbf{r}_j|) \right) e^{-\beta \sum_{i<j} u_A(|\mathbf{r}_i - \mathbf{r}_j|)} \quad (7)$$

give the expression of the function $S(x)$.

(c) Show that the attractive energy of one realization of the system, which appears in Eq. 7 :

$$U_A = \sum_{i<j} u_A(|\mathbf{r}_i - \mathbf{r}_j|) \quad (8)$$

can be rewritten, using the counting operator, as :

$$U_A = \frac{1}{2} \int d^3\mathbf{r} d^3\mathbf{r}' \hat{\rho}(\mathbf{r}) u_A(|\mathbf{r} - \mathbf{r}'|) \hat{\rho}(\mathbf{r}'). \quad (9)$$

In particular, show that U_A can be written introducing an effective potential U_{eff}

$$U_A = \frac{1}{2} \int d^3\mathbf{r} U_{eff}(r) \hat{\rho}(\mathbf{r}) \quad (10)$$

Specify the functional form of U_{eff} .

(d) Up to now, everything is exact. Let's introduce a mean field approximation to simplify the problem. This approximation consist of replacing the local density with its average :

$$\hat{\rho}(\mathbf{r}) \simeq \langle \hat{\rho}(\mathbf{r}) \rangle = \rho \quad (11)$$

Show the effective potential can be expressed as

$$U_{eff} \simeq -\rho\alpha \quad (12)$$

where α is a constraint. What is the condition for having a finite α ? Using, this result show that :

$$U_A = -\frac{1}{2} \alpha \rho N = -\frac{1}{2} \alpha \rho^2 V \quad (13)$$

What are we neglecting with this approximation?

(e) Show that in this case the partition function becomes :

$$Z_N \simeq Z_{HS} \exp\left(\beta \frac{\alpha N^2}{2V}\right). \quad (14)$$

With this you can derive the pressure that takes the form :

$$P = P_{HS} - \frac{\alpha}{2v^2}. \quad (15)$$

Using Clausius approximation :

$$\frac{\beta P_{HS}}{\rho} = 1 + B_2^{HS} \rho \simeq \frac{1}{1 - B_2^{HS} \rho} = \frac{1}{1 - B_2^{HS}/v} \quad (16)$$

Where B_2^{HS} is the Hard Spheres virial coefficient :

$$B_2^{HS} = \frac{2\pi}{3} d^3 \quad (17)$$

Show that we obtain the VdW equation (Eq. 2). We can now discuss the relation between the parameter a and b and the microscopic variables of the systems.

2 Electrostatics in Soft Matter

2.1 Poisson-Boltzmann Equation

One of the main equation in the treatment of electrostatics in soft matter is the Poisson-Boltzmann Equation.

- Describe the basic assumption on which it is derived and what are the founding principles.
- Give a rapid idea of the derivation of the PBE (*a full derivation is a bonus*).

2.2 Linearized Poisson-Boltzmann Equation or Debye-Huckel (DH)

In general, a solution of this equation can be achieved only in few cases. It is for this reason that we use a linearized approximation

- Linearize the PBE to obtained his linearized version (LPBE, or Debye-Huckel theory).
- Solve the LPBE theory and derive an expression for the electrostatic potential.
- A characteristic length, the Debye length λ_D , emerges. Discuss its physical interpretation.
- Discuss in details what are the conditions under which the PBE can be linearized.
- Show that for a spherical macro ion of charge $Q = Ze$ and diameter d in a solution of $N/2$ NaCl molecules (i.e. N total ions), the LPBE can be solved. Show (briefly!) that the potential can be derived as :

$$\psi(r) = \frac{Ze}{4\pi\epsilon(1 + \frac{d}{\lambda_D})} \frac{e^{-\frac{(r-d)}{\lambda_D}}}{r} \quad (18)$$

2nd PART

3 Lecture questions

Each question can be answered within few lines.

1. Explain the entropic driven phase transition of a system of hard-spheres : how entropy can favorize cristallization of spherical particles with hard-core repulsion ?
2. What is the definition of the Critical Micellar Concentration (CMC) ? Should the CMC increase or decrease with the temperature ?

4 Micelle morphologies

Surfactant molecules in solvent self-assemble to form larger objects, called micelles. Depending on the “geometry” of the surfactant molecules, micelles can have different morphologies, *e.g.*: spherical, cylindrical, lamella (see Fig. 2). The goal of this exercise is to show that the micelle morphology depends primarily on the dimensionless *micelle packing parameter* $g = v/(a_0 l_0)$, where v is the volume of one surfactant molecule, a_0 is the equilibrium area per hydrophilic head at the aggregate interface, and l_0 is the maximal length (*i.e.*: when fully stretched) of the hydrophobic tail of one molecule.

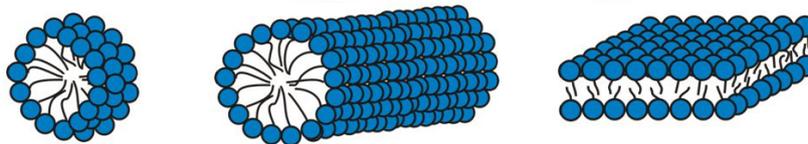


FIGURE 2 – Schematic illustration of the three most commonly observed geometrical shapes of surfactant micelles in aqueous solution : spherical, cylindrical, and planar (lamella).

1. We consider a spherical micelle with radius R made of q molecules. Establish a first relation between v , q , R , and a second relation between a_0 , q , R .
2. The radius of the micelle must satisfy $R \leq l_0$. Deduce that a spherical micelle morphology is possible only for a packing parameter g smaller than a given value g_s to determine.
3. We now consider a cylindrical micelle with radius R_c , length L_c . We suppose $L_c \gg R_c$, so the contributions of the two ends of the cylinder to its volume and surface area are negligible. As before, find the maximal possible value g_c for the micelle packing parameter corresponding to a cylindrical micelle morphology.
4. Similarly, find the maximal possible value g_l for the packing parameter corresponding to a planar micelle (lamella) with thickness $2h_l$, and lateral size $L_l \gg h_l$.
5. When $g \leq g_s$, the three micelle morphologies (sphere cylinder, lamella) are possible in theory. Similarly, when $g_s \leq g \leq g_c$ both cylindrical and planar morphologies are possible. Use entropic arguments to explain why spherical micelles are favoured over cylindrical and lamellar ones as long as $g \leq g_s$, and cylindrical micelles over lamellar ones when $g_s \leq g \leq g_c$ (we assume that the gain of energy corresponding to the inclusion of one surfactant molecule within a micelle is the same for the three micelle morphologies).

5 Entropic undulation interactions of membranes

When two (or more) membranes are in the vicinity of each other their steric repulsions constraint their thermal fluctuations and hence decrease the entropy as compared with the far away configuration. . This situation arises, *e.g.* when two vesicles are close together, or in the lamellar phase of lyotropic liquid systems. This is this last system that we consider here : the lamellar phase is a pile of fluid membranes which are parallel on the average (see Fig. 3(b)). The aim of this exercise is to determine the dependence of the entropic undulation interaction $\Delta f_s(d)$ with the inter-membrane spacing d .

5.1 One membrane between two rigid walls

In this first approach, we simplify the problem and assume that a given membrane feels the influence of neighbouring ones as if it was constrained between two rigid walls separated by a distance equal to $2d$ (see Fig. 3(a)). This will allow us to derive the expression for the entropic undulation interaction, using two different semi-quantitative approaches .

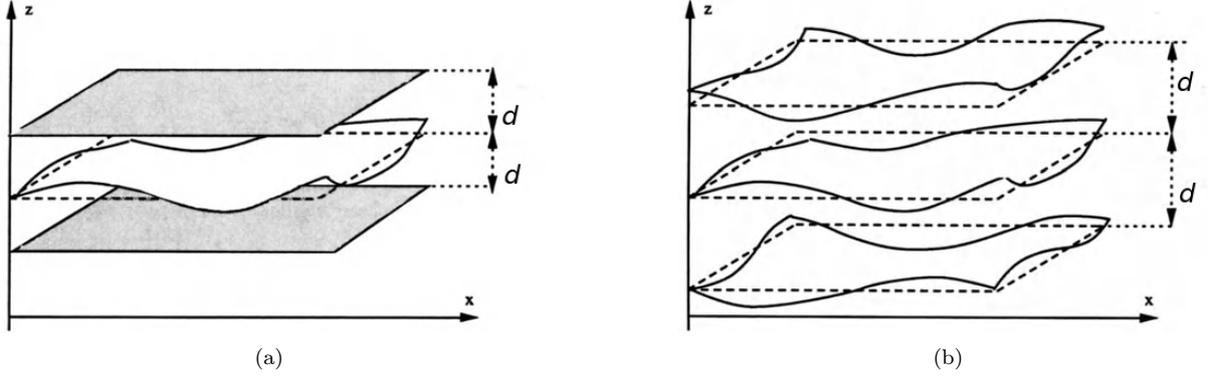


FIGURE 3 – a : single membrane trapped between two rigid walls ; b : stack of membranes, separated by an average distance d .

5.1.1 Ideal gas analogy

Let n be the average number of contacts between the membrane and the walls, at any time. The simplest argument making use of the ideal gas analogy is the following : consider the undulating membrane with lateral size L as a set of n independent “particles”, each one corresponding to a piece of membrane of area $L_z^2 = L^2/n$ where L_z is such that the root mean square (r.m.s.) displacement of membranes of size L_z is on the order of d , i.e. ,

$$\langle u^2 \rangle_{L_z} = \mu d^2,$$

where μ is a number of the order of unity. The subscript L_z of $\langle u^2 \rangle$ refers to the fact that the r.m.s. displacement due to thermal undulations is computed for a piece of membrane of surface area L_z^2 . The collisions generated by these pieces of membranes result in a kinetic pressure similar to the one generated by an ideal gas of particles.

1. Justify that the volume per contact is $V/n = 2dL_z^2$.
2. Using the ideal gas law, express the pressure p as a function of $k_B T$, $\langle u^2 \rangle_{L_z}$, μ and L_z .
3. We recall the expression for the r.m.s. displacement of a unconstrained membrane of size L_z :

$$\sqrt{\langle u^2 \rangle_{L_z}} = \sqrt{\frac{k_B T}{4\pi\sigma} \ln \left[\frac{L_z^2 + \pi^2 \lambda_c^2}{\Lambda^2 + \pi^2 \lambda_c^2} \right]},$$

where Λ is a microscopic length related to the surfactant molecule size, and $\lambda_c = \sqrt{\kappa_b/\sigma}$.

Simplify this expression in the limit of vanishing surface tension ($\lambda_c \gg L_z \gg \Lambda$) which is the relevant regime here.

4. Deduce from the last two questions the expression of p as a function of $k_B T$, μ , κ_b and d in this regime.
5. By calculating the work required to bring the rigid walls from $-\infty$ to d , show that the steric interaction energy per unit membrane surface (i.e.: the increase of free energy per unit surface due to the presence of the walls) is :

$$\Delta f_s = \frac{a}{d^2},$$

and give the expression of the constant a .

6. How the range of this entropic interaction compares with other interactions between two parallel surfaces, e.g.: Van der Waals interactions ?

5.1.2 Steric constraint in Fourier space

An alternative argument introduces a cutoff in the mode wavevectors. The idea is that the steric constraint hinders essentially all fluctuations of wavevector $\mathbf{q}_\perp = (q_x, q_y)$ smaller than a cut-off q_\perp^* , such that

$$\langle u^2 \rangle = \sum_{\substack{\mathbf{q}_\perp \\ |\mathbf{q}_\perp| \geq q_\perp^*}} |\tilde{u}(\mathbf{q}_\perp)|^2 = \mu d^2.$$

1. We recall that, from equipartition theorem : $\langle |\tilde{u}(\mathbf{q}_\perp)|^2 \rangle L^2 \kappa_b q_\perp^4 = k_B T$, for each allowed mode. Deduce the expression of \mathbf{q}_\perp^* as a function of $k_B T$, κ_b and d , using continuous approximation.
2. the interaction energy per unit area corresponds the average energy of the suppressed modes, *i.e.*:

$$\Delta f_s = \frac{1}{L^2} \sum_{\substack{\mathbf{q}_\perp \\ |\mathbf{q}_\perp| \leq q_\perp^*}} \left\langle \frac{1}{2} |\tilde{u}(\mathbf{q}_\perp)|^2 L^2 \kappa_b q_\perp^4 \right\rangle.$$

Using again equipartition theorem and continuous approximation, show that $\Delta f_s = a'/d^2$, where the coefficient a' is slightly different from the coefficient a above.

5.2 Stack of membranes

We now come back to the initial problem of a stack of N fluid membranes which are parallel on the average, with lattice spacing d as shown in Fig. 3(b). A given membrane has an absolute height $h_n = nd + u_n(x, y)$, where n is an integer which indexes the lattice positions and $u_n(x, y)$ is the local deviation of the membrane from its average value, $\langle h_n \rangle = nd$.

1. Let $f_{int}(h_n, h_{n+1})$ be the interaction energy (per unit surface) between membranes n and $n+1$. We will use for expression :

$$f_{int} \simeq \text{cst} + \frac{B}{2} (u_{n+1} - u_n)^2.$$

Give the approximations or assumptions on which this expression is built.

2. For membrane system with gentle undulations ($\nabla h_n \ll 1$) and with vanishing membrane tension, the coarse-graining Hamiltonian of the system is then :

$$\mathcal{H} = \sum_n \left\{ \frac{\kappa_b}{2} \iint_{A_p} (\nabla_\perp^2 u_n)^2 dx dy + \frac{B}{2} \iint_{A_p} (u_{n+1} - u_n)^2 dx dy \right\},$$

where A_p is the projected area and $\nabla_\perp^2 \equiv \partial^2/\partial x^2 + \partial^2/\partial y^2$. We introduce the Fourier expansion of $u_n(x, y)$:

$$u_n(x, y) = \sum_{\mathbf{q}_\perp, q_z} e^{i(\mathbf{q}_\perp \cdot \boldsymbol{\rho} + q_z n d)} \tilde{u}(\mathbf{q}_\perp, q_z),$$

where $\mathbf{q}_\perp = (q_x, q_y)$ and $\boldsymbol{\rho} = (x, y)$. We use periodic boundary conditions in the three directions.

What are the values allowed for q_x, q_y ? And for q_z ? For the latter we choose allowed values in the interval $] -\pi/d, \pi/d[$.

3. Show that the coarse-grained Hamiltonian can be rewritten :

$$\mathcal{H} = A_p N \sum_{\mathbf{q}_\perp, q_z} |\tilde{u}(\mathbf{q}_\perp, q_z)|^2 \left[\frac{1}{2} \kappa_b q_\perp^4 + B (1 - \cos q_z d) \right].$$

We recall the identities : $\sum_{n=-N/2+1}^{N/2} e^{i(l-p)2\pi n/N} = N \delta_{l,p}$ and : $\iint_{A_p} e^{i(\mathbf{q}_\perp - \mathbf{q}'_\perp) \cdot \boldsymbol{\rho}} dx dy = A_p \delta_{\mathbf{q}_\perp, \mathbf{q}'_\perp}$.

4. Show that the free energy can be written formally as :

$$\mathcal{F}(B) = \mathcal{F}_0 + \frac{k_B T}{2} \sum_{\mathbf{q}_\perp, q_z} \ln [\kappa_b q_\perp^4 + 2B (1 - \cos q_z d)],$$

where \mathcal{F}_0 is some constant (unimportant).

5. We are interested in the excess free energy (per unit surface area and per membrane) Δf_s of the stack as compared to the separate membranes. To which value of B corresponds the non-interacting membranes state? Using again the continuous approximation, deduce that

$$\Delta f_s = \frac{dk_B T}{16\pi} \int_{-\pi/d}^{\pi/d} dq_z \sqrt{\frac{2B(1 - \cos q_z d)}{\kappa_b}} = \frac{k_B T}{2\pi} \sqrt{\frac{B}{\kappa_b}}.$$

We give : $\int_0^\infty \ln \left[\frac{x^2+c}{x^2} \right] dx = \pi \sqrt{c}$.

6. The equation above constitutes a self-consistent equation : B itself is related to the second derivative of the free energy with respect to the average layer spacing ; *i.e.*, imagine a uniform expansion or compression of the system. The restoring force is just the effective value of B which is proportional to the macroscopic compressibility of the system :

$$B = \frac{\partial^2 \Delta f_s}{\partial d^2}.$$

Show that $\Delta f_s = \alpha/d^2$ is solution of the self-consistent equation, and determine α . Is it consistent with the simple models developed in 5.1.1 and 5.1.2?