

Experimental Soft Matter (M. Durand, G. Foffi)

Nota Bene

Exam duration : 3H30

Lecture notes, cell phones and other electronic devices are not allowed.

Accepted languages : english, french.

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

1st Part

This part is composed of questions on what we have seen in class. For each question, explain your reasoning in a concise yet precise way explaining each step carefully. Each section has the same weight for the final mark.

1 Electrostatics in Soft Matter

1.1 Poisson-Boltzmann Equation

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

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

1.2 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

- (a) Linearize the PBE to obtain his linearized version (LPBE, or DH theory).
- (b) Solve the LPBE theory and derive an expression for the electrostatic potential.
- (c) A characteristic length, the Debye length λ_D , emerges. Discuss its physical interpretation.
- (d) Discuss in details what are the conditions under which the PBE can be linearized.
- (e) Show that for a spherical macro ion of charge $Q = Ze$ and diameter d in a solution of NaCl of ionic strength I , the LBE can be solved. Show (briefly!) that the potential can be derived as :

$$\psi(r) = \frac{Ze}{4\pi\epsilon(1 + \frac{d/2}{\lambda_D})} \frac{e^{-\frac{(r-d/2)}{\lambda_D}}}{r} \quad (1)$$

2 Solutions, Osmotic Pressure and depletion interactions

The difference in Gibbs energy of mixing for a regular solution is given by :

$$\Delta G_{mix} = Wx_Ax_B + Nk_B T [x_A \ln x_A + x_B \ln x_B] \quad (2)$$

where x is the molar fraction and W is a constant.

- (a) Discuss the different terms in Eq. 2 and briefly describe their derivation. What is the main assumption behind the regular solution free energy?

- (b) Discuss the concept of osmotic pressure and discuss its physical consequences. Show that, in ideal conditions, van't Hoff equation :

$$\Pi = RTc_B \quad (3)$$

where c_B is the concentration, holds. Show the analogy to Boyle equation. What happen in non ideal conditions? How can we correct Eq.3.

- (c) We discuss a case in which the PB equation can be solved analytically, the Guoy-Chapman theory for the double layer. Discuss this fundamental result.

Imagine two plates placed of surface A in a solution of spherical particles of diameter d . We work in with N spheres in a volume V . The situation is depicted in Fig. 1.

- (a) Imagine that the spheres do not interact between them, but they are excluded by the plates. What is the interaction between them ?
- (b) Derive the effective force between the two plates as a function of the distance h using the osmotic pressure of the solution. Justify, the approximation, you made.
- (c) Can you sketch the derivation of the same results in the canonical ensemble? (*A full derivation is a bonus*)
- (d) In the real word, the spheres could be some nano-particles or polymers. When does the ideal solution approximation holds? What happen when it breaks? Can you imagine how the force between the plates would change?

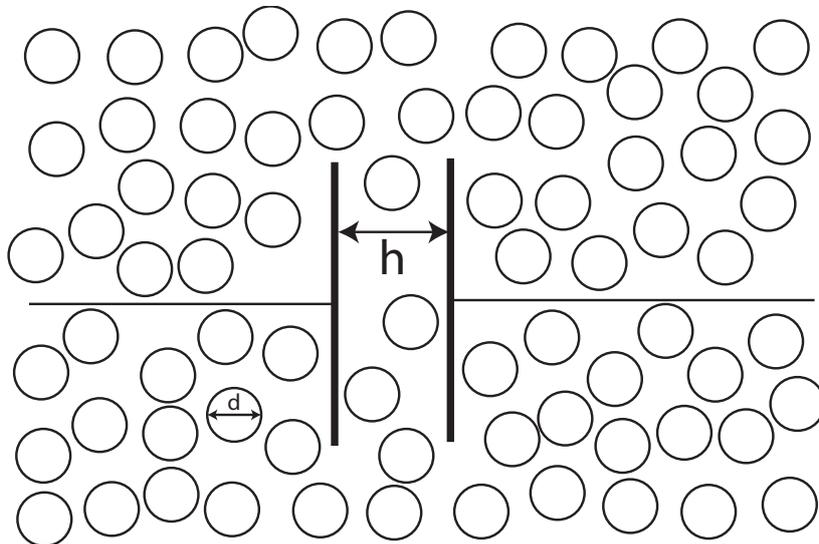


FIGURE 1 – Two planes in a *sea* of ideal spheres.

3 Structure of a simple/complex liquid.

In this section we will discuss the tools that we introduced to describe the structure of a simple or a complex system.

- (a) Explain the general difficulties of treating an interacting systems in the context of the canonical ensemble.
- (b) Define the distribution functions, $\rho^{(n)}(r)$, in the canonical ensemble and discuss what is the advantage in introducing the distribution functions.
- (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 ?
- (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 $S(q)$.
- (f) Discuss how scattering can be used to measure the structure of a fluid.

2nd Part : On Bubbles and Foam...

The two exercises of this part are independent.

4 Equilibrium configuration of a bubble

For a very small bubble with low surface energy, thermal fluctuations can alter the bubble shape, as sketched in Fig. 2. For simplicity, we will consider a “two-dimensional” bubble; this may correspond to a bubble squeezed between two parallel plates. The surrounding gas is at constant pressure P_0 and constant temperature T . We assume that the inside gas and the outside gas are the same. We note γ the surface tension between the gas and the liquid, and h the height between the two parallel plates. We use a coarse-grained description in which every microstate L of the bubble

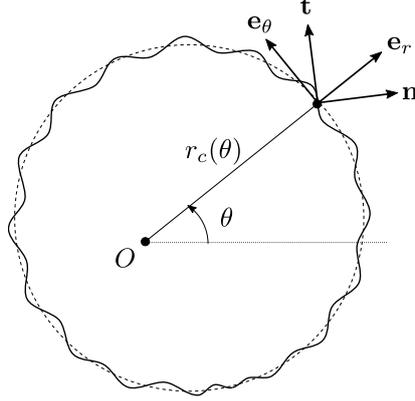


FIGURE 2 – Thermal fluctuations of a small two-dimensional bubble.

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

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

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

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

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

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

3. Let A_0 be the area that the encapsulated gas would occupy for its pressure to be equal to the surrounding pressure P_0 . Show that for small values of $P_L - P_0$, G_L can then be expanded as :

$$G_L \simeq G_0 + 2\gamma h \mathcal{L} + \frac{B(T, P_0) h (A - A_0)^2}{2 A_0}, \quad (4)$$

and give the physical interpretation of G_0 .

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

We now want to determine the average bubble configuration.

5. Justify that the average bubble configuration is obtained by looking for the contour that minimizes the partial free enthalpy [Eq. (4)].
6. To describe the bubble contour, we use the polar parametrization $\theta \mapsto r_c(\theta)$, as shown in Fig. 2. The origin O can be any point within the bubble. Does this parametrization allow to consider all possible configurations of the contour?
7. Let ds be the length of an elementary piece of the contour. Express $ds/d\theta$ in terms of $r_c(\theta)$ and its derivative $\dot{r}_c(\theta)$.
8. Deduce the integral expression for the partial free enthalpy of the liquid film $G_L^{(f)} = 2\gamma h\mathcal{L}$.
9. We admit that the area of the bubble is $A = \oint r_c^2(\theta)d\theta/2$. Show that the change of partial free enthalpy [Eq. (4)] associated with the elementary change of contour $r_c(\theta) \rightarrow r_c(\theta) + \delta r_c(\theta)$ can be written :

$$\delta G = \oint f(r_c, \dot{r}_c)\delta r_c(\theta)d\theta + \oint g(r_c, \dot{r}_c)\delta \dot{r}_c(\theta)d\theta, \quad (5)$$

where functions f and g have to be expressed.

10. What is the relation between $\delta r_c(\theta)$ and $\delta \dot{r}_c(\theta)$? Using integration by parts on the second integral, finally show that the contour that extremizes the partial free enthalpy is given by :

$$2\gamma \left[\frac{1}{(r_c^2 + \dot{r}_c^2)^{1/2}} - \frac{1}{r_c} \frac{d}{d\theta} \left(\dot{r}_c (r_c^2 + \dot{r}_c^2)^{-1/2} \right) \right] + B \frac{A - A_0}{A_0} = 0. \quad (6)$$

11. To interpret this equation, it is useful to introduce the local curvature $\kappa(\theta)$ of the contour, defined through :

$$\frac{d\mathbf{t}}{ds} = -\kappa(\theta)\mathbf{n},$$

where $\mathbf{t} = \frac{d\mathbf{r}}{ds}$ and \mathbf{n} are the unit vectors locally tangent and normal to the contour respectively, as depicted in Fig. 2. Express the components of \mathbf{t} , $\frac{d\mathbf{t}}{ds}$ and \mathbf{n} on the polar vector basis $(\mathbf{e}_r, \mathbf{e}_\theta)$, and show that the local curvature is given :

$$\kappa(\theta) = (r_c^2 + \dot{r}_c^2)^{-1/2} - \frac{1}{r_c} \frac{d}{d\theta} \left(\dot{r}_c (r_c^2 + \dot{r}_c^2)^{-1/2} \right).$$

12. Rewrite Eq. (6) by introducing $\kappa(\theta)$. How is called the obtained relation? What is the average shape of the bubble?
13. Without doing all the calculations, what would have changed in Eq. (6) if, instead of taking the contribution of the compressive term into account in the partial free enthalpy, we would have consider that the inside gas was incompressible (*i.e.* $A = \text{constant}$)?

5 Foam coarsening

The pressure differences between the bubbles of a disordered foam drive the diffusion of gas through the thin films which separate them (see Fig. 3). A single bubble will shrink and disappear for this reason, and a similar fate awaits each bubble in a foam. While some will initially grow at the expense of others, all must eventually perish. This process is called *coarsening*. In this problem, we want to derive the equations of foam coarsening and study the so-called self-similar regime of coarsening.

5.1 Von-Neumann's law

We note γ the surface tension between the liquid and the gas phases.

1. Express the rule on the number of adjoining films and the angle condition at every vertex of a two-dimensional foam at mechanical equilibrium (Plateau's laws).
2. By counting the total turning angle made by a tangent vector traveling over the contour of bubble i , establish the Gauss-Bonnet formula which relates the number of sides n_i of this bubble, and κ_{ij} , l_{ij} (with $j \in \{1, \dots, n_i\}$), respectively the curvature and length of the side shared by bubbles i and j .

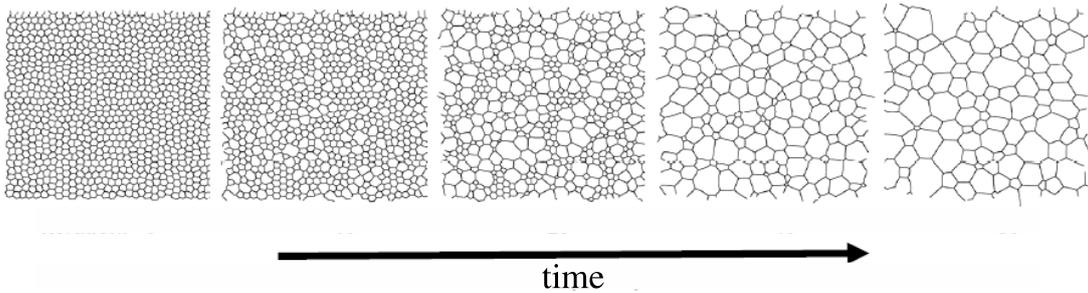


FIGURE 3 – Coarsening of an initially monodisperse foam. Pictures are taken at regular time intervals. Self-similar growth appears only at sufficiently long time.

3. As a very good approximation, the gas flow-rate between adjacent bubbles i and j is $\phi_{ij} = Dl_{ij}(p_i - p_j)$, where D is the permeability of the soap film. Deduce that the growth rate of the area A_i of a bubble having n_i sides is given by the so-called Von Neumann's law :

$$\frac{dA_i}{dt} = k(n_i - 6), \quad (7)$$

with $k = \frac{2\pi\gamma D}{3}$.

4. Statistically, smaller bubbles in a foam have $n_i < 6$ and larger bubbles $n_i > 6$. What Eq. (7) tells us about the “destiny” of a bubble depending on its size?

5.2 Foam coarsening equations and self-similar regime

Let $f(A, n, t)dA$ be the number of bubbles having n sides and area $\in [A, A + dA]$ at time t .

1. Suppose first that every bubble keeps its number of sides fixed in time. Show that the distribution $f(A, n, t)$ then follows the following continuity equation, for any value of n :

$$\frac{\partial f}{\partial t} + k(n - 6) \frac{\partial f}{\partial A} = 0.$$

2. In fact, due to the space-filling constraints and the disappearance of bubbles with time, the number of sides of every bubble evolves with time. This effect can be included in the preceding equation by introducing $I_{mn}(A, t)$, the rate of m -sided bubbles with area A that become n -sided. Such “topological transitions” are taken to be instantaneous, and the bubble area A does not change at the moments they occur. Continuity equation then becomes :

$$\frac{\partial f}{\partial t} + k(n - 6) \frac{\partial f}{\partial A} = I_n(A, t),$$

where $I_n = \sum_m I_{mn}$.

We assume that all vanishings of bubbles are due to the decrease of the areas to zero; bubbles cannot leave the system due to topological transitions. Hence, what is the value of $\sum_n I_n$?

So-called self-similar regime is defined as temporal evolution in which the dimensionless statistical distributions remain stationary. That is, the foam structure at two different times within this regime has statistical characteristics which differ only in their length-scale, *i.e.* the average bubble size. Two successive photos of the foam, if the scale is not specified, appear alike.

3. To study the self-similar regime, one introduces $p(\alpha, n, t)$, the fraction of bubbles having n sides and relative area $\alpha = A/\langle A \rangle(t)$ at time t . $\langle A \rangle(t)$ is the average bubble area at time t . Express the relation between $p(\alpha, n, t)$, $f(A, n, t)$, $\langle A \rangle(t)$, and $N(t)$, the number of bubbles in the foam.
4. Then show that the continuity equation for the dimensionless area distribution $p(\alpha, t) = \sum_n p(\alpha, n, t)$ is :

$$\langle A \rangle \left(\frac{\partial}{\partial t} p(\alpha, t) + \frac{1}{N} \frac{dN}{dt} p(\alpha, t) \right) - \frac{d\langle A \rangle}{dt} \left(p(\alpha, t) + \alpha \frac{\partial}{\partial \alpha} p(\alpha, t) \right) + k \frac{\partial}{\partial \alpha} [(\bar{n}(\alpha) - 6)p(\alpha, t)] = 0,$$

where $\bar{n}(\alpha, t) = \sum_n np(\alpha, n, t) / \sum_n p(\alpha, n, t)$ denotes the mean number of sides of a bubble with relative area α at time t .

To solve this equation, we need first to determine the evolution of $N(t)$ and $\langle A \rangle(t)$.

5. Using Von Neumann's law [Eq. 7], show that the number of bubbles whose area decrease to 0 (and thus disappear) in the infinitesimal time interval dt is $\frac{N(t)}{\langle A \rangle} \sum_{n \leq 6} p(0, n, t) k(6 - n) dt$.
6. In the self-similar regime, the normalized distribution function $p(\alpha, n, t)$ does not explicitly depend on time. Deduce that

$$\frac{1}{N} \frac{dN}{dt} = -\frac{Ck}{\langle A \rangle(t)},$$

where C is some constant.

7. Suppose that the foam fills a container with fixed total area $A_{tot} = N(t)\langle A \rangle(t)$ ($\gg \langle A \rangle(t)$). Deduce the time evolution of $\langle A \rangle(t)$ and $N(t)$ in the self-similar regime. Are your findings in agreement with the experimental observation of Fig. 4.

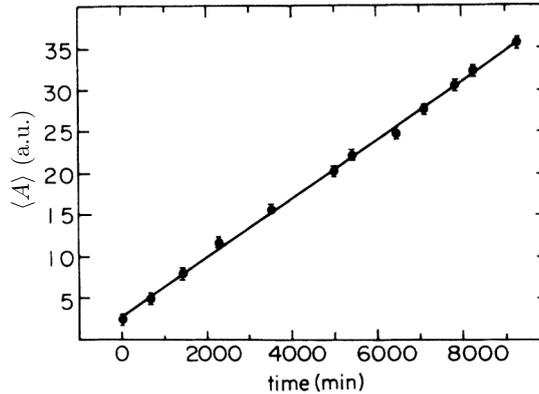


FIGURE 4 – Average bubble area $\langle A \rangle$ vs time in a coarsening two-dimensional foam, in the self-similar regime. J. Stavans, *Physical Review A* **42**, 5049-5051 (1990).

8. Actually, the scaling-law between $\langle A \rangle$ and t can be obtained with another argument : suppose that all lengths in a foam structure are magnified by a factor λ . According to Laplace's law, how is scaled the pressure difference between two adjacent bubbles? Therefore, how is scaled the rate of gas transfer between the two bubbles? Conclude on the variation of $\langle A \rangle$ with t .
9. Using your preceding results, show that in this regime the continuity equation simplifies to :

$$-C \left(2p(\alpha) + \alpha \frac{\partial}{\partial \alpha} p(\alpha) \right) + \frac{\partial}{\partial \alpha} [(\bar{n}(\alpha) - 6)p(\alpha)] = 0.$$

10. Experience reveals an exponentially decreasing distribution of bubble areas in the self-similar regime : $p(\alpha) = e^{-\alpha}$. Derive the corresponding expected shape for $\bar{n}(\alpha)$.