

EXAM

3 HOURS ; DOCUMENTS AND POCKET CALCULATORS NOT ALLOWED

Tentative scale : 7 points for problem I, 7 points for problem II and 6 points for problem III

I On the fluctuation theorem*N.B. The different questions are, to a large extent, independent.*

We consider a classical Hamiltonian system, initially in thermal equilibrium at temperature T . The goal of this problem is to show that the free energy difference between two states of the system can be obtained from *non equilibrium averages*, taken over a large number of realizations of the same experiment, where an external parameter λ is modified (λ can be, for instance, the system volume, or any other quantity that can be controlled by the experimentalist). Between the initial time $t = 0$ and the final time t_f , λ changes from $\lambda = 0$ (the system is then in the macroscopic state A_0) to $\lambda = 1$ (the system is then in the macroscopic state A_1), following a temporal evolution $\lambda(t)$ that is given once and for all. During that operation, the work received by the system reads

$$W = \mathcal{H}_1(\Gamma(t_f)) - \mathcal{H}_0(\Gamma(0)) \quad (1)$$

where $\Gamma(t)$ denotes the point in phase space where the system sits at time t , and $\mathcal{H}_\lambda$ is the Hamiltonian, parameterized by λ . The partition function associated to $\mathcal{H}_\lambda$ at temperature T is denoted Z_λ . From a realization of the experiment to the next (in all realizations, the system is brought from state A_0 to state A_1), the work W fluctuates, e.g. because initial conditions correspond to different starting points $\Gamma(0)$ in phase space. We denote $\overline{(\dots)}$ average values taken over all possible realizations of the experimental protocol, that is encoded in the function $\lambda(t)$ (it is not necessary to specify its time dependence). In the following, we suppose that at $t = 0$, the system is decoupled from the thermostat and subsequently evolves following Hamilton equations of motion.

1. Jarzynski equality

(a) We have

$$\overline{e^{-\beta W}} = \int e^{-\beta W} \rho(\Gamma(0)) d\Gamma(0) \quad (2)$$

where $\beta^{-1} = kT$ and the integral runs over all phase space. What is the expression of the probability density $\rho(\Gamma(0))$?

(b) In expression (2), the work W only depends on $\Gamma(0)$. Using definition (1), and invoking some properties of Hamiltonian systems, show that

$$\overline{e^{-\beta W}} = e^{-\beta \Delta \phi}. \quad (3)$$

What is the meaning of $\Delta \phi$? The identity (3) bears the name of Jarzynski, and we shall admit that it remains valid when the system remains in contact with the thermostat during the experiment.

(c) Obtain from (3) an inequality between $\overline{W}$ and $\Delta \phi$. What does it mean?

2. Limiting cases

(a) In the reversible limit (where $t_f \rightarrow \infty$ and the system can be considered at thermal equilibrium at all times), what is the expression of $\overline{W}$? How can this result be compatible with equality (3)?

- (b) (more difficult) We would like to explicitly check the above result. First express W as an integral of $\partial\mathcal{H}_\lambda/\partial\lambda$ and show that

$$\frac{\partial \log Z_\lambda}{\partial \lambda} = -\beta \left\langle \frac{\partial \mathcal{H}_\lambda}{\partial \lambda} \right\rangle_\lambda, \quad (4)$$

where the meaning of the average $\langle \dots \rangle_\lambda$ should be specified. Conclude.

- (c) Conversely, in the limit where the transformation is instantaneous ($t_f \rightarrow 0^+$), (3) has a particular meaning. Under such circumstances, we indeed have

$$W = \mathcal{H}_1(\Gamma(0)) - \mathcal{H}_0(\Gamma(0)) \quad (5)$$

and it can be noted that the definition (2) yields $\overline{e^{-\beta W}} = \langle e^{-\beta W} \rangle_0$. Show that Jarzynski's equality is recovered.

3. Crooks relation

We denote $p(W)$ the probability density function of W , obtained from the ensemble of realizations of the experimental protocol. We then have

$$\overline{e^{-\beta W}} = \int e^{-\beta W} p(W) dW. \quad (6)$$

It is possible to derive a more general relation than Jarzynski's. It relates the probability density $p_F(W)$ holding for the “direct” experiment, to $p_B(W)$ characteristic of the “inverse” process (F stands for “forward”, and B for “backward”, in which case the system goes from state A_1 to A_0 , where λ changes from 1 (at $t = 0$) to 0 (at $t = t_f$) following the law $\lambda(t_f - t)$).

- (a) On general grounds, it is possible to express the probability density function of a given random variable from an appropriate average of a Dirac distribution. Specifically, this gives here :

$$p_F(W) = \frac{1}{Z_0} \int e^{-\beta \mathcal{H}_0(\Gamma(0))} \delta(W - \mathcal{H}_1(\Gamma(t_f)) + \mathcal{H}_0(\Gamma(0))) d\Gamma(0). \quad (7)$$

In such conditions, how is $p_B(W)$ defined ?

- (b) Show that

$$p_F(W) e^{-\beta W} = e^{-\beta \Delta F} p_B(-W), \quad (8)$$

where ΔF is the free energy difference $F(A_1) - F(A_0)$. We again assume here that during the transformation, the system is decoupled from the thermostat, and we admit that the results obtained still hold when the system remains in thermal contact with the heat bath.

- (c) Show that Jarzynski equality (3) can be readily recovered from (8).
(d) Discuss briefly the reversible limit.

4. The case of Gaussian fluctuations

We are interested here only in the direct process (“forward”). In the limit where the transformation is sufficiently slow (without being necessarily reversible), $p(W)$ takes a Gaussian form. We denote $\overline{W}$ its mean, and σ the corresponding standard deviation.

- (a) Show that equation (3) implies that

$$\overline{W} = \Delta F + \alpha \beta \sigma^2 \quad (9)$$

where α is a constant that should be precised.

- (b) In what sense can the previous relation be coined “fluctuation-dissipation” ? Briefly discuss the reversible limiting case.

5. ... where one measures the length of time's arrow ...

Reminder : the Kullback-Leibler distance between two discrete probability distributions $\{p_i\}$ and $\{q_i\}$ reads :

$$D(p||q) = \sum_i p_i \log \left(\frac{p_i}{q_i} \right). \quad (10)$$

Generalize the above definition in the continuous case, and give the expression of the distance between the distributions $p_F(W)$ and $p_B(-W)$. Establish then a connection between the irreversibility on the one hand, and the distinguishability of forward and reverse protocols (as measured by their distances) on the other hand.

6. Application to single molecule experiments

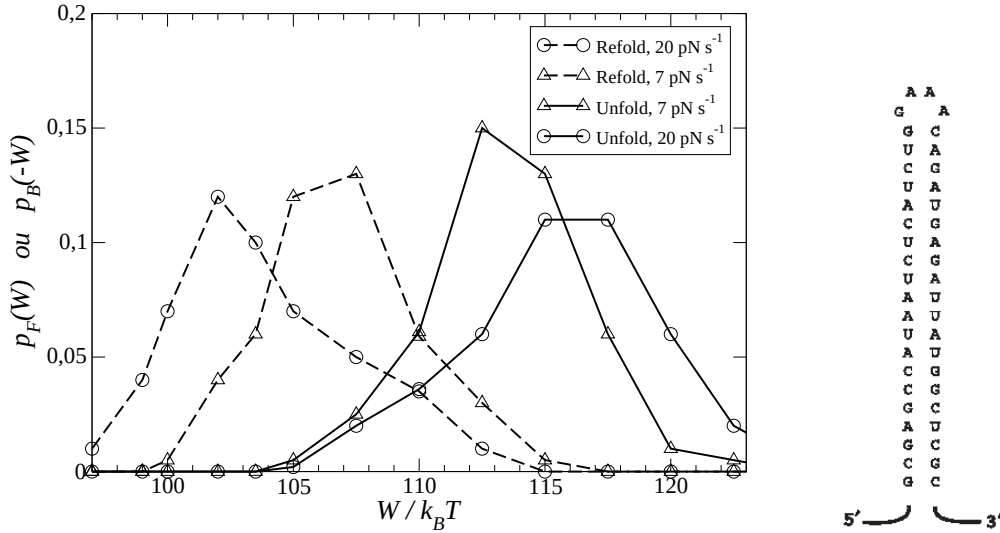


FIG. 1 – Left : plots of probability densities $p_F(W)$ (continuous curves) and $p_B(-W)$ (dashed curves) in an experiment of unfolding/refolding of an RNA strand. Right : the RNA strand in its hairpin configuration. From Collin *et al.*, Nature **437**, 231 (2005).

Figure 1 represents work distributions as measured in experiments where an RNA strand in a folded configuration (forming an hairpin) is unfolded by a mechanical force applied on both ends (denoted 3' and 5' on figure 1). The reverse process (folding) is spontaneous (with mostly negative values of W). The results shown have been obtained using two different experimental protocols : one is fast (data at 20 pN s^{-1} , corresponding to the circles), and the other is slow (data at 7 pN s^{-1} , corresponding to the triangles).

- Invoking Crooks relation, the free energy difference for unfolding can be directly read on figure 1. What is this difference ?
- How can the offset between folding and unfolding curves be explained ? Are the data shown in figure 1 compatible with the body of results obtained earlier ?

References :

- *Nonequilibrium equality for free energy differences*, C. Jarzynski, Physical Review Letters **78**, 2690 (1997).
- *Entropy production fluctuation theorem and the non-equilibrium work relation for free energy differences*, G.E. Crooks, Physical Review E **60**, 2721 (1999).

II Shape of liquid droplets

Question 3 is independent from the previous ones.

Our interest goes to the shape of a droplet on a solid substrate, in the gravitational field $\mathbf{g}$. For the sake of simplicity, we assume the droplet to be translationally invariant along a direction parallel to the substrate, and perpendicular to the plane of Fig. 2. We are then led to a two-dimensional problem, where the droplet is entirely characterized by the profile $\zeta(x)$ (see figure 2). In what follows, we will assume the dimension perpendicular to the plane of the figure to be unity.

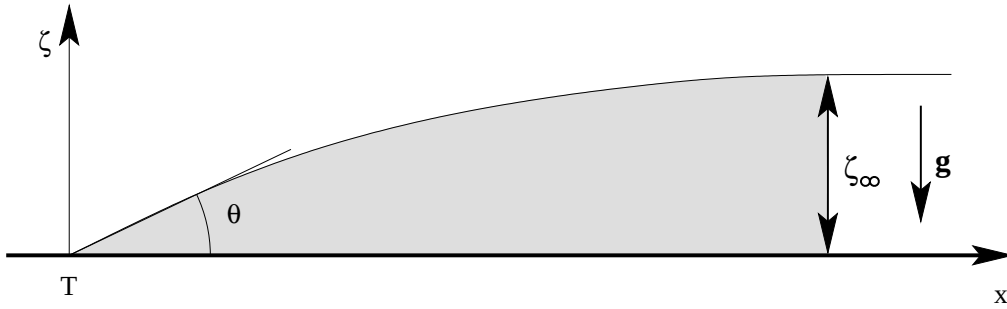


FIG. 2 – Profile of a liquid drop on a substrate.

The liquid/vapor, substrate/liquid and substrate/vapor interfacial tensions are respectively written γ_{LV} , γ_{SL} and γ_{SV} . As a reminder, we recall the mechanical interpretation of surface tension γ . On Fig. 3, the right part of the interface (seen from above) exerts on the left part a force per unit length γ .

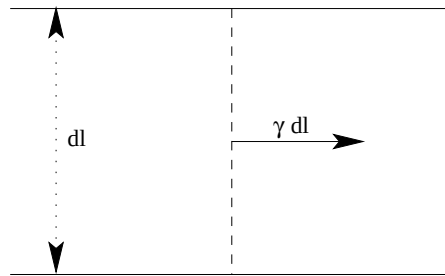


FIG. 3 – Force due to interfacial tension.

For numerical estimations, we shall consider that for water : $\gamma_{LV} = 70 \text{ mN m}^{-1}$ and that the density is $\rho_L = 1000 \text{ kg m}^{-3}$.

1. Young-Dupré relation

The contact line (point T on figure 2) is the line where the three interfaces meet. Balancing the different capillary forces felt by the contact line, write the relation between the contact angle θ (defined on figure 2) and the three interfacial tensions.

2. Macroscopic shape of the droplet

- (a) For a sufficiently small droplet, it is possible to neglect gravity effects. What is then the shape of the drop (no calculation asked) ?
- (b) For a sufficiently big drop, gravity forces have a tendency to flatten the apex. We assume here that the drop reaches a constant height ζ_∞ (on the right hand side of figure 2).
 - i. We denote by P_∞ the pressure in the vicinity of the apex (top of the drop). Assuming mechanical equilibrium, what is the height (z) dependence of the pressure inside the vapor ($P_V(z)$) and inside the liquid ($P_L(z)$) ? The result should be expressed as a function of vapor (ρ_V) and liquid (ρ_L) densities.

- ii. We suppose $\rho_V \ll \rho_L$. What is the net horizontal pressure force felt by the grey portion of the drop on figure 2?
 - iii. Write (without calculations) the net capillary force felt by the same fluid portion (grey zone on figure 2. This force is horizontal.
 - iv. Enforcing mechanical equilibrium of the drop grey portion, obtain the maximal height ζ_∞ , as a function of γ_{LV} , ρ_L , g and θ .
 - v. *Numerical estimation.* A glass of water is spilled over a flat surface. The contact angle is $\theta = 5^\circ$. Estimate the spread of the puddle (film of water).
- (c) What is the characteristic length discriminating the regimes of “small” and “large” droplets? No calculation is asked here.

3. Shape of the droplet near the contact line

After the previous macroscopic arguments, we are now interested in the microscopic details in the vicinity of the contact line. We study a thin drop, forming a liquid film, that partially wets the substrate : the *macroscopic* contact angle is θ , with $0 < \theta \ll 1$. The word *macroscopic* indicates that this angle is an apparent angle, when observed sufficiently far from the contact line (see figure 4). In the immediate vicinity of this line, interactions with the substrate significantly alter the profile. The goal here is to quantify this effect.

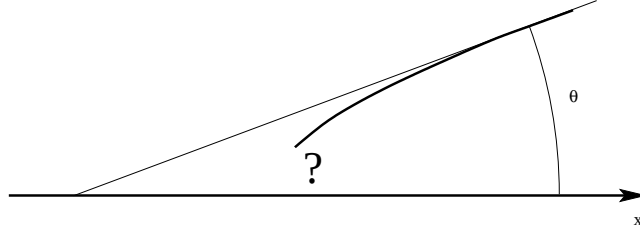


FIG. 4 – Deformation of the drop boundary.

It is admitted that the free energy of a drop having a given profile $\zeta(x)$ ($0 \leq x \leq x_M$) can be written :

$$f = f_0 + \int_0^{x_M} dx \left[C + \frac{A}{12\pi\zeta^2} + K \left(\frac{d\zeta}{dx} \right)^2 + G(\zeta) \right] \quad (11)$$

where f_0 , C , A , and K are constants. We assume $A > 0$.

(a) Interpretation of the different factors

- i. $G(\zeta) dx$ is the gravitational potential energy of the liquid slice between x and $x + dx$. What is the expression of $G(\zeta)$?
- ii. The quantity C represents the interfacial energy excess between the substrate covered by a thick film (of uniform thickness), and the dry substrate. Provide C as a function of interfacial tensions.
The term $A/(12\pi\zeta^2)$ accounts for Van der Waals interactions that become relevant for thin films. It is not asked to justify this term.
- iii. The quantity $K(d\zeta/dx)^2$ corresponds to the excess area of the liquid-vapor interface, with respect to a constant thickness film. For a given curve $\zeta(x)$, it is reminded that the length of an infinitesimal section as measured by the curvilinear abscissa ds , reads $(ds)^2 = (dx)^2 + (d\zeta)^2$. What is then the expression of K ?

(b) Equilibrium drop profile

- i. The drop is in equilibrium with a thermostat. The liquid is assumed incompressible and non volatile, so that the volume and number of particles in the drop are fixed. What is then the relevant thermodynamic potential? How is equilibrium determined from the above potential?

- ii. Obtain the differential equation obeyed by $\zeta(x)$ at equilibrium. NB : for simplicity, it is admitted that there is no need to impose constraints for volume or particle number conservation.
- iii. Show that the above equation can be integrated to yield

$$K \left(\frac{d\zeta}{dx} \right)^2 = \frac{\gamma_{LV}}{2} \left(\frac{a}{\zeta} \right)^2 + G(\zeta) + D \quad (12)$$

where D is an integration constant (yet unspecified). What is the expression of quantity a ?

- iv. *Numerical estimation* For water on most solids, $A \simeq 10^{-19}$ J. Estimate a .

We now search for a solution of equation (12) in the vicinity of the contact line. $G(\zeta)$ can then be safely neglected, and we do so in the remainder.

- v. It is admitted that $D = \gamma_{LV} \theta^2 / 2$. What is the profile ζ of the drop, as a function of x , a and θ ? Draw schematically the graph of this solution.
- vi. The previous arguments hold provided $d\zeta/dx \ll 1$. Under which conditions on ζ is the profile found earlier acceptable?
- vii. Estimate the height below which the profile departs from a straight line.
Numerical estimation. Taking $A \simeq 10^{-19}$ J and $\theta = 1^\circ$, what is the corresponding value of that length?
- viii. In the complete wetting case, $\theta \rightarrow 0$ and we admit that $D = 0$. Solve equation (12) and find the corresponding profile ζ as a function of x and a . Draw it schematically.

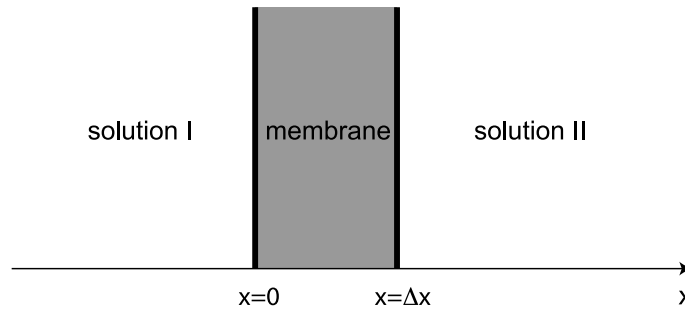
Reference : *Gouttes, bulles, perles et ondes*, P.-G. de Gennes, F. Brochard-Wyart et D. Quéré, Belin, 2002.

III Filtration properties of a membrane

We consider a membrane of thickness Δx , that separates two compartments. Each compartment is filled with a solution made up of an incompressible solvent, and a neutral solute having a small concentration. We note n^I the particle concentration per unit volume in compartment I , while n^{II} stands for its counterpart in compartment II . Likewise, we denote c^I the (dimensionless) relative solute fraction in compartment I , c^{II} is the solute fraction in compartment II (and so on and so forth for other quantities). The concentration in each compartment is supposed spatially homogeneous. We will denote with Δ the differences of any quantity between compartment II and I : for instance, $\Delta c = c^{II} - c^I$. Temperature T is constant and spatially uniform. We simplify the problem assuming all spatial variations to take place along the x coordinate. v and v_s will respectively stand for the solvent and solute volume per particle (and more generally, the subscript s will be used for solvent properties). The following results for dilute solutions are reminded

$$\begin{aligned} \mu_s &= \mu_0(T, P) - kT c \\ \mu &= \psi(P, T) + kT \log c, \end{aligned}$$

where μ_0 is the pure solvent chemical potential and the energy ψ is not specified.



1. For a membrane that is permeable to the solvent and impermeable to the solute, what is the expression of the equilibrium pressure difference $\Delta\pi$ between both compartments? $\Delta\pi$ can be written first as a function of Δc , and then of Δn . How is $\Delta\pi$ called usually?

We now consider a membrane that is permeable to the solute. In an out of equilibrium situation, the chemical potentials of both constituents can have different values in the two compartments, so that currents may appear. We denote J the solute current density (along x axis) in the membrane. Likewise, J_s is for the solvent current density. The chemical potentials μ and μ_s are assumed continuous at $x = 0$ and $x = \Delta x$.

2. Write the local entropy production rate per unit volume $\dot{s}$ in the membrane as a function of temperature T , currents J , J_s and chemical potentials μ , μ_s .
3. In the stationary case, what is the x dependence of the currents?
4. In a stationary situation again, integrating over the membrane thickness provides the expression for the entropy production rate σ per unit surface of the membrane, as a function of μ , μ_s , J , J_s and T .

In what follows, we assume that Δx is small, and we elaborate on the previous expression for σ .

5. Write $\Delta\mu_s$ as a function (among other quantities) of ΔP , the pressure difference between both compartments, and $\Delta\pi$ (obtained in question 1).
6. Show that $v = \left. \frac{\partial\psi}{\partial P} \right|_T$. In what follows, we shall assume v independent of the pressure.
7. Write the expression of $\Delta\mu$ as a function of ΔP and $\Delta\pi$. We introduce the mean concentration $\bar{n} = (n^{II} + n^I)/2$ and we also suppose that $\Delta n \ll \bar{n}$.
8. Infer from the above that the entropy production rate σ can be written :

$$\sigma T = -(J_s v_s + J v) \Delta P - \left(\frac{J}{\bar{n}} - v_s J_s \right) \Delta\pi. \quad (13)$$

We define $J_1 = (v_s J_s + v J)$ and $J_2 = \left(\frac{J}{\bar{n}} - v_s J_s \right)$.

9. What is the physical interpretation of current J_1 ?
10. From $\Delta n \ll \bar{n}$, write J_2 as a function of the mean velocities of solute and solvent (respectively u and u_s) in the membrane. What is the physical meaning of flux J_2 ?
11. In the same approximation, write J_1 as a function of u_s . Refine the interpretation of J_1 .
12. The currents are written in the form :

$$J_1 = -L_{11}\Delta P - L_{12}\Delta\pi \quad (14)$$

$$J_2 = -L_{21}\Delta P - L_{22}\Delta\pi \quad (15)$$

Justify such a relation and provide the important properties of coefficients L_{ij} , indicating (without proof) the physical origin of those properties.

13. We assume here that $\Delta\pi = 0$. How is this achievable experimentally? Provide the physical interpretation of coefficients L_{11} and L_{21} . We define $r = -\frac{L_{21}}{L_{11}}$. Express u/u_s as a function of r . Discuss the properties of the membrane as parameterized by r .
14. Write J as a function of ΔP and $\Delta\pi$.
15. Under which conditions on the coefficients L_{ij} does the membrane behave as an ideal semi-permeable membrane?
16. Write J in the form

$$J = a J_1 - \omega \Delta\pi. \quad (16)$$

Provide the expressions of a and ω . What is the sign of ω ? What does this coefficient mean?

17. We impose $J_1 = 0$. How can that be achieved in practice? What is the time evolution of $\Delta\pi$? The result makes use of the macroscopic volumes of both compartments V^I and V^{II} , and of the membrane surface as well.
18. Propose an experimental method to measure r and ω .