### EXAM

# 3 HOURS; DOCUMENTS AND POCKET CALCULATORS NOT ALLOWED Tentative scale : 10 points for problem I, 10 points for problem II

## I The Potts model

The multinomial expansion formula, that can prove useful here, is reminded in the annex below. In addition, question 15 may be treated almost independently from the others.

We consider a variant of Ising model, the so-called Potts model, where the N degrees of freedom (spins)  $\sigma_1, \ldots, \sigma_N$  may each take q different values,  $\sigma_i \in \{1, \ldots, q\}$ , where q is, for the time being, an arbitrary integer  $\geq 2$ . The spins interact with the following hamiltonian

$$H(\sigma_1, \dots, \sigma_N) = -\sum_{i,j=1}^N J_{i,j} \delta_{\sigma_i, \sigma_j} - \sum_{i=1}^N h_{\sigma_i} , \qquad (1)$$

where  $J_{i,j}$  is the coupling constant between spins *i* and *j*,  $\delta$  denotes Kronecker symbol and  $h_1, \ldots, h_q$  can be seen as magnetic fields acting on the *q* possible values of the spins. Such an approach is useful to study theoretically a variety of condensed matter problems in a unified framework, and is also relevant to model some experimental systems such as Krypton adsorbed on graphite. In the remainder, we shall work in the canonical ensemble, the system being in equilibrium at temperature *T*. We denote the Boltzmann constant by  $k_{\rm B}$  and averages over the Boltzmann-Gibbs distribution by  $\langle \cdot \rangle$ .

1. We consider here the q = 2 case. Establish that Potts model is then equivalent, up to a constant, to Ising model with variables  $\sigma_i^{(I)} = \pm 1$  and a hamiltonian

$$H(\sigma_1^{(\mathrm{I})}, \dots, \sigma_N^{(\mathrm{I})}) = -\sum_{i,j=1}^N J_{i,j}^{(\mathrm{I})} \sigma_i^{(\mathrm{I})} \sigma_j^{(\mathrm{I})} - h^{(\mathrm{I})} \sum_{i=1}^N \sigma_i^{(\mathrm{I})} .$$
<sup>(2)</sup>

Express  $J_{i,j}^{(\mathrm{I})}$  and  $h^{(\mathrm{I})}$  as functions of parameters pertaining to Potts model.

2. From now on, we consider a generic value for q, and we take  $J_{i,j} = \frac{J}{N}$  for all values (i, j), with J > 0. Why can such an approach be coined "mean-field"? Show then that the partition function associated to the hamiltonian (1) can be written in the form

$$Z = \sum_{x_1,\dots,x_q} \mathcal{N}_{x_1,\dots,x_q}^N e^{-N\beta e(x_1,\dots,x_q)} , \quad \text{with} \ e(x_1,\dots,x_q) = -J \sum_{\sigma=1}^q x_{\sigma}^2 - \sum_{\sigma=1}^q h_{\sigma} x_{\sigma} . \tag{3}$$

What are the possible values for  $x_1, \ldots, x_q$ ? Write explicitly the expression of  $\mathcal{N}_{x_1,\ldots,x_q}^N$ .

3. Stirling's formula  $\ln(X!) \sim X \ln X - X$  for  $X \to \infty$  is reminded. Show that the free energy per spin reads, in the thermodynamic limit :

$$f(T) = -\frac{1}{\beta} \lim_{N \to \infty} \frac{1}{N} \ln Z = \inf_{x_1, \dots, x_q} \widehat{f}(x_1, \dots, x_q, T), \quad \text{with}$$

$$\tag{4}$$

$$\widehat{f}(x_1, \dots, x_q, T) = e(x_1, \dots, x_q) - Ts(x_1, \dots, x_q) \quad \text{and} \quad s(x_1, \dots, x_q) = -k_B \sum_{\sigma=1}^q x_\sigma \ln x_\sigma .$$
 (5)

What is the domain where the minimization should be performed? Comment on the expression of  $s(x_1, \ldots, x_q)$ .

- 4. We denote by  $(x_1^*, \ldots, x_q^*)$  the point where the minimum of  $\widehat{f}$  is reached. Show that in the thermodynamic limit, one has  $\langle \delta_{\sigma_i,\sigma} \rangle = x_{\sigma}^*$  for all i and all  $\sigma$ .
- 5. What is the value of  $(x_1^*, \ldots, x_q^*)$  for high temperatures? How can we call the corresponding phase of the system?
- 6. We assume in what follows that  $h_1 = \cdots = h_q = 0$ , and it is reminded that J > 0. What are the possible values of  $(x_1^*, \ldots, x_q^*)$  at vanishing temperature? How can we call the corresponding phases? What is the degeneracy of the ground state?

We now wish to study the transition between the low T and high T regimes. We assume that the spontaneous symmetry breaking that occurs at low T, takes place along the  $\sigma = 1$  direction, and does not distinguish among the other q - 1 possible values. We thus write  $x_1 = x$ , together with  $x_2 = \cdots = x_q$ .

7. Express the common value  $x_2 = \cdots = x_q$  as a function of x. Show then that with the above parametrisation, we have  $f(T) = \inf_x \widehat{f}(x,T)$ , with  $\widehat{f}(x,T) = e(x) - Ts(x)$ . Provide the expressions of the functions e(x) and s(x).

From now on, q is taken as an arbitrary real number  $\geq 2$ , not necessarily an integer (there indeed exists a microscopic alternative definition to (1), that is meaningful for all possible real q).

- 8. Plot schematically and separately the functions e(x) and s(x) for an arbitrary q > 2, emphasizing the behaviour close to the boundaries of their support (lower and upper bound), as well as the behaviour in the vicinity of their extrema (the position of which will be indicated).
- 9. What is the value of x that minimizes  $\widehat{f}(x,T)$  at high temperature? This value will be denoted  $x_0$  in the remainder. Below which temperature, denoted  $T_c^{(2)}$ , is  $x_0$  no longer a local minimum of  $\widehat{f}(x,T)$ ? It may prove useful to show

$$\frac{\partial^2 \hat{f}}{\partial x^2}\Big|_T = -\gamma J \frac{q}{q-1} + k_{\rm B} T \frac{1}{x(1-x)} , \quad \text{where } \gamma \text{ is a constant that will be given.}$$
(6)

- 10. Expand  $\hat{f}(x, T_c^{(2)})$  to third order around  $x = x_0$ . Show then that if q > 2, there exists a temperature  $T_c^{(1)} > T_c^{(2)}$  such that  $x_0$  no longer is the global minimum of  $\hat{f}$  for all temperatures  $T < T_c^{(1)}$ .
- 11. Plot schematically the graphs of  $\widehat{f}(x,T)$  as a function of x for different temperatures.
- 12. In the case q > 2, write the conditions that determine the value of  $T_c^{(1)}$ , and the position of the global minimum  $x^{(1)}$  of  $\hat{f}$  at temperature  $T_c^{(1)^-}$ , i.e. infinitesimally below  $T_c^{(1)}$ . Show that the conditions are met by

$$x^{(1)} = 1 - \frac{\alpha}{q}$$
,  $k_{\rm B}T_{\rm c}^{(1)} = J \frac{q-2}{(q-1)\ln(q-1)}$ . (7)

What is the value of  $\alpha$ ?

- 13. Sketch the graph of the position of  $x^*(T)$ , the global minimum of  $\hat{f}$ , as a function of T. The cases q = 2 and q > 2 should be distinguished. Write down an admissible order parameter. In each case, what is the order of the transition and, if applicable, what is the value of the critical exponent  $\beta$  associated to the critical behaviour of  $x^*(T)$ ?
- 14. Explain qualitatively what would happen if one would consider the exact solution of the Potts model on a given lattice at  $T = T_c^{(1)}$ , imposing a fraction of spins  $\sigma_i = 1$  between  $x_0$  and  $x^{(1)}$ . It will be assumed that the mean-field scenario for q > 2 holds.
- 15. **Application**. The physisorption of Krypton atoms onto a graphite plane provides a possible realization of Potts model. In such a plane, carbon atoms are organized in an hexagonal structure, and Krypton preferentially adsorbs in the center of the hexagonal rings (shown by circles on figure 1-a)). For steric reasons, an adsorbed Krypton atom makes adsorption on nearest neighbouring sites less likely, and we



FIGURE 1 – a) Sketch of a graphite surface, where possible adsorption sites for Krypton atoms are represented by the circles. b) A possible ground state at filling fraction 1/3 (the sites occupied by Krypton correspond to the black disks. c) Groups of triplets of adsorption sites, to define the sites considered in the Potts model (where a q-states spin lives).



FIGURE 2 – An instantaneous configuration of adsorbed Kr atoms on graphite, at filling fraction 1/3; the question is to identify the different ground states coexisting, and the domain walls between them...

shall consider a 1/3 coverage (one site occupied on average out of three). In this case, a possible ground state is shown in Fig. 1-b). There thus exist three equivalent positions for the lattice of adsorbed Kr, and we admit that such a system can be described by a Potts model, where a site corresponds to a triplet of original adsorption sites (see figure 1-c)), and where the spin indicates which of the three original sites is occupied. We therefore exclude the possibility that Kr atoms desorb, which certainly happens at high T. What is then the value of q? Figure 2 shows a configuration of Kr on the graphite plane, in which the possible ground states coexist, and occupy well defined domains. Show on the figure the domain walls (you can use page 7 below and don't forget to give this sheet back!). Which type of wall is the most energy consuming?

Annex : the multinomial expansion reads

$$\sum_{k_1+k_2+\ldots+k_m=n} \frac{n!}{k_1! k_2! \ldots k_m!} x_1^{k_1} x_2^{k_2} \ldots x_m^{k_m} = (x_1+x_2+\ldots+x_m)^n$$

#### **References** :

For question 15, see the cover of *Statistical Mechanics of Phase Transitions* by J. Yeomans (Oxford University Press), inspired from *Commensurate-incommensurate phase diagrams for overlayers from a helical Potts model*, M. Kardar and A. Berker, Phys. Rev. Lett. **48**, 1552 (1982).

# II Thermodiffusion, depletion and localisation of colloids

The different sections of the problem can be treated independently. Moreover, many questions in parts B, C and D can be answered at a very qualitative level. Part D may be slightly easier than part C.

Our interest goes here to thermodiffusion (also referred to as thermophoresis or Soret effect), that is the motion induced by a temperature gradient. More generally, the controlled gradient of thermodynamic variables such as the chemical potential or temperature, induces the migration of colloids in fluids. It is hence possible to separate some molecules, localize them in different stationary states, or obtain efficient transport strategies upon coupling several gradients. We shall work here in the framework of the linear thermodynamics of irreversible processes.

#### A General results on transport coefficients

We are interested in a mixture of two species A (molecules of a certain type), and B (the fluid, which is the majority species). We denote by  $n_A$  and  $n_B$  the corresponding volume densities, from which we define the concentration of species A :  $c = n_A/(n_A + n_B)$ . We assume that the majority species is at rest (no flow) and we shall work in the frame linked to B, where the only non-vanishing current density is that of species A denoted  $\vec{j}$ .

- 1. In what follows, the pressure is constant and uniform. What are the variables on which the chemical potential  $\mu$  of species A depends?
- 2. Provide, without further justification, the expression of the entropy production rate  $\sigma$ , as a function of the energy current  $\vec{j}_U$ ,  $\vec{j}$ , and the gradients of  $\mu/T$ , 1/T.
- 3. Put  $\sigma$  in the form

$$\sigma = -\vec{j} \cdot \left( \frac{1}{T} \frac{\partial \mu}{\partial c} \bigg|_T \vec{\nabla} c \right) + \vec{j}_1 \cdot \vec{\nabla} \left( \frac{1}{T} \right)$$
(8)

What is the expression and meaning of  $\vec{j_1}$ ?

4. Within linear response formalism, we have

$$\vec{j} = L_{11} \vec{\nabla} \left( -\frac{\mu}{T} \right) + L_{12} \vec{\nabla} \left( \frac{1}{T} \right) \tag{9}$$

$$\vec{j}_U = L_{21} \vec{\nabla} \left( -\frac{\mu}{T} \right) + L_{22} \vec{\nabla} \left( \frac{1}{T} \right)$$
(10)

What are the properties of the matrix  $L_{ij}$ ? No justification is asked.

5. It is furthermore customary to write

$$\vec{j} = -D\vec{\nabla}c - D_T\vec{\nabla}T \tag{11}$$

$$\vec{j}_1 = -\beta_T \vec{\nabla} c - \kappa \vec{\nabla} T \tag{12}$$

What do D and  $\kappa$  represent? What can be said about their sign? Same question with the coefficients  $D_T$  and  $\beta_T$ . Write the transport coefficients  $(D, D_T, \beta_T, \kappa)$  as functions of the  $L_{ij}$  and the chemical potential. Calculate the ratio of crossed terms  $\beta_T/D_T$ . What is its sign?

#### **B** Application to DNA manipulation : Soret effect

In the parameter range considered (room temperature, concentration  $c \ll 1$ ), a reasonable approximation for  $D_T$  is provided by  $D_T = D S_T c$ ; one then writes the current of A particles (minority species) as

$$\vec{j} = -D\left(\vec{\nabla}c + cS_T\vec{\nabla}T\right).$$
(13)

The Soret coefficient  $S_T$  does not change much with c and T, and will be henceforth considered as constant.



FIGURE 3 – a) Sketch of the temperature and concentration profiles, and geometry of the experiment. The point indicated by the black disk at x = 0 is the heating spot. b) Depletion factor  $1 - (\Delta c)/c_0$  as a function of the temperature increment, measured in Kelvin, for two types of DNA molecules.

1. At a reference point where the temperature is  $T_0$ , we denote the concentration by  $c_0$ . Making use of relation (13), express  $c/c_0$  as a function of  $T - T_0$ , in steady state, without any current.

The previous treatment allows for an understanding of experimental results pertaining to the thermophoresis of DNA, that plays here the role of species A. The suspending fluid, water, is species B. A laser locally heats the solution. By a fluorescence technique, it is possible to measure the local temperature, and in the geometry considered (Braun&Libchaber, 2002), one obtains the profiles given in Figure 3, where the experimental setup is schematized. The interplate distance H is sufficiently small to allow for the neglect of other spatial coordinates than x for the observables of interest.

- 2. What is the sign of  $S_T$ ?
- 3. With a slab thickness  $H = 25 \,\mu\text{m}$ , one obtains  $\Delta T \simeq 7.1 \,\text{K}$ , and it is measured that  $|S_T| \simeq 0.14 \,\text{K}^{-1}$ . What is the corresponding value of  $(\Delta c)/c_0$ ? Hint :  $\exp(-1) \simeq 0.37$ .
- 4. Figure 3-b) shows the theoretical extrapolation of the concentration drop for more vigorous heating. Two types of DNA strands have been considered : long molecules (5kbp, i.e. 5000 base pairs) or short molecules (27 bp, i.e. 27 base pairs). Which type of strands have been used for the experiment reported in question 3? What do we learn here on the dependence of Soret coefficient  $S_T$  on the strand length? Hint :  $\ln(10) \simeq 2.3$ .

### C Application to DNA manipulation : localization by convection

For wider inter-plate distances H and more intense laser intensities, the heating induces a fluid flow, in the form of convection rolls. The confining plates are horizontal while gravity acts in the direction perpendicular to the x axis.

- 1. Sketch the form of the velocity field in a plane perpendicular to the plates and containing the hot spot.
- 2. Explain qualitatively the effect of the flow on the suspended DNA.
- 3. We are interested in the transient regime. At time t = 0, the laser is switched on, while the system is in equilibrium (hence  $c = c_0$  everywhere for t < 0). The concentration profiles measured in a plane parallel to the plates are shown in Figure 4. Explain qualitatively the observed sequence of images.

а	0s	b	10s	С	60s
DNA	1 <u>00µm</u>		9		

FIGURE 4 – Visualisation of iso-concentration regions, at different times, for  $H = 50 \,\mu\text{m}$ . The grey intensity level measures the concentration (whiter regions are those where c is higher).

## D Application to DNA manipulation : localisation by polymer depletion

Related experiments have been performed in the presence of a polymer (polyethylene-glycol, PEG), in large amounts compared to DNA. The heating induces a depletion of PEG, with a concentration profile  $c_{PEG}$  that does not depend on DNA presence (in this respect, PEG thermopheresis can be understood along similar lines as above; it is however not necessary to have treated the previous questions to proceed). The PEG gradient thereby created, though, induces a force on DNA strands. This force is proportional to  $\nabla c_{PEG}$ , which translates into an additional term in the current  $\vec{j}$ :

$$\vec{j} = -D\left(\vec{\nabla}c + cS_T\vec{\nabla}T\right) - \alpha c\vec{\nabla}c_{PEG},\tag{14}$$

where  $\alpha$  is a positive quantity.

- 1. Write down the expression of DNA concentration as a function of  $c_{PEG}$  and T, in the steady state.
- 2. Explain qualitatively the experimental snapshots of Figure 5.



FIGURE 5 – Measured DNA concentration (c) levels, in a plane parallel to the plates, in presence of a polymer (PEG). Three distinct experiments with different PEG concentrations have been performed (from left to right : no PEG, volume fraction 2.5%, then 5%). As in Fig. 4, the darker regions are those with smaller values of the concentration.

#### **Références** :

Trapping of DNA by thermophoretic depletion and convection,

D. Braun, A. Libchaber, Phys. Rev. Lett. **89**, 188103 (2002). Thermal Separation : Interplay between the Soret effect and entropic force gradient,

Y.T. Maeda, A. Buguin, A. Libchaber, Phys. Rev. Lett. to appear (2011).

## Name :



FIGURE 6 – Same as Fig. 2, to answer question 15 of problem I.

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