## STATISTICAL PHYSICS

## Maximising the Missing Information

## **Tutorial Sheet 1**

The questions that follow on this and succeeding sheets are an integral part of this course. Cross references to the questions are given in the lecture notes. The code beside each question has the following significance:

- K: key question explores core material
- R: review question an invitation to consolidate
- C: challenge question going beyond the basic framework of the course
- S: standard question general fitness training!
- 1.1 The missing Information Function [K] Consider the missing information function

$$S(\{p_i\}) = -k \sum_{i=1}^{r} p_i \ln p_i$$

where the set  $\{p_i\}$  represents the probabilities associated with the r mutually exclusive and exhaustive outcomes of some procedure.

- (a) Sketch the form of S as a function of  $p_1$  for r = 2
- (b) Show that S has its maximum value when  $p_i = 1/r \quad \forall i$
- (c) Show that the value of S is increased when any two of the probabilities are changed in such a way as to reduce their difference
- 1.2 Simple application [S] In a certain game a player can score any integer n = 0, 1, ...and it is known that the mean score is  $\mu$ . Use the method of Lagrange multipliers to show that, knowing the mean, the rational probability distribution for the score is

$$p_n = A \exp(-\lambda n)$$

where  $A, \lambda$  are constants. By imposing the relevant constraints determine these constants and show that

$$p_n = \frac{\mu^n}{(1+\mu)^{n+1}}$$

1.3 **Extensivity of Missing Information** [K] Consider a 'compound' event  $i = (i_1, i_2)$ . The probability of event *i* may be written as  $p(i) = p(i_1|i_2)p(i_2)$  where  $p(i_1|i_2)$  is the conditional probability of  $i_1$  given  $i_2$ .

If the events are *uncorrelated* show that

$$S(\{p_i\}) = S_1(\{p_{i_1}\}) + S_2(\{p_{i_2}\}) .$$

If the events are *correlated* explain on general information theoretic grounds why

$$S(\{p_i\}) \le S_1(\{p_{i_1}\}) + S_2(\{p_{i_2}\})$$
.

Now interpret i as the state of an assembly and  $i_1$  and  $i_2$  as the states of two halves of the assembly. Identifying S as the Gibbs entropy think about the conditions under which the entropy is extensive.

1.4 **Relation of Gibbs to Boltzmann entropies** [**C**] In an assembly the Boltzmann entropy of any macrostate is given by

$$S = k \ln \Omega$$

where  $\Omega$  is the weight of the macrostate (number of associated microstates).

Now consider an *ensemble*, which consists of a very large number m of such assemblies. The assemblies are identical and each has q possible microstates available. By the law of large numbers we expect the number of such assemblies in each possible microstate i is  $m_i = mp_i$  where  $p_i$  is the probability of an assembly being in microstate i and  $i = 1 \dots q$ .

Derive an expression for the Boltzmann entropy of the *ensemble* (macro)state specified by  $\{m_i\}$ . You will need to determine the number of ways of assigning the states to the *m* assemblies. [Hint: you need to use a multinomial coefficient

$$\Omega = \frac{m!}{m_1! \, m_2! \dots m_q!}$$

Show that the Boltzmann entropy of the ensemble per assembly may be written as

$$S(\{p_i\}) = -k \sum_{i=1}^{r} p_i \ln p_i$$

[Help: You will need Stirling's approximation  $\ln m! \simeq m \ln m - m$ ]

1.5 **Thermodynamic representation of the chemical potential**[**R**] We have defined the chemical potential as

$$\mu = \left(\frac{\partial E}{\partial \overline{N}}\right)_{S,V}$$

show that equivalent representations are

$$\mu = -T\left(\frac{\partial S}{\partial \overline{N}}\right)_{\overline{E},V} = \left(\frac{\partial F}{\partial \overline{N}}\right)_{V,T} = \left(\frac{\partial G}{\partial \overline{N}}\right)_{P,T}$$

Hence establish that  $G(T, P, \overline{N}) = \overline{N}\mu$ . For this part (tricky) you will have to invoke extensivity of the Gibbs free energy.

- 1.6 Microscopic significance of the chemical potential [S] Show, by maximising the missing information, that two assemblies juxtaposed so that particles may be freely exchanged between them, have equilibrium grand canonical distributions characterised by the same value of  $\mu$ . Hint: you should consider the composite system of the two assemblies.
- 1.7 Canonical distribution for an assembly with free boundaries[S] Consider a fluid in a container whose walls are flexible so that its volume may take on any of a set of values  $\{V_{\alpha}\}$ . Suppose that the temperature and pressure of the environment are such that the mean energy and mean volume of the assembly are  $\overline{E}$ ,  $\overline{V}$  respectively. Establish the probability  $p_{i,\alpha}$  of finding the fluid to be in eigenstate *i* of volume  $V_{\alpha}$ . Identify the two Lagrange multipliers appearing in your results.

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