Faculty of Engineering and Physical Sciences
Department of Physics

Year 2, Energy and Entropy
Problem Set 2

Probability and Combinatorics

1. The quantity x can take on discrete values of -20, -10 and 30 with respective probabilities 3/10, 1/5 and 1/2. Determine the average value of x, denoted $\langle x \rangle$, and $\langle x^2 \rangle$.

2. For the continuous probability distribution $p(x) = \alpha e^{-\alpha x}$ where $0 < x < \infty$ calculate

(a) $\langle x \rangle$,

(b) $\langle x^2 \rangle$,

3. (a) If six different coloured inks are available, in how many ways can we select three colours for a printing job?

(b) How many ways can one choose five objects out of twelve if either the order of the choice is important, or the order of the choice is not important only the objects chosen?

(c) How many ways can the letters of the word "statisticians" be arranged?

(d) If the letters of the word "minimum" are arranged in a line at random, what is the probabiliity that the three "m"s are together at the beginning of the arrangement?

4. Stirling's approximation is given by $\ln x! \approx x \ln x - x$. Calculate the derivative of this expression, i.e. an approximation to $\frac{d(\ln x!)}{dx}$.

Note: this piece of mathematics will come up quite often.

Microcanonical ensemble

The theme of these questions is very similar, so you need not do them all if you are short of time.

5. For an assembly of n quantum simple harmonic oscillators sharing m quanta, calculate the entropy as a function of the total energy $U = m\hbar\omega$ and n (we calculated the expression for W in lectures). By applying Stirling's approximation to $\ln W$ and replacing $n-1$ with n, use this to show that the total energy at temperature T is

$$U \approx \frac{n\hbar\omega}{e^{\hbar\omega/k_B T} - 1},$$

the Planck distribution.

Hint: recall from thermodynamics that $\frac{1}{T} = \frac{\partial S}{\partial U}$, *then substitute the results from above into this expression.*

6. In thermal equilibrium at temperature T, a crystal with N atoms can have a certain number n of lattice sites vacant. Obtain an expression for the number of ways W in which this situation can arise by considering the different arrangements of the n vacant sites chosen from N possibilities.

Hint: we have $N + n$ sites in total, N are occupied and n are vacant.

Assuming that $S = k_B \ln W$ and that the internal energy $U = n\epsilon$, find a expression for the vacancy concentration n/N by minimising the free energy $F = U - TS$. Estimate the vacancy concentration in copper at 1300K if $\epsilon = 1\text{eV}$.

For this free energy method to be valid, the vacancies have to be created while the system is at constant volume. You should satisfy yourself that this can be achieved if the system consists of the crystal placed in an evacuated box of fixed volume. Would the analysis be significantly affected by including the number of ways in which the n atoms displaced to make vacancies can be found new sites e.g. on the crystal surfaces?

7. A paramagnet in one dimension can be modelled as a linear chain of $N + 1$ spins. Each spin interacts with its neighbours in such a way that the energy is $U = n\epsilon$ where n is the number of domain walls separating regions of up spins from down as shown by a vertical line in the representation below.

$$\uparrow\uparrow\uparrow \mid \downarrow\downarrow\downarrow\downarrow \mid \uparrow\uparrow\uparrow\uparrow\uparrow\uparrow \mid \downarrow\downarrow\downarrow \mid \uparrow\uparrow \mid \downarrow\downarrow \mid \uparrow\uparrow \mid \downarrow\downarrow\downarrow\downarrow\downarrow\downarrow$$

How many ways can n domain walls be arranged? *Hint: we have N spaces between the spins, of which n domain walls and $N - n$ are not.*

Calculate the entropy $S(U)$, and hence show that the energy is related to the temperature as

$$U = \frac{N\epsilon}{\exp(\epsilon/k_B T) + 1}$$

Sketch the energy and heat capacity as a function of temperature, paying particular attention to the asymptotic behaviour for low and for high temperatures.

8. A $1 - D$ model of a rubber consists of $2N$ links, each of length a, and each link can point left or right. If there are $N + r$ links pointing to the right, and $N - r$ pointing to the left, calculate an expression for the entropy.

The first law states that $TdS = dU - f dl$, where $l = 2ra$ is the length of the rubber, and f is the tension. Assuming that U is independent of l show that the force is given by

$$f = \frac{k_B T l}{2Na^2}$$

Hint: Apply stirling's approximation to your expression for entropy recall from thermodynamics that $f = -T\frac{\partial S}{\partial l}$.