Mathematical Tripos Part II Christopher Thomas

STATISTICAL PHYSICS Examples 1 Lent 2024

1. Establish Stirling's formula as follows. Start with

$$n! = \int_0^\infty e^{-x} x^n \, dx \equiv \int_0^\infty e^{-F(x)} \, dx \, .$$

Let the minimum of F be at x_0. Approximate $F(x)$ by $F(x_0) + F''(x_0)(x - x_0)^2/2$. (One further approximation is needed.) Hence obtain $n! \sim \sqrt{2\pi n}\, n^n e^{-n}$, and the statistical physics approximation $\ln n! \sim n \ln n - n$.

2. A cubic box is described by a three-dimensional infinite square well with $0 \le x, y, z \le a$ and corresponding single-particle energy eigenstates

$$E = \frac{\hbar^2 \pi^2}{2ma^2}(p^2 + q^2 + r^2)$$

where p, q, r are positive integers. Assume that the box contains N non-interacting distinguishable particles of mass m. Let $G(E)$ be the number of states with energy less than E. For $E \gg \hbar^2\pi^2/(2ma^2)$ show that $G(E) \approx cE^{\alpha N}$ for some positive constants c and α. Determine the value of α.

[*Hint*: a microstate can be parameterized by $3N$ positive integers and states with energy less than E are those for which these integers lie inside some sphere in the corresponding $3N$ dimensional space. How does the volume of this sphere depend on N?]

3. Consider two systems, for which the total number of states with energy within a small range δE around E is given by the functions $\Omega_1(E)$ and $\Omega_2(E)$ with $\Omega_i(E) = c_i E^{\alpha_i N_i}$ where N_1, N_2 are the number of particles in each system and c_i, α_i are positive constants. Using the approximation $S_i(E) \approx k_B \ln \Omega_i(E)$ consider the probability that, in equilibrium, the first system has energy E_1 and the second has energy $E - E_1$ (where E is the total energy):

$$p(E_1) = \frac{\Omega_1(E_1)\Omega_2(E - E_1)}{\Omega(E)} = \frac{1}{\Omega(E)} \exp\left[\frac{S_1(E_1)}{k_B} + \frac{S_2(E - E_1)}{k_B}\right] .$$

(i) Determine the value E_1^* which maximizes this probability. (ii) By expanding the exponent to second order around E_1^* show that $p(E_1)$ is negligible for $|E_1 - E_1^*| \gg E/\sqrt{N}$ (where N is the total number of particles and $N_1, N_2 \sim N$).

4. (a) Show that two coupled systems in the microcanonical ensemble, each with heat capacity C, maximize their entropy at equal temperature only if C is positive.

(b) In the canonical ensemble, show that the fluctuations in energy, $(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2$, are proportional to the heat capacity.

(c) Show that in the canonical ensemble the Gibbs entropy can be written as $S = k_B \frac{\partial}{\partial T}(T \ln Z)$.

5. Gas in an insulated container of fixed volume V is divided into two parts of volumes V_1 and V_2 by a thin, movable barrier (i.e. energy can pass through the barrier). Show using the first law in the form

$$dS = \frac{dE}{T} + \frac{p\,dV}{T}$$

that the temperatures and pressures in the two parts are equal in equilibrium.

6. A system consists of N spin-$\frac{1}{2}$ particles with fixed positions. Each particle can be in one of two quantum states: spin "up" or "down", labelled by $s_z \in \{\frac{1}{2}, -\frac{1}{2}\}$. There is a magnetic field of strength B in the z-direction so the energy of a particle is $-\mu B s_z$ where μ is a constant.

(a)(i) How many states are there with $N_\uparrow$ spin "up" particles and $N_\downarrow = N - N_\uparrow$ spin "down" particles? Express the energy of such a state as a function of $N_\uparrow$ and hence calculate the Boltzmann entropy $S(E)$, expressing your answer in terms of $N_\uparrow$. When $N, N_\uparrow$ and $N_\downarrow$ are all large use Stirling's approximation $n! \sim \sqrt{2\pi n}\, n^n e^{-n}$ to show that

$$S(E) \approx -k_B \left[(N - N_\uparrow) \ln \left(\frac{N - N_\uparrow}{N} \right) + N_\uparrow \ln \left(\frac{N_\uparrow}{N} \right) \right] .$$

Plot S as a function of E.

(ii) Calculate the temperature T as a function of E and plot $\frac{1}{T}$ against E. What happens in the limits $T \to 0$ and $T \to \infty$? Show that the temperature is *negative* for $E > 0$.

[Negative temperature occurs if Ω decreases with E, which is the case here for $E > 0$. For most systems, kinetic energy ensures that Ω always increases with E, so negative temperatures do not usually occur.]

(b) Now consider this system in the canonical ensemble. Show that the partition function is

$$Z = 2^N \cosh^N \left(\frac{\beta \mu B}{2} \right) .$$

Find the average energy E and entropy S. Show that your results for $E(T)$ and $S(T)$ agree with the microcanonical calculations of part (a).

(c) The *magnetisation* of the system, is defined by $M = \mu(N_\uparrow - N_\downarrow)/2$. Compute M as a function of (T, B). The magnetic susceptibility is defined as $\chi \equiv (\partial M / \partial B)_T$. Show that, at high temperature, the system obeys *Curie's Law*: $\chi \sim \frac{1}{T}$.

7. * Consider a system of N interacting spins. At low temperatures, the interactions ensure that the spins are either all aligned or all anti-aligned with the z-axis, even in the absence of an external field. At high temperatures, the interactions become less important and the spins can be either aligned or anti-aligned with the z-axis. The heat capacity takes the form

$$C_V = C_{\max}\left(\frac{2T}{T_0} - 1\right) \quad \text{for} \quad \frac{T_0}{2} < T < T_0 \quad \text{and} \quad C_V = 0 \quad \text{otherwise}\,.$$

Determine $C_{\max}$.

8. Compute the partition function of a quantum harmonic oscillator with frequency ω and energy levels

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)\,, \qquad n = 0, 1, 2, \ldots\,.$$

Find the average energy E as a function of temperature T.

Einstein constructed a simple model of a solid as N atoms, each of which vibrates with the same frequency ω. Treating these vibrations as harmonic oscillators, show that at high temperatures, $k_B T \gg \hbar\omega$, the Einstein model correctly predicts the *Dulong-Petit* law for the heat capacity of a solid,

$$C_V = 3Nk_B\,.$$

At low temperatures, the heat capacity of many solids is experimentally observed to tend to zero as $C_V \sim T^3$. Was Einstein right about this?

9. Consider the Gibbs entropy for a probability distribution $p(n)$,

$$S = -k_B \sum_n p(n) \ln p(n)$$

(a) By implementing the constraint $\sum_n p(n) = 1$ through the use of a Lagrange multiplier show that, when restricted to states of fixed energy E, the entropy is maximised by the microcanonical ensemble in which all such states are equally likely. Further show that in this case the Gibbs entropy coincides with the Boltzmann entropy.

(b) Show that at fixed *average* energy $\langle E\rangle = \sum_n p(n)E_n$, the entropy is maximised by the canonical ensemble. Moreover, show that the Lagrange multiplier imposing the constraint is proportional to β, the inverse temperature. Confirm that maximizing the entropy is equivalent to minimizing the free energy.

(c) Show that at fixed average energy $\langle E\rangle$ and average particle number $\langle N\rangle$, the entropy is maximised by the grand canonical ensemble. What is the interpretation of the Lagrange multiplier in this case?

10. Let Z_N be the canonical partition function for N particles. Show that the grand partition function $\mathcal{Z}$ can be written as

$$\mathcal{Z}(\mu, V, T) = \sum_{N=0}^{\infty} \xi^N Z_N(V, T)$$

where $\xi = e^{\beta\mu}$ is called the *fugacity.* Show that

$$\langle N\rangle = \xi \frac{\partial}{\partial \xi} \ln \mathcal{Z}\,, \quad (\Delta N)^2 = \left(\xi \frac{\partial}{\partial \xi}\right)^2 \ln \mathcal{Z}\,.$$

If $Z_N = Z_1^N/N!$ show that $\mathcal{Z}(\xi, V, T) = e^{\xi Z_1(V,T)}$. For this case, show also that

$$\frac{\Delta N}{\langle N\rangle} = \frac{1}{\langle N\rangle^{1/2}}\,.$$

11. Make use of the fact that the free energy $F(T, V, N)$ of a thermodynamic system must be extensive, to explain why

$$F = V\left(\frac{\partial F}{\partial V}\right)_{T,N} + N\left(\frac{\partial F}{\partial N}\right)_{T,V}\,.$$

The *Gibbs free energy* is defined as $G = F + pV$. Use the result above for F to show that the Gibbs free energy can be expressed as $G = \mu N$. Explain why this result was to be expected from the scaling behaviour of G.

12. A neutral gas consists of N_e electrons e^-, N_p protons p^+ and N_H hydrogen atoms H. An electron and proton can combine to form Hydrogen,

$$e^- + p^+ \leftrightarrow H$$

At fixed temperature and volume, the free energy of the system is $F(T, V; N_e, N_p, N_H)$. We can define a chemical potential for each of the three species as

$$\mu_i = \frac{\partial F}{\partial N_i}$$

By minimizing the free energy, together with suitable constraints on the particle numbers, show that the condition for equilibrium is

$$\mu_e + \mu_p = \mu_H$$

Such reactions usually take place at constant pressure, rather than constant volume. What quantity should you consider instead of F in this case?

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