MATHEMATICAL TRIPOS PART II *Dr M Wingate*

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Statistical Physics - Examples I *Lent 2007*

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 get $n! \sim \sqrt{2\pi n}\; n^n e^{-n}$.

2. The air in a bicycle pump is in equilibrium at pressure p. The piston is pushed in slowly an infinitesimal distance so that the volume of air contained is decreased by an amount dV. Show that the work done on the gas is pdV. Generalize this result to the case of a volume of gas of any shape, when a general element $d\mathbf{S}$ of its surface at $\mathbf{r}$ is displaced through $d\mathbf{r}$.

3. Consider a system consisting of N spin-$\frac{1}{2}$ particles (where N is large and even), each of which can be in one of two quantum states, 'up' and 'down'. (The particles are at fixed sites and there are no other degrees of freedom and no interactions.) Suppose that $\frac{N}{2} + m$ are 'up' and $\frac{N}{2} - m$ are 'down'.

(a) Find the number of ways, $g(N, m)$, in which this situation can occur.

(b) Use Stirling's formula to show that $g(N, m) \sim g(N, 0) \exp(-2m^2/N)$.

(c) Estimate $\langle m^2 \rangle = \sum_m g(N, m) m^2 / \sum_m g(N, m)$ by using the approximation in (b), and show that $\sqrt{\langle m^2 \rangle} \ll N$. [Alternatively you could calculate $\langle m^2 \rangle$ exactly if you wish.]

4. (a) By considering dE, dF, dH and dG, obtain four different Maxwell relations for the partial derivatives of S, P, T and V.

(b) Obtain the partial derivative identity

$$\left.\frac{\partial S}{\partial T}\right|_p = \left.\frac{\partial S}{\partial T}\right|_V + \left.\frac{\partial S}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_p .$$

(c) Obtain the partial derivative identity

$$\left.\frac{\partial p}{\partial T}\right|_V \left.\frac{\partial T}{\partial V}\right|_p \left.\frac{\partial V}{\partial p}\right|_T = -1\,.$$

5. Consider a specimen of gas with a fixed number of molecules. Derive the following set of results which are useful for many thermodynamic problems where what is known is the equation of state. (The results of question 4 are needed.)

(a) $\quad C_p - C_V = T \left.\frac{\partial V}{\partial T}\right|_p \left.\frac{\partial p}{\partial T}\right|_V = -T \left.\frac{\partial V}{\partial T}\right|_p^2 \left.\frac{\partial p}{\partial V}\right|_T ,$

(b) $\quad \left.\frac{\partial E}{\partial V}\right|_T = T \left.\frac{\partial p}{\partial T}\right|_V - p\,,$

(c) $\left.\frac{\partial E}{\partial p}\right|_T \quad = -T\left.\frac{\partial V}{\partial T}\right|_p - p\left.\frac{\partial V}{\partial p}\right|_T,$

(d) $\left.\frac{\partial C_V}{\partial V}\right|_T \quad = T\left.\frac{\partial^2 p}{\partial T^2}\right|_V,$ (e) $\left.\frac{\partial C_p}{\partial p}\right|_T = -T\left.\frac{\partial^2 V}{\partial T^2}\right|_p.$

6. Consider an ideal gas, with equation of state $pV = NkT$ and constant heat capacity $C_V = Nk\alpha$. Use the results of Ex. 5(a) to show that $C_p = Nk(\alpha + 1)$, and that the entropy is

$$S = Nk\ln\left(\frac{V}{N}\right) + Nk\alpha\ln T + \text{const}.$$

Deduce that, for an adiabatic process ($\Delta S = 0$), VT^{α} is constant and, equivalently, pV^{γ} is constant, where $\gamma = C_p/C_V$.

7. A (non-ideal) gas has constant heat capacities C_V and C_p. Use parts (a), (d) and (e) of question 5, to show that its equation of state can be written as

$$(C_p - C_V)T = (p + a)(V + b).$$

Show also that E is of the form $E = C_V T + f(V)$, find $f(V)$ and calculate the entropy as a function of V and T.

8. *The Joule-Thomson or Joule-Kelvin Process.* Consider a thermally insulated pipe which has a porous barrier separating two halves of the pipe. A gas of volume V_1, initially on the left-hand side of the pipe, is forced by a piston to go through the porous barrier using a constant pressure p_1. As a result the gas flows to the right-hand side, resisted by another piston which applies a constant pressure p_2 ($p_2 < p_1$). Eventually all of the gas occupies a volume V_2 on the right-hand side.

(a) Show that enthalpy, $H = E + pV$, is conserved.

(b) Find the Joule-Thomson coefficient $\mu_{\mathrm{JT}} \equiv (\frac{\partial T}{\partial p})_H$ in terms of T, V, the heat capacity at constant pressure C_p, and the volume coefficient of expansion $\alpha \equiv \frac{1}{V}(\frac{\partial V}{\partial T})_p$. [You will need to use a Maxwell relation.]

(c) What is μ_{JT} for an ideal gas?

(d) If we wish to use the Joule-Thomson process to cool a real (non-ideal) gas, what must the sign of μ_{JT} be?

9. Consider a relativistic gas of N spinless particles obeying the energy-momentum relation $\varepsilon = pc$, where c is the speed of light in vacuum. Show that the partition function is given by

$$Z(V,T) = \frac{1}{N!}\left[\frac{V}{\pi^2}\left(\frac{kT}{\hbar c}\right)^3\right]^N.$$

10. Show that the energy fluctuation in a canonical distribution is given by

$$\left\langle (E - \langle E\rangle)^2 \right\rangle = kT^2 C_V.$$

Then show, for an ideal gas of N monatomic particles, that

$$\frac{\left\langle (E - \langle E\rangle)^2 \right\rangle}{\langle E\rangle^2} = \frac{2}{3N}.$$