

DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY, MADRAS

PH350 Classical Physics

Problem Set 6

24.9.2009

1. (a) **Formula for the internal energy of a system:** The quantity U that you are familiar with in thermodynamics is nothing but the *mean* or *average* value of the energy of the system in thermal equilibrium (at some temperature T). We know that the *probability* that the system has an energy E under such conditions is $(1/Z) \exp(-\beta E)$, where Z is its canonical partition function and $\beta = k_B T$. The average value of the energy is defined as

$$\langle E \rangle = \frac{\sum_{\text{states } r} (E_r e^{-\beta E_r})}{\sum_{\text{states } r} (e^{-\beta E_r})}$$

It is this average value that's denoted by U in thermodynamics. The denominator in the above expression is of course the canonical partition function Z . Show that

$$U = \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \quad ,$$

a *fundamental* formula that you should commit to memory because it's so useful.

- (b) Show also that the mean square value of the energy is given by

$$\langle E^2 \rangle = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = \frac{1}{Z} \frac{\partial}{\partial \beta} \left(Z \frac{\partial}{\partial \beta} \ln Z \right) \quad ,$$

and hence the *variance* of the energy is given by

$$\langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Z = -\frac{\partial}{\partial \beta} \langle E \rangle \quad ,$$

another very useful formula.

- (c) **Physical significance of the variance of E :** Show that the variance in the energy found above is equal to $k_B C_v T^2$. Hence show that, for a gas of N particles, the ratio of the standard deviation in the energy to the average value of the energy is of the order of $1/\sqrt{N}$. This verifies the assertion about the smallness of the *relative fluctuations* made in class.
2. A system has energy values in the range $0 \leq E < \infty$. Its density of states is given to be $\rho(E) \propto E^\alpha$, where α is a positive number. Find the specific heat $C = (\partial U / \partial T)$ of the system.

3. **Model for paramagnetism:** A paramagnetic solid consists of N mutually noninteracting elementary or ‘atomic’ magnetic moments, each of which can be in one of *three* states in an applied magnetic field B (taken to be along the positive z direction, say). In state 1, the energy is $-\mu B$ and the magnetic moment is $+\mu$ (in the direction of the applied field). In state 2, the energy is 0, and so is the moment. In state 3, the energy is $+\mu B$ and the magnetic moment is $-\mu$. *The system is in thermal equilibrium at a constant temperature T .* The N moments are located at the sites of a crystal lattice and are thus distinguishable.

Find

- the magnetic contribution to the partition function Z of the system,
- its internal energy U ,
- its specific heat $C = (\partial U / \partial T)$,
- its magnetization M (defined as N times the average magnetic moment of the atom), and
- the isothermal paramagnetic susceptibility

$$\chi_T = \left[\left(\frac{\partial M}{\partial B} \right)_T \right]_{B=0} .$$

(The $1/T$ dependence of χ_T on temperature is called **Curie’s law**, after Pierre Curie.)

- Sketch M as a function of B for both positive and negative B for two different temperatures T_1 and T_2 , where $T_1 > T_2$.

4. **Ideal gas in an external force field:** An ideal gas of N molecules (such as the one considered in class) is placed in a conservative field of force $\vec{F}(\vec{r}) = -\vec{\nabla}\Phi(\vec{r})$, where $\Phi(\vec{r})$ is a scalar function of the coordinates. The volume of the container is V . Write down an expression for the partition function of the gas.

5. **The entropy of mixing of two gases:**

We found that that the entropy of an ideal gas of N particles in a volume V at temperature T is given by

$$S = Nk_B \left(\ln(V/N) + \frac{5}{2} + \frac{3}{2} \ln(2\pi k_B T / h^2) \right) .$$

Suppose we have two different ideal gases, 1 and 2, in two containers separated by a partition in the middle as shown in the figure below:

N_1, V_1, T	N_2, V_2, T
(gas 1)	(gas 2)

$$(V_1 + V_2 = V; N_1 + N_2 = N)$$

Clearly, if the partition is removed and the gases are allowed to mix, many more configurations are available to the system – each molecule of the gas 1 can now be anywhere in the total volume V , rather than in V_1 alone; a similar statement holds good for each molecule of gas 2. The *disorder* certainly increases after mixing – *compared* to the mixture, the state before mixing is *more ordered*, because all the particles of gas 1 are segregated in V_1 , and all the particles of gas 2 are segregated in V_2 . The total entropy of the system thus *increases* after mixing of the gases. This increase in the entropy is called the *entropy of mixing*. We assume, of course, that the two molecular species do not undergo any chemical reaction, but merely mix physically.

- (a) Show that the entropy of mixing in the situation shown in the figure is

$$\Delta S_{\text{mixing}} = N_1 k_B \ln(V/V_1) + N_2 k_B \ln(V/V_2) \quad ,$$

which is *positive* as required.

- (b) Verify that if the specific volumes V_1/N_1 and V_2/N_2 are equal, then if gases 1 and 2 actually refer to the *same* gas, there is *no* entropy of mixing, as we should require on physical grounds. (Placing or removing a partition in a container of an ideal gas should not change the entropy!) Thus there is no “Gibbs paradox”, because we’ve included the correct combinatorial factor ($1/N!$) in writing $Z = z^N/N!$.
- (c) Let the specific volumes of the two gases be equal before mixing, i.e., let $V_1/N_1 = V_2/N_2$. Of course, this means also that each of these ratios is equal to V/N . Let’s call the concentration $c \equiv N_1/N$. Then $N_2/N = (1 - c)$. The entropy of mixing can be rewritten as

$$\Delta S_{\text{mixing}}/Nk_B = -[c \ln c + (1 - c) \ln(1 - c)] \quad .$$

Sketch the LHS as a function of the concentration c (evidently, $c \in [0, 1]$ is the physical range of c). Is there a maximum? If so, at what value of c does it occur, and why?

- (d) If N_1 and N_2 correspond to one mole each of two ideal gases at NTP, find the value of the entropy of mixing in calories per degree.