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PHYS 403: HOMEWORK ASSIGNMENT No. 2: CANONICAL and GRAND CANONICAL ENSEMBLES

(FEB 15th, 2023)

HOMEWORK DUE: WEDNESDAY, MARCH 8th, 2023

To be uploaded by 11.59 pm, Wednesday March 8th - Late Homework will not be accepted

QUESTION (1) DIATOMIC GAS: A diatomic molecule has 3 degrees of freedom, viz., translational motion of the molecular centre of mass, rotational motion abut the centre of mass, and vibrations in distance between the 2 atoms. We will treat these different degrees of freedom as being independent, ie., with no coupling between them. We assume the diatom is made from 2 atoms, each with mass m, and mean separation a_o.

(i): The moment of inertia of the rotating diatom is $I = 1/2ma_o^2$. We also suppose that the frequency of small harmonic oscillation of the distance x around the mean a_o between the atoms is ω_o.

Show that we can write the total canonical partition function $\mathcal{Z}$ for a gas of N such diatoms as $\mathcal{Z} = Z_{tr}Z_{rot}Z_{vib}$, where Z_{tr} comes from the translational degrees of freedom, where $Z_{rot} = z_I^N$ and $Z_{vib} = z_{\omega_o}^N$, and show that

$$z_I \;=\; \sum_{j=0}^{\infty}(2j+1)\exp[-\beta\hbar^2 j(j+1)/2I]\;; \qquad\qquad z_{\omega_o} \;=\; \sum_{n=o}^{\infty}\exp[-\beta\hbar(n+1/2)\omega_o] \tag{0.1}$$

You do not have to evaluate the translational term Z_{tr}.

(ii) Let us first consider the vibrational modes. Evaluate the partition function $z_{\omega_o}(\beta)$, and then show that the vibrational contribution to the energy of the system is $U_{vib}(\beta) = (N/2)\hbar\omega_o\coth(\beta\hbar\omega_o/2)$. From this find also the contribution $C_V^{vib}(\beta)$ to the specific heat.

Finally, sketch the behaviour of both $U_{vib}(\beta)$ and $C_V^{vib}(\beta)$ as functions of the temperature T.

(iii) Now let's look at Z_{rot} for the rotational motion of the diatom. The low T behaviour is easy, because the terms in the sum in the expression for $z_I(\beta)$ decrease rapidly with increasing j. By taking just the first 2 terms in the sum, find a simple low-T result for $z_I(\beta)$, and from this find expressions for $U_{rot}(T)$ and $C_V^{rot}(T)$ for the N diatoms in the low T regime.

For the high-T behaviour we need to approximate the sum as an integral. Using the result $\int_0^\infty dx\, x\, e^{-x^2} = 1/2$, find a simple result for $z_I(\beta)$ in the high-T regime where $kT \gg \hbar^2/2I$, with the result $\propto kT$. Then, from this result, find the energy U_{rot} and $C_V^{rot}(T)$ for the N diatoms in the high T regime.

Finally, plot sketches for U_{rot} and $C_V^{rot}(T)$ for the N diatoms as a function of T; you can use the expression you found for the low-T and high-T results, and then just simply interpolate between them.

(iv) The "third" contribution to the specific heat coming from the translational degrees of freedom is just that from a 3-dimensional classical Maxwell-Boltzmann gas. Typically, the vibrational zero point energy $\hbar\omega_o/2 \gg \hbar E_o$, where $E_o = \hbar^2/2I$ is the rotational zero point energy. Using the results you have derived above for $C_V^{rot}(T)$ and $C_V^{vib}(T)$, sketch the result you expect for the TOTAL specific heat $C_V(T)$ for a gas of N diatoms, as a function of T. Explain the limiting behaviour you find for $C_V(T)$ for (i) high T (ie., for $T \gg \hbar\omega_o/2$) and for low T (ie., for $kT \ll \hbar^2/2I$)?

QUESTION (2) INTERSTELLAR GRAIN: The space in galaxies is full of 'interstellar grains', ie., particles made of carbon or silicate materials which drift through a very rarified interstellar gas, largely composed of Hydrogen atoms. They are tpically microns in size, sometimes larger. The H atoms can stick to the grains and react with the C to form hydrocarbon molecules - this leads to the gradual synthesis of very complex hydrocarbons on the grains, a fact which may be important for the origin/evolution of life.

Let's assume that the gas of H atoms in the interstellar medium, with density ρ and temperature T, is in thermodynamic equilibrium with the H atoms stuck to the grain surface. Suppose also that on a given grain there are N_o sites available for H atoms to stick, one for each site - for simplicity we assume the (negative) binding energy is U_o.

2(a): Suppose that the chemical potential of the H atoms on the grain and in space is μ; what is the grand partition function for the atoms?

2(b): What is the expectation value $\langle m \rangle$ of the fraction M/N_o, where M is the number of atoms which are stuck to the grain surface, as a function of μ, U_o, and the temperature T?

2(c): If the chemical potential of a gas of H atoms of mass m at temperature T and number density $\rho = p/kT$ per unit volume is given by

$$\rho \;=\; \frac{1}{4\pi^2}(2m)^{3/2}\int_0^\infty \frac{dE}{\hbar^3}E^{1/2}e^{-\beta(E-\mu)} \tag{0.2}$$

then we can determine $\langle m \rangle$, now in terms of pressure p, U_o, and the temperature T. Find this result, and evaluate it for a pressure $p = 10^{-18}$ atmospheres, a temperature of 40 K, and assuming $U_o = 5$ eV (recalling that 1 eV $\sim 11,604$ K). You will need to find out what is atmospheric pressure from the literature.

END of 1ST HOMEWORK ASSIGNMENT