

PHYS 403 HW2 Model Solution

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1 Diatomic gas

A diatomic molecule has 3 degrees of freedom, viz., translational motion of the molecular centre of mass, rotational motion about 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_0 .

(15pts)(i). The moment of inertia of the rotating diatom is $I = \frac{1}{2}ma_0^2$. We also suppose that the frequency of small harmonic oscillation of the distance x around the mean a_0 between the atoms is ω_0 .

Show that we can write the total canonical partition function \mathcal{Z} for a gas of N such diatoms as $\mathcal{Z} = Z_{\text{tr}}Z_{\text{rot}}Z_{\text{vib}}$, where Z_{tr} comes from the translational degrees of freedom, $Z_{\text{rot}} = z_I^N$ and $Z_{\text{vib}} = z_{\omega_0}^N$ and show that

$$z_I = \sum_{j=0}^{\infty} (2j+1) \exp[-\beta\hbar^2 j(j+1)/2I]; \quad z_{\omega_0} = \sum_{n=0}^{\infty} \exp[-\beta\hbar(n+1/2)\omega_0] \quad (1.1)$$

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

Solution:

First notice this is a quantum statistics problem, since we have \hbar in the partition function. Recall the definition of partition function in quantum statistics:

$$\mathcal{Z} = \text{Tr}(e^{-\beta\hat{H}}) \quad (1.2)$$

Here the Hamiltonian(energy) is $H = H_{\text{tr}} + H_{\text{rot}} + H_{\text{vib}} = \sum_i h_{\text{tr},i} + \sum_i h_{\text{rot},i} + \sum_i h_{\text{vib},i}$, where $h_{\text{tr}}, h_{\text{rot}}, h_{\text{vib}}$ are the single particle Hamiltonians:

$$h_{\text{tr}} = \frac{\vec{P}^2}{2M}; \quad h_{\text{rot}} = \frac{\vec{L}^2}{2I}; \quad h_{\text{vib}} = \frac{p^2}{2M} + \frac{1}{2}M\omega_0^2 x^2. \quad (1.3)$$

then

$$\mathcal{Z} = \text{Tr} (e^{-\beta \sum_i (h_{\text{tr},i} + h_{\text{rot},i} + h_{\text{vib},i})}) \quad (1.4)$$

$$= \text{Tr} (e^{-\beta (h_{\text{tr}} + h_{\text{rot}} + h_{\text{vib}})})^N \quad (1.5)$$

$$= \text{Tr} (e^{-\beta h_{\text{tr}}})^N \text{Tr} (e^{-\beta h_{\text{rot}}})^N \text{Tr} (e^{-\beta h_{\text{vib}}})^N \quad (1.6)$$

$$= Z_{\text{tr}} Z_{\text{rot}} Z_{\text{vib}} \quad (1.7)$$

$$\text{where } Z_{\text{tr}} = \text{Tr} (e^{-\beta h_{\text{tr}}})^N = z_{\text{tr}}^N, \quad (1.8)$$

$$Z_{\text{rot}} = \text{Tr} (e^{-\beta h_{\text{rot}}})^N = z_{\text{I}}^N, \quad (1.9)$$

$$Z_{\text{vib}} = \text{Tr} (e^{-\beta h_{\text{vib}}})^N = z_{\omega_o}^N. \quad (1.10)$$

Next we calculate $z_{\text{I}}, z_{\omega_o}$. Energy levels of $h_{\text{rot}} = \vec{L}^2/(2I)$ are $1/(2I)$ times the eigenvalues of L^2 , which are $\hbar^2 l(l+1)$, with degeneracy $2l+1$, therefore

$$z_{\text{I}} = \sum_{l=0}^{\infty} (2l+1) e^{-\beta \hbar^2 l(l+1)/(2I)}. \quad (1.11)$$

Energy levels of h_{vib} are $\hbar\omega_o(n + \frac{1}{2})$ with no degeneracy, therefore

$$z_{\omega_o} = \sum_{n=0}^{\infty} e^{-\beta \hbar\omega_o(n+1/2)} \quad (1.12)$$

Marking scheme

- 2pts for showing understanding of definition of partition function
- 2pts for showing understanding of the Hamiltonian of the system
- 3pts for showing the partition function splits into products of 3 factors.
- 3pts for identifying the energy levels of the rotation mode.
- 2pts for identifying the degeneracy of the rotation energy.
- 3pts for identifying the energy levels of the vibration mode.
- Rigorousness is not required for getting full marks.
- You get half the mark if results differ by a numerical factor.

(20pts)(ii) Let us first consider the vibrational modes. Evaluate the partition function z_{ω_o} , and then show that the vibrational contribution to the energy of the system is $U_{\text{vib}}(\beta) = N/2\hbar\omega_o \coth(\beta\hbar\omega_o/2)$. From this find also the contribution $C_V^{\text{vib}}(\beta)$ to the specific heat. Finally, sketch the behaviour of both

$U_{\text{vib}}(\beta)$ and $C_V^{\text{vib}}(\beta)$ as functions of the temperature T.

Solution

$$U_{\text{vib}}(\beta) = -\frac{1}{Z_{\text{vib}}} \frac{\partial Z_{\text{vib}}}{\partial \beta} = -\frac{1}{z_{\omega_o}^N} \frac{\partial z_{\omega_o}^N}{\partial \beta} = -\frac{1}{z_{\omega_o}} \frac{N \partial z_{\omega_o}}{\partial \beta} \quad (1.13)$$

now z_{ω_o} is

$$z_{\omega_o} = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_o (n+1/2)} = e^{-\beta \hbar \omega_o / 2} \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_o n} \quad (1.14)$$

$$= e^{-\beta \hbar \omega_o / 2} \frac{1}{1 - e^{-\beta \hbar \omega_o}} = \frac{1}{e^{\beta \hbar \omega_o / 2} - e^{-\beta \hbar \omega_o / 2}} = \frac{1}{2 \sinh(\beta \hbar \omega_o / 2)} \quad (1.15)$$

therefore internal energy is

$$U_{\text{vib}}(\beta) = -\frac{1}{z_{\omega_o}} \frac{N \partial z_{\omega_o}}{\partial \beta} = -N 2 \sinh(\beta \omega_o / 2) \left(-\frac{1}{2 \sinh(\beta \hbar \omega_o / 2)^2} \right) \cosh(\beta \hbar \omega_o / 2) \hbar \omega_o / 2 \quad (1.16)$$

$$= N \hbar \omega_o / 2 \coth(\beta \hbar \omega_o / 2). \blacksquare \quad (1.17)$$

The specific heat is

$$C_V^{\text{vib}}(\beta) = \frac{\partial U}{\partial T} = \frac{d\beta}{dT} \frac{\partial U}{\partial \beta} = -\frac{1}{k_B T^2} \frac{\partial U}{\partial \beta} = -k_B \beta^2 \frac{\partial U}{\partial \beta} \quad (1.18)$$

$$= -k_B \beta^2 N \hbar \omega_o / 2 \frac{-1}{\cosh^2(\beta \hbar \omega_o / 2)} \hbar \omega_o / 2 \quad (1.19)$$

$$= k_B N \beta^2 \hbar^2 \omega_o^2 / 4 \frac{1}{\cosh^2(\beta \hbar \omega_o / 2)} \quad (1.20)$$

Now to plot $U(T)$, notice when $T \rightarrow +\infty$, $\beta \rightarrow 0^+$, $\coth(\beta \hbar \omega_o / 2) = \frac{e^{\beta \hbar \omega_o / 2} + e^{-\beta \hbar \omega_o / 2}}{e^{\beta \hbar \omega_o / 2} - e^{-\beta \hbar \omega_o / 2}} \sim \frac{1}{\beta \hbar \omega_o}$, therefore $U(\beta) \sim N \hbar \omega_o / 2 \frac{1}{\beta \hbar \omega_o} = \frac{N}{2} k_B T$; when $T \rightarrow 0^+$, $\beta \rightarrow +\infty$, $\coth(\beta \hbar \omega_o / 2) \sim 1$, so $U(\beta) \sim N \hbar \omega_o / 2$.

To plot $C_V(T)$, notice when $T \rightarrow +\infty$, $\beta \rightarrow 0^+$, $\cosh(\beta \hbar \omega_o / 2) = \frac{e^{\beta \hbar \omega_o / 2} + e^{-\beta \hbar \omega_o / 2}}{2} \sim \beta \hbar \omega_o / 2$, thus $C_V \sim k_B N \beta^2 \hbar^2 \omega_o^2 / 4 \frac{4}{\beta^2 \hbar^2 \omega_o^2} = N k_B$; when $T \rightarrow 0^+$, $\beta \rightarrow +\infty$, and $\cosh(\beta \hbar \omega_o / 2) = \frac{e^{\beta \hbar \omega_o / 2} + e^{-\beta \hbar \omega_o / 2}}{2} \sim \frac{e^{\beta \hbar \omega_o / 2}}{2}$, then $\frac{\beta^2}{e^{\beta \hbar \omega_o / 2}} \sim 0 \Rightarrow C_V(T = 0) = 0$.

Marking scheme

- 2pt for knowing the definition of internal energy.
- 2pts for getting the correct partition function.
- 3pts for getting the correct internal energy.

- 2pt for knowing the definition of specific heat.
- 3pts for getting the correct specific heat.
- 2pt if the plot of energy starts at a nonzero point at $T = 0$.
- 2pt if the plot of energy grows linearly when T is large.
- 2pt if the plot of specific heat starts at 0 when $T = 0$.
- 2pt if the plot of specific heat goes to a constant when T is large.
- You get half mark if results differ by a numerical constant.

((20pts)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 $U_{\text{rot}}(T)$ and $C_{\text{rot}}(T)$ 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 $C_{\text{rot}}(T)$ for the N diatoms in the high T regime. Finally, plot sketches for U_{rot} and $C_{\text{rot}}(T)$ 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.

Solution

Low T limit: take the first two terms in the sum, we have $z_I = 1 + 3e^{-\beta\hbar^2/I}$, therefore

$$U_{\text{rot}} = -N \frac{1}{z_I} \frac{\partial z_I}{\partial \beta} = -N \frac{1}{1 + 3e^{-\beta\hbar^2/I}} (-3\hbar^2/I) e^{-\beta\hbar^2/I} = \frac{3N\hbar^2/I}{3 + e^{\beta\hbar^2/I}} \sim 0, \quad (1.21)$$

and

$$C_{\text{rot}} = -k_B \beta^2 \frac{\partial U}{\partial \beta} = -k_B \beta^2 3N\hbar^2/I \left(-\frac{1}{(3 + e^{\beta\hbar^2/I})^2} \hbar^2/I e^{\beta\hbar^2/I} \right) = \frac{3k_B \beta^2 N \hbar^4 / I^2 e^{\beta\hbar^2/I}}{(3 + e^{\beta\hbar^2/I})^2} \sim 0. \quad (1.22)$$

High T limit:

$$z_I = \sum_{j=0}^{+\infty} (2j+1) e^{-\beta\hbar^2 j(j+1)/2I} \sim \int_0^{+\infty} (2j+1) e^{-\beta\hbar^2 j(j+1)/2I} dj \quad (1.23)$$

Next we perform a change of variable, let $x^2 = \frac{\beta\hbar^2}{2I} j(j+1)$, $2x dx = \frac{\beta\hbar^2}{2I} (2j+1) dj$, we then have

$$z_I = \int_0^{+\infty} \frac{4I}{\beta\hbar^2} x dx e^{-x^2} = \frac{4I}{\beta\hbar^2} \frac{1}{2} = \frac{2I}{\beta\hbar^2}, \quad (1.24)$$

from which we can extract the energy and specific heat in the high T limit:

$$U_{\text{rot}} = -N \frac{1}{z_I} \frac{\partial z_I}{\partial \beta} = -N \frac{\beta \hbar^2 2I - 1}{2I \hbar^2 \beta^2} = N k_B T \quad (1.25)$$

$$C_{\text{rot}} = \frac{\partial U}{\partial T} = N k_B. \quad (1.26)$$

Marking Scheme

- 2 for knowing definition of the internal energy
- 3 for getting the correct energy in small T limit.
- 2 for knowing definition of the specific heat.
- 3 for getting the correct specific heat in small T limit.
- 3 for knowing how to express partition function as an integral.
- 3 for evaluating the integral correctly.
- 2 for getting the energy in the large T limit.
- 2 for getting the specific heat in the large T limit.
- You get half mark if results differ by a numerical constant.

(10pts)(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 $\hbar\omega_o/2 \gg E_o$, where $E_o = \hbar^2/2I$ is the rotational zero point energy. Using the results you have derived above for $C_V^{\text{rot}}(T)$ and $C_V^{\text{vib}}(T)$, 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 $kT \ll \hbar^2/2I$)?

Solution

There will be three regions of interests: $k_B T \ll \hbar^2/2I$, $\hbar^2/2I \ll k_B T \ll \hbar\omega_o/2$ and $k_B \gg \hbar\omega_o/2$. In the low T region, $C_V^{\text{rot}} \sim C_V^{\text{vib}} \sim 0$, thus $C_V \sim C_V^{\text{tr}} = \frac{3}{2} N k_B$; in the middle region $C_V^{\text{rot}} \sim N k_B$, $C_V^{\text{vib}} \sim 0$, thus $C_V \sim C_V^{\text{rot}} + C_V^{\text{tr}} = \frac{5}{2} N k_B$; in the high T limit $C_V^{\text{vib}} \sim N k_B$, thus $C_V \sim C_V^{\text{tr}} + C_V^{\text{rot}} + C_V^{\text{vib}} = \frac{7}{2} N k_B$

Marking Scheme

- 1pts for understanding the existence of 3 different temperature regions.
- 3pts for getting the value correct in the low T limit.
- 3pts for getting the value correct in the middle T region.
- 3pts for getting the value correct in the high T limit.

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 typically 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 .

(12pts)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?

Solution

There are N_o sites, each can either be occupied by an H atom or not. When a site is occupied, the particle number is 1 and the energy is $-U_o$. Therefore the grand canonical partition function for a single site is $\xi = 1 + e^{-\beta(-U_o)+\beta\mu \times 1} = 1 + e^{\beta U_o + \beta\mu}$, the total grand canonical partition function for n_o sites is then

$$\Xi(\beta, \mu) = \xi^{N_o} = (1 + e^{\beta U_o + \beta\mu})^{N_o} \quad (2.1)$$

Marking Scheme

- 2pts for knowing the definition of grand canonical partition function.
- 5pts for getting the single site partition function.
- 5pts for getting the total partition function.

(10pts)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 ?

Solution

the average number of atoms in a single site is:

$$\langle M_0 \rangle = 0 \times \frac{1}{\xi} + 1 \times \frac{e^{\beta U_o + \beta \mu}}{\xi} = \frac{e^{\beta U_o + \beta \mu}}{1 + e^{\beta U_o + \beta \mu}} = \frac{1}{1 + e^{-\beta U_o - \beta \mu}} \quad (2.2)$$

then since particle number is extensive, the total average number of particles is:

$$\langle M \rangle = N_o \langle M_0 \rangle = \frac{N_o}{1 + e^{-\beta U_o - \beta \mu}}, \quad (2.3)$$

and the fraction M/N_o is just $\langle M_0 \rangle$.

Marking Scheme

- 5pts for showing understanding of how to calculate average values of quantities.
- 5pts for getting the correct average value of m .

(13pts)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

$$\rho = \frac{1}{4\pi^2} (2m)^{3/2} \int_0^{+\infty} \frac{dE}{\hbar^3} E^{1/2} e^{-\beta(E-\mu)} \quad (2.4)$$

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 $U_o = 5eV$ (recalling that $1eV \sim 11,604K$). You will need to find out what is atmospheric pressure from the literature.

Solution

The question is essentially asking you to change variable from (β, μ, U_o) to (β, p, U_o) using the relation given above. First we solve the integral:

$$\rho = \frac{1}{4\pi^2} (2m)^{3/2} e^{\beta \mu} / \hbar^3 \int_0^{+\infty} dE E^{1/2} e^{-\beta E} \quad (2.5)$$

$$= \frac{1}{4\pi^2} (2m)^{3/2} e^{\beta \mu} / \hbar^3 \frac{\sqrt{\pi}}{2\beta^{3/2}} = \left(\frac{m}{2\pi\beta\hbar} \right)^{3/2} e^{\beta \mu} \quad (2.6)$$

$$\Rightarrow e^{\beta \mu} = \rho \left(\frac{2\pi\beta\hbar}{m} \right)^{3/2} \quad (2.7)$$

therefore the average atom number can be expressed as

$$\langle m \rangle = \frac{1}{1 + e^{-\beta U_0 - \beta \mu}} = \frac{1}{1 + e^{-\beta U_0} \frac{1}{\rho} \left(\frac{m}{2\pi\beta\hbar} \right)^{3/2}} \sim 1 \quad (2.8)$$

Marking Scheme

- 5 for doing the integration correctly.
- 3 for expressing μ in terms of other variables.
- 3 for getting the correct expression for $\langle m \rangle$
- 2 for evaluating $\langle m \rangle$ correctly