

PHY5524 Problem Set 5: Solution

Problem 1

(a) The partition function for a single molecule described by the given “rigid-rotor” Hamiltonian is

$$Q_1(T, V) = \int \frac{d^3r d^3p}{h^3} \int \frac{d\theta d\phi dp_\theta dp_\phi}{h^2} e^{-\beta \left(\frac{p^2}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} \right)} \quad (1)$$

$$= \left(\int \frac{d^3r d^3p}{h^3} e^{-\beta \vec{p}^2 / 2m} \right) \left(\int \frac{d\theta d\phi dp_\theta dp_\phi}{h^2} e^{-\beta \left(\frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} \right)} \right) \quad (2)$$

The integral over \vec{r} and \vec{p} is just the familiar integral for an ideal monatomic gas which gives $V(2\pi mk_B T/h^2)^{3/2}$. To do the remaining integral over θ , ϕ , p_θ and p_ϕ we can make a change of variables from p_ϕ to p'_ϕ where $p'_\phi = p_\phi/\sin\theta$.

$$\int \frac{d\theta d\phi dp_\theta dp_\phi}{h^2} e^{-\beta \left(\frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta} \right)} = \int \frac{\sin \theta d\theta d\phi dp_\theta dp'_\phi}{h^2} e^{-\beta \left(\frac{p_\theta^2}{2I} + \frac{p_\phi'^2}{2I} \right)} \quad (3)$$

$$= \frac{4\pi}{h^2} \frac{2\pi I}{\beta} \quad (4)$$

$$= \frac{8\pi^2 I k_B T}{h^2} \quad (5)$$

Putting everything together we find

$$Q_1 = V \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{8\pi^2 I k_B T}{h^2} \right) \quad (6)$$

(b) For N noninteracting indistinguishable molecules the partition function is

$$Q_N = \frac{1}{N!} Q_1^N \quad (7)$$

and the Helmholtz free energy (using $\ln N! = N \ln N - N$) is,

$$A = -k_B T \ln Q_N = N k_B T \left(\frac{3}{2} \ln \left(\frac{h^2}{2\pi m k_B T} \right) + \ln \left(\frac{h^2}{8\pi^2 I k_B T} \right) \right) + k_B T (N \ln N - N) \quad (8)$$

$$= N k_B T \left(\ln \left(\frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \left(\frac{h^2}{8\pi^2 I k_B T} \right) \right) - 1 \right) \quad (9)$$

(c) The pressure is

$$P = - \left(\frac{\partial A}{\partial V} \right)_{T, N} = \frac{N k_B T}{V} \quad (10)$$

from which we see that the ideal gas law $PV = N k_B T$ is satisfied.

The entropy is

$$S = - \left(\frac{\partial A}{\partial T} \right)_{N, V} \quad (11)$$

$$= k_B T \left(\ln \left(\frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \left(\frac{8\pi^2 I k_B T}{h^2} \right) \right) + \frac{7}{2} \right) \quad (12)$$

and the energy is

$$E = - \frac{\partial}{\partial \beta} \ln Q_N = \frac{5}{2} N k_B T \quad (13)$$

(consistent with the equipartition theorem).

(d) The specific heat at constant volume is

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{5}{2} N k_B \quad (14)$$

and the specific heat at constant pressure is

$$C_P = \left(\frac{\partial(E + PV)}{\partial T} \right)_{N,P} = \frac{7}{2} N k_B \quad (15)$$

The ratio of the two is then

$$\gamma = C_P/C_V = 7/5 \quad (16)$$

(d) From the expression for S obtained in (b) we see that for any process in which S is constant it must also be the case that

$$T^{5/2} V = \text{Const.} \quad (17)$$

Using the ideal gas law ($PV = Nk_B T$) we then find

$$(PV)^5/2V = \text{Const.} \quad (18)$$

and raising both sides of the equation to the power $2/5$ yields the expected result

$$PV^{7/5} = \text{Const.} \quad (19)$$

Problem 2.

(a) The partition function for N quantum rigid rotors is

$$Q_N(T) = Q_1(T)^N \quad (20)$$

where

$$Q_1(T) = \sum_{j=0}^{\infty} (2j+1) e^{-\beta \hbar^2 j(j+1)/2I} \quad (21)$$

Here the factor of $2j+1$ is due to the degeneracy of the states with angular momentum j . Given Q_1 , the energy can be obtained using

$$E = -\frac{\partial}{\partial \beta} \ln Q_N = -N \frac{\partial \ln Q_1}{\partial \beta} \quad (22)$$

(b) Let $\alpha = \beta \hbar^2/2I$. We are interested in how Q_1 behaves in the limit $\alpha \rightarrow 0$. To determine this let $x_j = \alpha^{1/2} j$. The sum for Q_1 can then be expressed

$$Q_1 = \alpha^{-1/2} \sum_{j=0}^{\infty} (2x_j + \alpha^{1/2}) e^{-x_j(x_j + \alpha^{1/2})} \quad (23)$$

If we let $\Delta x = x_{j+1} - x_j = \alpha^{1/2}$ the above expression can be written

$$Q_1 = \alpha^{-1} \sum_{j=0}^{\infty} (2x_j + \alpha^{1/2}) e^{-x_j(x_j + \alpha^{1/2})} \Delta x \quad (24)$$

In the limit $\alpha \rightarrow 0$ the sum becomes an integral and we have

$$Q_1 \simeq \alpha^{-1} \int_0^{\infty} (2x + \alpha^{1/2}) e^{-x(x + \alpha^{1/2})} dx \quad (25)$$

Making the change of variables $y = x(x + \alpha^{1/2})$, for which $dy = (2x + \alpha^{1/2})dx$, then yields

$$Q_1 \simeq \alpha^{-1} \int_0^\infty e^{-y} dy = \frac{2Ik_B T}{\hbar^2} = \frac{8\pi^2 Ik_B T}{h^2} \quad (26)$$

Reassuringly, this is the same result obtained for the classical rotor in Problem 1.

Given Q_1 we can find the energy of the system

$$E = -N \frac{\partial \ln Q_1}{\partial \beta} = Nk_B T \quad (27)$$

and the specific heat

$$C = \frac{\partial E}{\partial T} = Nk_B \quad (28)$$

Both results are in agreement with the classical result, as we should expect in the limit $k_B T \gg \hbar^2/(2I)$.

(d) In the low temperature limit we need only keep the first two terms in the expression for Q_1

$$Q_1 \simeq 1 + 3e^{-\beta\hbar^2/I} \quad (29)$$

The energy E in this limit is then

$$E \simeq N \frac{\hbar^2}{I} \frac{3e^{-\beta\hbar^2/I}}{1 + 3e^{-\beta\hbar^2/I}} \simeq 3N \frac{\hbar^2}{I} e^{-\beta\hbar^2/I} \quad (30)$$

and the specific heat is

$$C(T) = \frac{\partial E}{\partial T} \simeq 3N \left(\frac{\hbar^2}{I} \right)^2 \frac{1}{k_B T^2} e^{-\beta\hbar^2/I} = 3Nk_B \left(\frac{\hbar^2/I}{k_B T} \right)^2 e^{-\beta\hbar^2/I} \quad (31)$$

Problem 3.

(a) The energy levels for a given cluster are

$$E_{\uparrow\uparrow} = \frac{J}{4} - 2\mu H \quad (32)$$

$$E_{\uparrow\downarrow} = E_{\downarrow\uparrow} = -\frac{J}{4} \quad (33)$$

$$E_{\downarrow\downarrow} = \frac{J}{4} + 2\mu H \quad (34)$$

The states $\uparrow\downarrow$ and $\downarrow\uparrow$ are degenerate.

(b) The partition function for a single cluster is

$$Q_1(T) = e^{-\beta E_{\uparrow\uparrow}} + e^{-\beta E_{\uparrow\downarrow}} + e^{-\beta E_{\downarrow\uparrow}} + e^{-\beta E_{\downarrow\downarrow}} \quad (35)$$

$$= 2e^{\beta J/4} + 2e^{-\beta J/4} \cosh(2\beta\mu H) \quad (36)$$

and so, for N clusters

$$Q_N(T) = \left(2e^{\beta J/4} + 2e^{-\beta J/4} \cosh(2\beta\mu H) \right)^N \quad (37)$$

(c) The magnetization is readily found to be

$$M = \frac{N}{\beta} \frac{\partial}{\partial H} \ln Q_1 \quad (38)$$

$$= \frac{2\mu e^{-\beta J/4} \sinh(2\beta\mu H)}{e^{\beta J/4} + e^{-\beta J/4} \cosh(2\beta\mu H)} \quad (39)$$

and the spin susceptibility is then

$$\chi = \lim_{H \rightarrow 0} \frac{\partial M}{\partial H} = \frac{4\mu^2 \beta}{1 + e^{\beta J/2}} \quad (40)$$

For $k_B T \gg J$ we have

$$\chi(T) \simeq \frac{4\mu^2 \beta}{1 + (1 + \beta J/2 \dots)} \simeq \frac{2\mu^2}{k_B(T + \frac{J}{4k_B})} = \frac{C}{T + \Theta} \quad (41)$$

where $C = 2\mu^2/k_B$ is the Curie constant and $\Theta = J/4k_B$.