PHY5524
Problem Set 5: Solution

Problem 1

(a) The partition function for a single molecule described by the given Hamiltonian is

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

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

The integral over $\vec{r}$ and $\vec{p}$ is just the familiar integral for an ideal monatomic gas which gives $V(2\pi mk_BT/h^2)^{3/2}$. To do the remaining integral over θ, ϕ, p_θ and p_ϕ we can make the change of variables p_ϕ let $p'_\phi = p_\phi/sin\theta$.

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

$$= \frac{4\pi}{h^2}\frac{2\pi I}{\beta} \tag{4}$$

$$= \frac{8\pi^2 Ik_BT}{h^2} \tag{5}$$

Putting everything together we find

$$Q_1 = V\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\left(\frac{8\pi^2 Ik_BT}{h^2}\right) \tag{6}$$

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

$$Q_N = \frac{1}{N!}Q_1^N \tag{7}$$

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

$$A = -k_BT\ln Q_N = Nk_BT\left(\frac{3}{2}\ln\left(\frac{h^2}{2\pi mk_BT}\right)+\ln\left(\frac{h^2}{8\pi^2 Ik_BT}\right)\right)+k_BT(N\ln N - N) \tag{8}$$

$$= Nk_BT\left(\ln\left(\frac{N}{V}\left(\frac{h^2}{2\pi mk_BT}\right)^{3/2}\left(\frac{h^2}{8\pi^2 Ik_BT}\right)\right)-1\right) \tag{9}$$

(c) The pressure is

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

from which we see that the ideal gas law $PV = Nk_BT$ is satisfied.

The entropy is

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

$$= k_BT\left(\ln\left(\frac{V}{N}\left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\left(\frac{8\pi^2 Ik_BT}{h^2}\right)\right)+\frac{7}{2}\right) \tag{12}$$

and the energy is

$$E = -\frac{\partial}{\partial\beta}\ln Q_N = \frac{5}{2}Nk_BT \tag{13}$$

(consistent with the equipartition theorem).
(d) The specific heat at constant volume is

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

and the specific heat at constant pressure is

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

The ratio of the two is then

$$\gamma = C_P/C_V = 7/5 \tag{16}$$

(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

$$T^{5/2}V = Const. \tag{17}$$

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

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

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

$$PV^{7/5} = Const. \tag{19}$$

Problem 2.
(a) The partition function for N quantum rigid rotors is

$$Q_N(T) = Q_1(T)^N \tag{20}$$

where

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

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

$$E = -\frac{\partial}{\partial\beta}\ln Q_N = -N\frac{\partial \ln Q_1}{\partial\beta} \tag{22}$$

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

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

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

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

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

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

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

$$Q_1 \simeq \alpha^{-1} \int_0^\infty e^{-y} dy = \frac{2Ik_BT}{\hbar^2} = \frac{8\pi^2 Ik_BT}{h^2} \tag{26}$$

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

$$E = -N\frac{\partial \ln Q_1}{\partial \beta} = Nk_BT \tag{27}$$

and the specific heat

$$C = \frac{\partial E}{\partial T} = Nk_B \tag{28}$$

Both results are in agreement with the classical result.

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

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

The energy E in this limit is then

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

and the specific heat is

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

Problem 3

(a) The energy levels for a given cluster are

$$E_{\uparrow\uparrow} = \frac{J}{4} - 2\mu H \tag{32}$$

$$E_{\uparrow\downarrow} = E_{\downarrow\uparrow} = -\frac{J}{4} \tag{33}$$

$$E_{\downarrow\downarrow} = \frac{J}{4} + 2\mu H \tag{34}$$

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

(b) The partition function for a single cluster is

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

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

and so, for N clusters

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

(c) The magnetization is readily found to be

$$M = \frac{N}{\beta}\frac{\partial}{\partial H}\ln Q_1 \tag{38}$$

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

and the spin susceptibility is then

$$\chi = \lim_{H\to 0}\frac{\partial M}{\partial H} = \frac{4\mu^2\beta}{1 + e^{\beta J/2}} \tag{40}$$

For $k_BT \gg J$ we have

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

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