

Problem Set 5
Solutions - McQuarrie Problems
3.20 MIT
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Problem 3-4

We have to derive the thermodynamic properties of an ideal monatomic gas from the following:

$$\Theta = e^{q\lambda}$$

$$\lambda = e^{\beta\mu} \text{ and } q = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V$$

Θ is the partition function for the grand canonical ensemble, where T, V, μ are fixed. The characteristic potential for the grand canonical ensemble is the "grand canonical potential"

$$\phi = E - TS - \mu N = -pV$$

(since $E = TS - pV + \mu N$)

$$d\phi = -SdT - pdV - Nd\mu$$

The thermodynamic properties for the grand canonical ensemble are:

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

$$p = - \left(\frac{\partial \phi}{\partial V} \right)_{T,\mu}$$

$$N = - \left(\frac{\partial \phi}{\partial \mu} \right)_{T,V}$$

The grand canonical potential is related to Θ according to

$$\phi = -kT \ln \Theta \quad (\text{see table 3-1})$$

but $\Theta = e^{q\lambda}$ so,

$$\phi = -kT \cdot q\lambda = -kT \cdot \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V \cdot e^{\beta\mu} = -(kT)^{\frac{5}{2}} \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V \cdot \exp\left(\frac{\mu}{kT}\right)$$

Starting with N ,

$$N = - \left(\frac{\partial \phi}{\partial \mu} \right)_{T,V} = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} V \cdot \exp\left(\frac{\mu}{kT}\right) \quad ((3-8-1))$$

and p

$$p = - \left(\frac{\partial \phi}{\partial V} \right)_{T,\mu} = kT \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \exp\left(\frac{\mu}{kT}\right)$$

Putting those together we can get the ideal gas equation of state, namely

$$p = \frac{N}{V} kT$$

Now S ,

$$S = - \left(\frac{\partial \phi}{\partial T} \right)_{N,V} = \frac{5}{2} k \cdot (kT)^{\frac{3}{2}} \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V e^{\beta\mu} + (kT)^{\frac{5}{2}} \left(\frac{2\pi m}{h^2} \right)^{\frac{3}{2}} V \left(\frac{-\mu}{kT^2} \right) e^{\beta\mu}$$

$$\begin{aligned}
S &= \frac{5}{2}k \cdot \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V e^{\beta\mu} - \frac{\mu}{T} \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V e^{\beta\mu} \\
S &= \left(\frac{5}{2}k - \frac{\mu}{T}\right) \underbrace{\left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V e^{\beta\mu}\right]}_N \\
S &= \left(\frac{5}{2}k - \frac{\mu}{T}\right) N \tag{3-8-2}
\end{aligned}$$

But from (3-8-1) we can get

$$\begin{aligned}
e^{\beta\mu} &= NV^{-1} \left(\frac{2\pi mkT}{h^2}\right)^{-\frac{3}{2}} \\
\mu &= -kT \cdot \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} \right]
\end{aligned}$$

Putting this into (3-8-2) we get

$$\begin{aligned}
S &= \left(\frac{5}{2}k + k \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} \right]\right) N = Nk \left\{ \ln \left(e^{\frac{5}{2}}\right) + \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} \right] \right\} \\
\boxed{S} &= Nk \ln \left[\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \frac{V}{N} \cdot e^{\frac{5}{2}} \right]
\end{aligned}$$

This is the same expression as that obtained in the canonical ensemble (see Chapter 5). This is due to the equivalence of ensembles when N is very large.

Problem 3-10

We are dealing with the isothermal-isobaric ensemble this time, with the partition function for an ideal monatomic gas given to us in the problem as

$$\Delta = \left[\frac{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{ph^3} \right]^N$$

- The isothermal-isobaric is for fixed (N, T, P) .
- The characteristic potential for this ensemble is the Gibbs free energy

$$G = E - TS + pV$$

$$dG = -SdT + VdP + \mu dN$$

- The thermodynamic properties are:

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p,N}$$

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,N}$$

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{p,T}$$

- G is related to the isothermal-isobaric partition function Δ according to (see Table 3-1):

$$G = -kT \ln \Delta = -NkT \ln \left[\frac{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{ph^3} \right]$$

$$G = -NkT \left\{ \ln (2\pi m)^{\frac{3}{2}} + \frac{5}{2} \ln (kT) - \ln h^3 - \ln p \right\}$$

Starting with V ,

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,N} = \frac{NkT}{p}$$

which is the ideal gas equation of state. Now for μ :

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{p,T} = kT \ln \left[\frac{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{ph^3} \right]$$

$$\mu = \underbrace{-kT \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} kT \right]}_{\mu_o} + kT \ln p$$

And now for S ,

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p,N} = Nk \ln \left[\frac{(2\pi m)^{\frac{3}{2}} (kT)^{\frac{5}{2}}}{ph^3} \right] + \frac{5}{2} Nk$$

$$S = Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} \right] + Nk \ln \left(e^{\frac{5}{2}} \right)$$

$$S = Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{V}{N} \cdot e^{\frac{5}{2}} \right]$$

These are the same expressions as obtained in the grand canonical ensemble (Problem 3-8) and in the canonical ensemble (see chapter 5). This is due to the equivalence of ensembles in the thermodynamic limit, i.e N is very large such that fluctuations are negligible.

Problem 3-12

When looking at fluctuations, we derived

$$P(\Delta E) \approx \frac{1}{\sqrt{2\pi kT^2 C_v}} \exp \left[- \frac{(E - \bar{E})^2}{2kT^2 C_v} \right]$$

For an ideal monatomic gas (derived explicitly in chapter 5)

$$\bar{E} = \frac{3}{2} NkT$$

$$C_v = \frac{\partial \bar{E}}{\partial T} = \frac{3}{2} Nk$$

We are now asked what is the probability that the N -particle system will sample an energy that differs by $10^{-4}\%$ from the average energy, $\bar{E} = \frac{3}{2} NkT$? (We can let $N = N_A = 6.022 \times 10^{23} M$)

$$\Delta E = \left(\frac{10^{-4}}{100} \right) \bar{E} = 10^{-6} \bar{E} = (10^{-6}) \frac{3}{2} NkT$$

$$\frac{(\Delta E)^2}{2kT^2 C_v} = \frac{(10^{-6})^2 \frac{9}{4} N^2 k^2 T^2}{2kT^2 \cdot \frac{3}{2} Nk} = \frac{3}{4} (10^{-6})^2 N$$

So now we can go back to $P(\Delta E)$,

$$P(\Delta E) \approx \frac{1}{kT \sqrt{3\pi N}} \exp \left[- \frac{3}{4} (10^{-6})^2 N \right]$$

$$P(\Delta E) \approx \frac{1}{kT\sqrt{3\pi N}} \exp[-4.5 \times 10^{11}]$$

This is an extremely small probability which validates our earlier assumptions.

Problem 3-18

Derive an expression for the fluctuation of the pressure in the canonical ensemble..

We know the pressure in state i is

$$p_i = - \left(\frac{\partial E_i}{\partial V} \right)$$

and by definition

$$\bar{p} = \frac{\sum_i - \left(\frac{\partial E_i}{\partial V} \right) \exp \left[\frac{-E_i}{kT} \right]}{\sum_i \exp \left[\frac{-E_i}{kT} \right]}$$

Fluctuation is defined as $\sigma_p^2 = \overline{(p - \bar{p})^2} = \overline{p^2} - \bar{p}^2$.

Using the methods developed in class:

Step 1: Multiply both sides by the partition function

$$\bar{p}Q = \sum_i p_i \exp \left[\frac{-E_i}{kT} \right]$$

Step 2: Get derivative with respect to mechanical variable's conjugate.

$$\begin{aligned} \frac{\partial}{\partial V} (\bar{p}Q) &= \frac{\partial}{\partial V} \left(\sum_i p_i \exp \left[\frac{-E_i}{kT} \right] \right) \\ \bar{p} \frac{\partial Q}{\partial V} + Q \frac{\partial \bar{p}}{\partial V} &= \frac{\partial}{\partial V} \left(\sum_i p_i \exp \left[\frac{-E_i}{kT} \right] \right) \\ \bar{p} \frac{\partial}{\partial V} \left(\sum_i \exp \left[\frac{-E_i}{kT} \right] \right) + Q \frac{\partial \bar{p}}{\partial V} &= \frac{\partial}{\partial V} \left(\sum_i p_i \exp \left[\frac{-E_i}{kT} \right] \right) \\ \bar{p} \sum_i \left[\exp \left[\frac{-E_i}{kT} \right] \cdot - \left(\frac{\partial E_i}{\partial V} \right) \cdot \frac{1}{kT} \right] + Q \frac{\partial \bar{p}}{\partial V} &= \sum_i \left[\frac{\partial p_i}{\partial V} \exp \left[\frac{-E_i}{kT} \right] \right] + \sum_i \left[p_i \exp \left[\frac{-E_i}{kT} \right] \cdot - \left(\frac{\partial E_i}{\partial V} \right) \cdot \frac{1}{kT} \right] \end{aligned}$$

Step 3: Divide through by the partition function

$$\begin{aligned} \frac{\bar{p} \sum_i \left[\exp \left[\frac{-E_i}{kT} \right] \cdot - \left(\frac{\partial E_i}{\partial V} \right) \cdot \frac{1}{kT} \right]}{Q} + \frac{Q \frac{\partial \bar{p}}{\partial V}}{Q} &= \frac{\sum_i \left[\frac{\partial p_i}{\partial V} \exp \left[\frac{-E_i}{kT} \right] \right]}{Q} + \frac{\sum_i \left[p_i \exp \left[\frac{-E_i}{kT} \right] \cdot - \left(\frac{\partial E_i}{\partial V} \right) \cdot \frac{1}{kT} \right]}{Q} \\ \frac{\bar{p}^2}{kT} + \frac{\partial \bar{p}}{\partial V} &= \overline{\left(\frac{\partial p_i}{\partial V} \right)} + \frac{\bar{p}^2}{kT} \end{aligned}$$

Rearranging a little...

$$\sigma_p^2 = \bar{p}^2 - \overline{p^2} = kT \left[\overline{\left(\frac{\partial p_i}{\partial V} \right)} - \left(\frac{\partial \bar{p}}{\partial V} \right) \right]$$

Note: $\overline{\left(\frac{\partial p_i}{\partial V} \right)}$ has no immediate macroscopic interpretation, it must be calculate in any specific case and depends on the particular spectrum of $\left(\frac{\partial^2 E_i}{\partial V^2} \right)$. This conclusion holds for all generalized forces in the form $A_i = \frac{\partial E_i}{\partial a}$, where a is an extensive displacement conjugate to A . Hence, we cannot make an unqualified assertion that fluctuations in all kinds of external forces will be small.

Compare this with fluctuations in extensive quantities such as E , H , or N which can be expressed in terms of thermodynamic response variables such as heat capacities or compressibilities.

Specific calculations of the fluctuations in p of a perfect gas by Fowler is estimated as

$$\frac{\overline{(p - \bar{p}^2)}}{\bar{p}^2} \approx 5 \times 10^{-12}$$

for a cubic centimeter of gas under standard conditions. This is approximately $\frac{1}{n^{\frac{2}{3}}}$, where n is the number of molecules in the gas.

(Source: The Principles of Statistical Mechanics, Richard C Tolman, Oxford University Press, first edition 1938)

Problem 3-24

Show that $\overline{H^2} - \bar{H}^2 = kT^2 C_p$ in an N, p, T ensemble.

- N, P, T fixed means we are working in the isothermal-isobaric ensemble..
- The partition function in this ensemble is

$$\Delta = \sum_V \sum_j e^{-\beta E_j - \beta pV}$$

Where the E_j 's are the energies of the system when it has volume V . We also remember that $H = E + pV$.

Using the methods developed in class:

Step 1: Multiply both sides by the partition function

$$\bar{H}\Delta = \sum_{V,j} (E_j + pV) e^{-\beta E_j - \beta pV}$$

Step 2: Get the temperature derivative at constant (N, P) (The conjugate variable to H in this case)

$$\left(\frac{\partial \bar{H}}{\partial T}\right)_{N,P} \Delta + \bar{H} \left(\frac{1}{kT^2} \sum_{V,j} (E_j + pV) e^{-\beta E_j - \beta pV}\right) = \frac{1}{kT^2} \sum_{V,j} (E_j + pV)^2 e^{-\beta E_j - \beta pV}$$

Step 3: Divide through by the partition function

$$\left(\frac{\partial \bar{H}}{\partial T}\right)_{N,P} + \frac{1}{kT^2} \bar{H} \underbrace{\left(\frac{\sum_{V,j} (E_j + pV) e^{-\beta E_j - \beta pV}}{\Delta}\right)}_{\bar{H}} = \frac{1}{kT^2} \underbrace{\left(\frac{\sum_{V,j} (E_j + pV)^2 e^{-\beta E_j - \beta pV}}{\Delta}\right)}_{\bar{H}^2}$$

or

$$\overline{H^2} - \bar{H}^2 = kT^2 \left(\frac{\partial \bar{H}}{\partial T}\right)_{N,P}$$

but we know $\left(\frac{\partial \bar{H}}{\partial T}\right)_{N,P} = C_p$. So,

$$\boxed{\overline{H^2} - \bar{H}^2 = kT^2 C_p}$$

Problem 3-26

Show that $\left(\frac{\partial \mu}{\partial N}\right)_{V,T} = -\frac{V^2}{N^2} \left(\frac{\partial p}{\partial V}\right)_{N,T} \dots$

From Gibbs-Duhem we have

$$SdT - Vdp + Nd\mu = 0$$

At constant T , we then get

$$\left(\frac{d\mu}{dp}\right) = \frac{V}{N}$$

We can use the chain rule and get:

$$\left(\frac{d\mu}{dp}\right) = \left(\frac{d\mu}{dN}\right)_{V,T} \left(\frac{dN}{dp}\right)_{V,T}$$

Using partial derivative manipulation

$$\left(\frac{dN}{dp}\right)_{V,T} = -\left(\frac{dN}{dV}\right)_{P,T} \left(\frac{dV}{dp}\right)_{N,T}$$

But for a single component system $\left(\frac{dV}{dN}\right)_{P,T}$ = the molar volume = $\frac{V}{N}$ and we get

$$\left(\frac{dN}{dp}\right)_{V,T} = -\frac{N}{V} \left(\frac{dV}{dp}\right)_{N,T}$$

Putting this all together we get

$$\left(\frac{d\mu}{dN}\right)_{V,T} = -\frac{V^2}{N^2} \left(\frac{dp}{dV}\right)_{N,T}$$

Problem 4-2

Show that $\frac{6N}{\pi V} \left(\frac{h^2}{12mkT}\right)^{\frac{3}{2}}$ given in table 4-1 is very large for electrons in metals at $T = 300K$.

- Take Na-metal having the following properties
 - stable in the bcc crystal structure with lattice constant $a = 4.23 \times 10^{-10}m$
 - two Na atoms per bcc unit cell
 - number of valance electrons per Na atom = 1
 - valance electrons in Na can be considered nearly free

So we can get the following values to substitute into the original equations:

$$\frac{N}{V} = \frac{2}{(4.23 \times 10^{-10})^3}$$

$$h = 6.6262 \times 10^{-34} J \cdot s$$

$$k = 1.3807 \times 10^{-23} \frac{J}{K}$$

$$m_e = 9.1095 \times 10^{-31} kg$$

Putting those all together we get

$$\frac{6N}{\pi V} \left(\frac{h^2}{12mkT}\right)^{\frac{3}{2}} = 1524 \gg 1$$

Therefore Boltzmann statistics cannot be applied to electrons in metals. Must use Fermi-Dirac statistics.

Problem 4-6

$$S = \sum_{N=0}^{\infty} \sum_{\{n_j\}^*} x_1^{n_1} x_2^{n_2}$$

with n_1 and $n_2 = 0, 1, \text{ and } 2$. The $\sum_{\{n_j\}^*}$ means $\sum_{n_1} \sum_{n_2}$ with the restriction that $n_1 + n_2 = N$.

Let's consider $\sum_{\{n_j\}^*} x_1^{n_1} x_2^{n_2}$ for several values of N .

$N = 0 \rightarrow$ possible combinations of n_1 and n_2 are 0 and 0.

$$\implies \sum_{\{n_j\}^*} = 1$$

$N = 1 \rightarrow$ possible combinations of n_1 and n_2 are

| | | |
|-------|-------|-----|
| n_1 | n_2 | N |
| 1 | 0 | 1 |
| 0 | 1 | 1 |

$$\implies \sum_{\{n_j\}^*} x_1^{n_1} x_2^{n_2} = x_1 + x_2$$

$N = 2 \rightarrow$ possible combinations of n_1 and n_2 are

| | | |
|-------|-------|-----|
| n_1 | n_2 | N |
| 0 | 2 | 2 |
| 1 | 1 | 2 |
| 2 | 0 | 2 |

$$\implies \sum_{\{n_j\}^*} x_1^{n_1} x_2^{n_2} = x_2^2 + x_1 x_2 + x_1^2$$

$N = 3 \rightarrow$ possible combinations of n_1 and n_2 are

| | | |
|-------|-------|-----|
| n_1 | n_2 | N |
| 1 | 2 | 3 |
| 2 | 1 | 3 |

$$\implies \sum_{\{n_j\}^*} x_1^{n_1} x_2^{n_2} = x_1 x_2^2 + x_1^2 x_2$$

$N = 4 \rightarrow$ possible combinations of n_1 and n_2 are

| | | |
|-------|-------|-----|
| n_1 | n_2 | N |
| 2 | 2 | 4 |

$$\implies \sum_{\{n_j\}^*} x_1^{n_1} x_2^{n_2} = x_1^2 x_2^2$$

For $N > 4 \rightarrow \sum_{\{n_j\}^*} x_1^{n_1} x_2^{n_2} = 0$ because $n_1 + n_2 \leq 4$

Putting everything together we get

$$\sum_N \sum_{\{n_j\}^*} x_1^{n_1} x_2^{n_2} = 1 + x_1 + x_2 + x_2^2 + x_1 x_2 + x_1^2 + x_1 x_2^2 + x_1^2 x_2 + x_1^2 x_2^2$$

Now lets consider

$$S = \prod_{k=1}^2 (1 + x_k + x_k^2)$$

$$S = (1 + x_1 + x_1^2) (1 + x_2 + x_2^2) = 1 + x_1 + x_2 + x_2^2 + x_1x_2 + x_1^2 + x_1x_2^2 + x_1^2x_2 + x_1^2x_2^2$$

This expression contains the exact same terms as that obtained with $\sum_N \sum_{\{n_j\}}^* x_1^{n_1} x_2^{n_2}$.

Problem 4-8

We need to show this (remember the upper (lower) signs is for Fermi-Dirac (Bose-Einstein)

:

$$S = -k \sum_j [\bar{n}_j \ln \bar{n}_j \pm (1 \mp \bar{n}_j) \ln (1 \mp \bar{n}_j)]$$

Start with the partition function and go from there. Because of the equivalence of ensembles in the thermodynamic limit, we can calculate the entropy using the ensemble that offers the most mathematical convenience. For Fermions or Bosons, this is the grand canonical ensemble. $(S = k \ln \Theta + kT (\frac{\partial \ln \Theta}{\partial T})_{V,\mu})$

$$\Theta = \prod_j \left(1 + \lambda e^{-\frac{\epsilon_j}{kT}}\right)^{\pm 1}$$

$$\ln \Theta = \pm \sum_j \ln \left(1 + \lambda e^{-\frac{\epsilon_j}{kT}}\right)$$

$$\frac{\partial \ln \Theta}{\partial T} = \pm \sum_j \frac{\frac{\partial}{\partial T} \left(\pm \lambda e^{-\frac{\epsilon_j}{kT}}\right)}{1 \pm \lambda e^{-\frac{\epsilon_j}{kT}}} = \sum_j \frac{\left(\frac{\epsilon_j - \mu}{kT^2}\right) \exp\left[-\frac{(\epsilon_j - \mu)}{kT}\right]}{1 \pm \lambda e^{-\frac{\epsilon_j}{kT}}}$$

$$S = k \sum_j \left\{ \pm \ln \left(1 \pm \lambda e^{-\frac{\epsilon_j}{kT}}\right) + \frac{\lambda e^{-\beta \epsilon_j} \left(\frac{\epsilon_j - \mu}{kT}\right)}{1 \pm \lambda e^{-\beta \epsilon_j}} \right\}$$

To make this a little easier to manipulate we can write this shorthand by making the following substitutions. Let:

$$u = 1 \pm \lambda e^{-\beta \epsilon_j} \text{ and } v = \lambda e^{-\beta \epsilon_j}$$

$$u = 1 \pm v \text{ and } u \mp v = 1$$

$$\bar{n}_j = \frac{v}{u}$$

So we now have

$$S = k \sum_j \{\pm \ln u - \bar{n}_j \ln v\} = k \sum_j \{\pm \ln u - \bar{n}_j \ln \bar{n}_j - \bar{n}_j \ln u\}$$

$$S = k \sum_j \{(\pm 1 - \bar{n}_j) \ln u - \bar{n}_j \ln \bar{n}_j\} = k \sum_j \left\{ -(\pm 1 - \bar{n}_j) \ln \left(\frac{1}{u}\right) - \bar{n}_j \ln \bar{n}_j \right\}$$

Remembering that $u \mp v = 1$

$$S = k \sum_j \{-(\pm 1 - \bar{n}_j) \ln (1 \mp \bar{n}_j) - \bar{n}_j \ln \bar{n}_j\}$$

$$S = -k \sum_j \{\bar{n}_j \ln \bar{n}_j \pm (1 \mp \bar{n}_j) \ln (1 \mp \bar{n}_j)\}$$

Problem 4-12

N -distinguishable independent particles, each of which can be in state $+\varepsilon_o$ or $-\varepsilon_o$.

$$\begin{aligned} N_+ &= \text{number of particles with energy } +\varepsilon_o \\ N_- &= \text{number of particles with energy } -\varepsilon_o \\ &\text{with } N_+ + N_- = N \end{aligned}$$

The total energy is given as:

$$E = N_+\varepsilon_o - N_-\varepsilon_o = 2N_+\varepsilon_o - N\varepsilon_o$$

We now have to evaluate the partition function Q by summing $\exp\left(\frac{-E}{kT}\right)$ over levels and compare it to the result $Q = q^N$.

- We know

$$Q = \sum_j \exp\left(\frac{-E_j}{kT}\right)$$

where j labels a state in which the system can reside.

- Instead of summing over the states that the system can be in, we can also sum over the possible energy levels, making sure we take account of the degeneracy of each energy level, i.e.

$$Q = \sum_E \Omega(E) \exp\left(\frac{-E}{kT}\right)$$

where $\Omega(E)$ is the number of states with energy E .

- For this system we have already stated the allowed energy levels are

$$E = 2N_+\varepsilon_o - N\varepsilon_o$$

where N_+ can vary from $0 \rightarrow N$.

- For each allowed energy level E , there are $\Omega(E)$ possible states compatible with this energy. Since the N particles are distinguishable,

$$\Omega(E) = \frac{N!}{N_+!N_-!} = \frac{N!}{N_+(N - N_+)!}$$

This represents the number of ways that N_+ particles out of N can be in the $+$ state.

- So now we can write

$$Q = \sum_E \Omega(E) \exp(-\beta E) \quad \text{Since } E \text{ is uniquely a function of } N_+ \implies \sum_{N_+} \frac{N!}{N_+(N - N_+)!} \exp[-\beta(2N_+\varepsilon_o - N\varepsilon_o)]$$

This can be rewritten in a nicer form if we remember the binomial expansion

$$(1 + x)^n = \sum_{n_1=0}^n \frac{n! \cdot x^{n_1}}{n_1!(n - n_1)!}$$

So we have

$$Q = e^{\beta N\varepsilon_o} \left(\sum_{N_+} \frac{N!}{N_+(N - N_+)!} (e^{-\beta 2\varepsilon_o})^{N_+} \right)$$

if we let $x = e^{-\beta 2\varepsilon_o}$ and rewrite using the binomial expansion we have

$$Q = e^{\beta N\varepsilon_o} (1 + e^{-\beta 2\varepsilon_o})^N$$

or

$$Q = (e^{\beta\varepsilon_o} + e^{-\beta\varepsilon_o})^N$$

- Now we need to compare this to $Q = q^N$, where q is the single particle partition function defined as

$$q = \sum_l e^{-\beta \epsilon_l}$$

where l labels the single particle states. In this example there are two single particle states, with energy $-\epsilon_o$ and $+\epsilon_o$.

$$\implies q = e^{-\beta \epsilon_o} + e^{\beta \epsilon_o}$$

and

$$Q = q^N = (e^{-\beta \epsilon_o} + e^{\beta \epsilon_o})^N$$

•The last part of this problem asks us to calculate and plot the heat capacity for this system. We know $C_v = \frac{\partial E}{\partial T}$ and E is given as

$$E = kT^2 \frac{\partial \ln Q}{\partial T} = kT^2 N \frac{\partial \ln (e^{-\beta \epsilon_o} + e^{\beta \epsilon_o})}{\partial T}$$

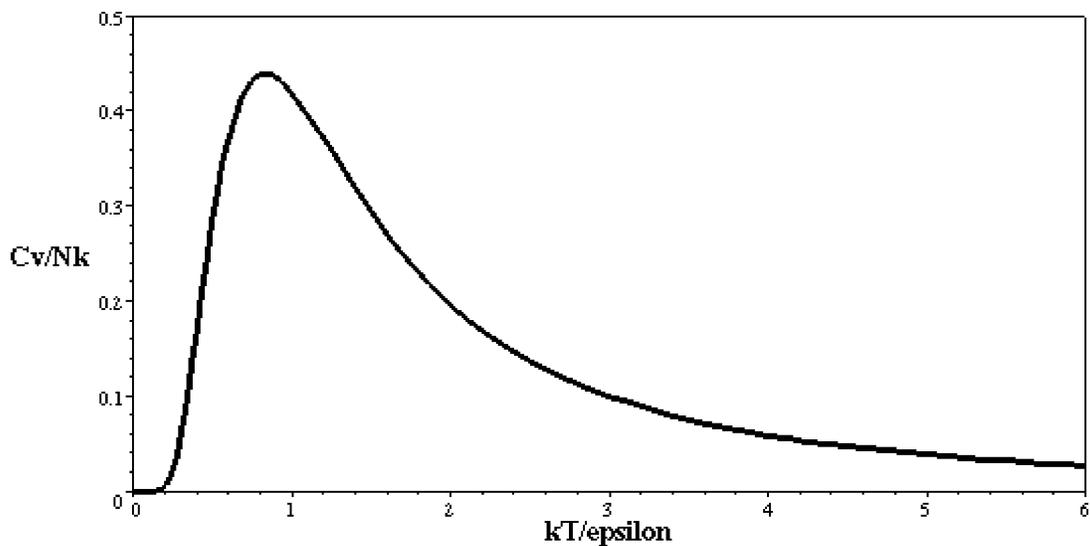
$$E = kT^2 N \frac{\frac{\epsilon_o}{kT^2} e^{-\beta \epsilon_o} - \frac{\epsilon_o}{kT^2} e^{\beta \epsilon_o}}{e^{-\beta \epsilon_o} + e^{\beta \epsilon_o}} = N \epsilon_o \left(\frac{e^{-\beta \epsilon_o} - e^{\beta \epsilon_o}}{e^{-\beta \epsilon_o} + e^{\beta \epsilon_o}} \right)$$

$$E = -N \epsilon_o \tanh(\beta \epsilon_o)$$

and C_v is then

$$C_v = \frac{\partial E}{\partial T} = Nk \left(\frac{\epsilon_o}{kT} \right)^2 \operatorname{sech}^2 \left(\frac{\epsilon_o}{kT} \right)$$

Plotting $\frac{C_v}{Nk}$ vs. $\left(\frac{kT}{\epsilon_o} \right)$



Problem 5-4

Calculate the entropy of Ne at 300K and 1 atm.

- The entropy of an ideal gas (eqn 5-20):

$$S = Nk \ln \left[\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \frac{V e^{\frac{5}{2}}}{N} \right]$$

Note this is neglecting electronic excitations (see Chapter 5).

Some data:

$$\begin{aligned} m &= 3.351 \times 10^{-26} \text{ kg} \\ k &= 1.3807 \times 10^{-27} \frac{\text{J}}{\text{K}} \\ h &= 6.6262 \times 10^{-34} \text{ J} \cdot \text{s} \\ p &= 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} \end{aligned}$$

Putting that together we can get

$$\begin{aligned} \frac{V}{N} &= \frac{kT}{p} = 4.0889 \times 10^{-26} \\ \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} &= 8.852 \times 10^{31} \end{aligned}$$

and

$$S = Nk \ln (4.41 \times 10^7)$$

$$S = k \ln \left[(4.41 \times 10^7)^N \right]$$

where N = the number of Ne atoms.

- We are now asked to estimate the translational degeneracy Ω

-From our study of fluctuation theory, we found that the fluctuation in energy of a thermodynamic system (with N very large) is exceedingly small.

-Therefore, the energy of the gas is essentially always very close to \bar{E} (see discussion on page 63 of McQuarrie) and we can use the expression for the entropy in the microcanonical ensemble.

$$S = k \ln \Omega$$

where Ω is the degeneracy at fixed energy \bar{E} . Compare this with

$$S = k \ln \left[(4.41 \times 10^7)^N \right]$$

and we get

$$\Omega = (4.41 \times 10^7)^N$$

which makes sense since it should be large because N is on the order of 10^{23} .

Problem 5-9

What is the DeBroglie wavelength of Ar at 298K?

$$\Lambda = \left(\frac{h^2}{2\pi mkT} \right)^{\frac{1}{2}}$$

Use:

$$\begin{aligned} m &= 6.634 \times 10^{-26} \text{ kg} \\ k &= 1.3807 \times 10^{-27} \frac{\text{J}}{\text{K}} \\ h &= 6.6262 \times 10^{-34} \text{ J} \cdot \text{s} \end{aligned}$$

and we get $\Lambda = 1.6 \times 10^{-11} \text{ m}$

- Now compare this with the inter-atomic distance

The volume per Ar atom is

$$\frac{V}{N} = \frac{kT}{p}$$

with $p = 1.013 \times 10^5 \text{ Pa}$. So $\frac{V}{N} = 4.06 \times 10^{-26} \text{ m}^3$. The interatomic distance $\sim \left(\frac{V}{N}\right)^{\frac{1}{3}} = 3.0 \times 10^{-9} \gg \Lambda$
(See page 83 on the relevance of this result.)

Problem Set 5
Additional Problems Solutions
3.20 MIT
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Problem 1

(a) A system of N non-interacting particles with two possible states either 0 or ε . A good rule is to assume "particles" (e.g. atoms, electrons, etc) are indistinguishable unless they are localized in a crystal or on a surface. The number of atoms in the excited state can be determined using Boltzmann statistics under the assumption that we are working at high temperature and/or low density::

$$N_\varepsilon = N\pi_\varepsilon$$

where π_ε is the probability an atom will be in state ε . This probability is determined using the single particle partition function and can be written as

$$\pi_\varepsilon = \frac{\exp\left[\frac{-\varepsilon}{kT}\right]}{\sum_i \exp\left[\frac{-\varepsilon_i}{kT}\right]} \quad (\text{McQuarrie 4-14})$$

But our system can be in only two states, so the sum in the denominator can be found explicitly:

$$\pi_\varepsilon = \frac{\exp\left[\frac{-\varepsilon}{kT}\right]}{\exp[0] + \exp\left[\frac{-\varepsilon}{kT}\right]}$$

So N_ε can be written as

$$N_\varepsilon = N\pi_\varepsilon = N \frac{\exp\left[\frac{-\varepsilon}{kT}\right]}{1 + \exp\left[\frac{-\varepsilon}{kT}\right]} = \frac{N}{1 + \exp\left[\frac{\varepsilon}{kT}\right]}$$

$$N_\varepsilon = \frac{N}{1 + \exp\left[\frac{\varepsilon}{kT}\right]}$$

(b) The total energy is simply $U = N\bar{\varepsilon} = N \sum_i \pi_i \varepsilon_i$ (McQuarrie 4-12 and 4-13)

$$U = N \sum_i \pi_i \varepsilon_i = N (\pi_1 \varepsilon_1 + \pi_2 \varepsilon_2) = N [(1 - \pi_2) \cdot 0 + \pi_2 \cdot \varepsilon]$$

$$U = N (\pi_2 \varepsilon) = N \left(\frac{\exp\left[\frac{-\varepsilon}{kT}\right]}{1 + \exp\left[\frac{-\varepsilon}{kT}\right]} \right) \varepsilon$$

$$U = \frac{N\varepsilon}{1 + \exp\left[\frac{\varepsilon}{kT}\right]}$$

Note: Since many particles will occupy the same state (either 0 or ε) these particles must be Bosons. At lower temperatures we would have to use Bose-Einstein statistics (McQuarrie 4-26) which would lead to a much more complicated problem since we would have to determine the chemical potential μ .

Problem 2

The magnetization is given as

$$M = \sum_{i=1}^N n_i \mu_o$$

•This is basically saying that we have atoms localized in a crystal and the magnetic moment at each site can be either up or down. The problem asks us to determine the thermodynamic properties as a function of T, N, H . Let us also assume for simplicity that we can work at constant volume. Therefore, our controlling variables are T, N, V, H .

•We need to make the appropriate Legendre transform to the entropy. Remember the entropy can be written starting from E :

$$E = TS - pV + HM + \mu N$$

rearranging to get things in terms of S and β we get

$$\frac{S}{k} = \beta E + \beta pV - \beta HM - \beta \mu N$$

Legendre transform such that our controlling variables are V, N, T, H

$$\frac{S}{k} - \beta E + \beta HM = \beta(TS - E + HM) = -\beta\psi = \ln \Gamma$$

where ψ is the characteristic potential for this ensemble with V, N, T, H constant and Γ is the partition function. Γ can be written as

$$\Gamma = \sum_{states} \exp[-\beta(E_{state} - M_{state}H)]$$

where we sum over all possible energy states and magnetizations M_{state} .

•Since the particles are non-interacting, the energy at $N, \beta = \text{constant}$ and $H = 0$ is constant. E is independent of the number or arrangement of up versus down spins. Since the absolute scale of energy is not important for thermodynamics, we can arbitrarily set the constant energy equal to zero giving us

$$\begin{aligned} \Gamma &= \sum_{states} \exp[\beta M_{state}H] = \sum_{n_1, n_2, \dots, n_N} \exp\left[\beta \sum_{i=1}^N n_i \mu_o H\right] = \sum_{n_1, n_2, \dots, n_N} \prod_{i=1}^N \exp[\beta n_i \mu_o H] \\ \Gamma &= \sum_{n_1, n_2, \dots, n_N} \prod_{i=1}^N \exp[\beta n_i \mu_o H] = \prod_{i=1}^N \sum_{n_i=-1}^{+1} \exp[\beta n_i \mu_o H] \end{aligned}$$

We can evaluate the sum since $n_i = \pm 1$ so,

$$\Gamma = (\exp[\beta \mu_o H] + \exp[-\beta \mu_o H])^N$$

We know the characteristic potential of an ensemble is related to the partition function for that ensemble according to

$$-\beta\psi = \ln \Gamma \rightarrow \psi = -kT \ln \Gamma$$

Furthermore, we know from thermo that

$$d\psi = -SdT - pdV + \mu dN - MdH$$

which gives us the following relationships for the properties of the system:

$$\begin{aligned} S &= -\left(\frac{\partial \psi}{\partial T}\right)_{V, N, H} \\ M &= -\left(\frac{\partial \psi}{\partial H}\right)_{V, N, T} \end{aligned}$$

$$\mu = \left(\frac{\partial \psi}{\partial N} \right)_{V,T,H}$$

$$p = - \left(\frac{\partial \psi}{\partial V} \right)_{T,N,H}$$

and from stat mech we have from above

$$\psi = -kTN \ln [\exp [\beta\mu_o H] + \exp [-\beta\mu_o H]]$$

• Lets get the entropy, S

$$S = - \left(\frac{\partial \psi}{\partial T} \right)_{V,N,H}$$

$$S = kN \ln (\exp [\beta\mu_o H] + \exp [-\beta\mu_o H]) + kTN \frac{\left(-\frac{\mu_o H}{kT^2} \right) (\exp [\beta\mu_o H] - \exp [-\beta\mu_o H])}{\exp [\beta\mu_o H] + \exp [-\beta\mu_o H]}$$

$$\boxed{S = kN \{ \ln (\exp [\beta\mu_o H] + \exp [-\beta\mu_o H]) - \beta\mu_o \tanh (\beta\mu_o H) \}}$$

• Now for the magnetization

$$M = - \left(\frac{\partial \psi}{\partial H} \right)_{V,N,T} = kTN\beta\mu_o \left\{ \frac{\exp [\beta\mu_o H] - \exp [-\beta\mu_o H]}{\exp [\beta\mu_o H] + \exp [-\beta\mu_o H]} \right\} = N\mu_o \tanh (\beta\mu_o H)$$

$$\boxed{M = N\mu_o \tanh (\beta\mu_o H)}$$

• The energy E

$$\psi = E - TS - HM$$

$$E = \psi + TS + HM = 0$$

• However if you define a quantity called the internal magnetic energy (which is a quantity analogous to the enthalpy in the T, p, N ensemble)

$$E_H = E - HM$$

you can get

$$E_H = -N\mu_o H \tanh (\beta\mu_o H)$$

• The last part of this problem asks you to determine the behavior of the energy and entropy as $T \rightarrow 0$.

$$E_H (T \rightarrow 0) = -N\mu_o H$$

$$\lim_{\beta \rightarrow \infty} S = \lim_{\beta \rightarrow \infty} kN \{ \ln (\exp [\beta\mu_o H] + \exp [-\beta\mu_o H]) - \beta\mu_o \tanh (\beta\mu_o H) \} = 0$$

$S(T \rightarrow 0) = 0$ is in accordance with the third law of thermodynamics.

Problem 3

(a)

$$M = \sum_{i=1}^N \mu_o n_i$$

(see solution to Problem 2 - Method 1)

$$M = - \left(\frac{\partial \psi}{\partial H} \right)_{V,N,T} = kTN\beta\mu_o \left\{ \frac{\exp [\beta\mu_o H] - \exp [-\beta\mu_o H]}{\exp [\beta\mu_o H] + \exp [-\beta\mu_o H]} \right\} = N\mu_o \tanh (\beta\mu_o H)$$

$$\boxed{M = N\mu_o \tanh (\beta\mu_o H)}$$

(b) The partition function for the N, V, H, T fixed ensemble is

$$\Gamma = \sum_s \exp[-\beta(E_s - M_s H)]$$

where $s = \text{states}$

We want to determine the fluctuations in the extensive quantity M . Use the 3-step procedure developed in class.

Step 1: Multiply both sides by the partition function

$$\overline{M}\Gamma = \sum_{\text{states}} M_s \exp[-\beta(E_s - M_s H)]$$

Because E_s is always constant (see comment in Problem 2) we can therefore arbitrarily set it to zero and write

$$\overline{M}\Gamma = \sum_{n_1, n_2, \dots, n_N} \left(\sum_{i=1}^N \mu_o n_i \right) \left(\exp \left[\beta \mu_o H \left(\sum_{i=1}^N n_i \right) \right] \right)$$

Step 2: Get derivative with respect to mechanical variable's conjugate.

$$\begin{aligned} \frac{\partial \overline{M}}{\partial H} \Gamma + \overline{M} \frac{\partial \Gamma}{\partial H} &= \sum_{n_1, n_2, \dots, n_N} \beta \left(\mu_o \sum_{i=1}^N n_i \right)^2 \left(\exp \left[\beta \mu_o H \left(\sum_{i=1}^N n_i \right) \right] \right) \\ \frac{\partial \overline{M}}{\partial H} \Gamma + \overline{M} \left\{ \sum_{n_1, n_2, \dots, n_N} \beta \left(\sum_{i=1}^N \mu_o n_i \right) \left(\exp \left[\beta \mu_o H \left(\sum_{i=1}^N n_i \right) \right] \right) \right\} &= \sum_{n_1, n_2, \dots, n_N} \beta \left(\mu_o \sum_{i=1}^N n_i \right)^2 \left(\exp \left[\beta \mu_o H \left(\sum_{i=1}^N n_i \right) \right] \right) \end{aligned}$$

Step 3: Divide through by the partition function

$$\frac{\partial \overline{M}}{\partial H} + \beta \overline{M}^2 = \beta \overline{M}^2$$

or we can write it like this

$$\langle (\delta M)^2 \rangle = \overline{M^2} - \overline{M}^2 = \frac{1}{\beta} \frac{\partial \overline{M}}{\partial H}$$

with:

$$\left(\frac{\partial \overline{M}}{\partial H} \right)_{\beta, N} = \beta N \mu^2 \{1 - \tanh^2(\beta \mu H)\}$$

(c) As $\beta \rightarrow \infty$, $\tanh(\beta \mu H) \rightarrow 1$. Therefore $\overline{M}_{T \rightarrow 0} = N \mu$ and $\langle (\delta M)^2 \rangle_{T \rightarrow 0} = \mu^2 \{1 - 1\} = 0$. In other words, the ground state with all the spins aligned has no fluctuations.

Problem 4

From the first and second law we have

$$dE = TdS - pdV + HdM + \mu dN$$

$$E = TS - pV - HM + \mu N \quad (\text{Euler Form})$$

We are working with fixed N, T, V, M in this problem. We need to make a Legendre transform because T is a controlling variable instead of E .

$$\frac{S}{k} - \beta E = -\beta F = \ln Q$$

$$Q = \sum_{\text{states}} \exp[-\beta E_{\text{state}}]$$

$$F = -kT \ln Q$$

From the differential form of F , namely

$$dF = -SdT - pdV + HdM + \mu dN$$

we get that

$$H = \left(\frac{\partial F}{\partial M} \right)_{T, V, N}$$

We are working under constant magnetization so

$$M = \mu_o \sum_{i=1}^N n_i = \mu_o (n_+ - n_-)$$

where n_+ = number of up spins and n_- = number of down spins. That means that the sum in the expression of Q must be performed over only those states with fixed M (i.e. fixed n_+ and n_-)

•Also the atoms in the system do not interact, meaning that the energy is independent of the number and arrangement of up/down spins and is therefore constant = E_o .

$$Q = \sum_{\substack{\text{states with} \\ \text{magnetization } M}} \exp[-\beta E_{\text{states}}] = \sum_{\substack{\text{states with} \\ \text{magnetization } M}} \exp[-\beta E_o] = \Omega \exp[-\beta E_o]$$

where Ω is the number of states that are consistent with a magnetization $M = \mu_o (n_+ - n_-)$.

$$\Omega = \frac{N!}{n_+! (N - n_+)!}$$

$$Q = \frac{N!}{n_+! (N - n_+)!} \exp[-\beta E_o]$$

$$F = -kT \ln \left(\frac{N!}{n_+! (N - n_+)!} \exp[-\beta E_o] \right) = E_o - kT \ln \left(\frac{N!}{n_+! (N - n_+)!} \right)$$

using Stirling's approximation,

$$F = E_o - kT \{ (N \ln N - N) - n_+ \ln n_+ + n_+ - (N - n_+) \ln (N - n_+) + (N - n_+) \}$$

but we know from above that

$$M = \mu_o (n_+ - n_-) = \mu_o (2n_+ - N) \implies n_+ = \frac{M + \mu_o N}{2\mu_o}$$

we can substitute this back into our expression for F to get F as a function of M

$$F = E_o - kT \left\{ N \ln N - \left(\frac{M + \mu_o N}{2\mu_o} \right) \ln \left(\frac{M + \mu_o N}{2\mu_o} \right) - \frac{\mu_o N - M}{2\mu_o} \ln \left(\frac{\mu_o N - M}{2\mu_o} \right) \right\}$$

Remembering that $H = \left(\frac{\partial F}{\partial M}\right)_{T,V,N}$

$$H = \left(\frac{\partial F}{\partial M}\right)_{T,V,N} = -kT \left\{ -\frac{1}{2\mu_o} \ln \left(\frac{M + \mu_o N}{2\mu_o} \right) - \frac{1}{2\mu_o} + \frac{1}{2\mu_o} \ln \left(\frac{\mu_o N - M}{2\mu_o} \right) + \frac{1}{2\mu_o} \right\}$$

$$H = \frac{kT}{2\mu_o} \left\{ \ln \left(\frac{M + \mu_o N}{2\mu_o} \right) - \ln \left(\frac{\mu_o N - M}{2\mu_o} \right) \right\}$$

$$2\mu_o \beta H = \ln \left(\frac{M + \mu_o N}{\mu_o N - M} \right)$$

and it is easy to show that $M = \mu_o N \tanh(\mu_o \beta H)$ which is the same result as in the other ensemble of Problems 2 and 3. This is due to the equivalence of ensembles in the thermodynamic limit.

Problem 5

(a) Grand canonical ensemble:

$$\Theta = \sum_{N=0}^{\infty} \underbrace{\sum_j \exp[-\beta E_j]}_{\text{This sum extends over all states with total \# of particles = N}} \exp[\beta \mu N] = \sum_{N=0}^{\infty} Q(N, V, T) \exp[\beta \mu N]$$

This sum extends over all states with total # of particles = N

$$\sum_j \exp[-\beta E_j] = Q(N, V, T) = \frac{q^N}{N!}$$

for a one component gas of non-interacting particles. We can write q in closed form as we have done before as

$$q = \left(\frac{2\pi m k T}{h^2} \right)^{\frac{3}{2}} V$$

So now Θ can be written as:

$$\Theta = \sum_{N=0}^{\infty} \frac{q^N}{N!} \exp[\beta \mu N] = \sum_{N=0}^{\infty} \frac{(q e^{\beta \mu})^N}{N!}$$

But if we let $a = q e^{\beta \mu}$ then we can write this sum in a form for which the solution is known, namely

$$\sum_{N=0}^{\infty} \frac{a^N}{N!} = e^a$$

If we now substitute in for q we can write Θ as

$$\Theta = e^{zV} \quad \text{with} \quad z = \frac{e^{\beta \mu}}{h^2} \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}}$$

(b) The characteristic potential for the grand canonical ensemble is

$$-pV = \phi = -kT \ln \Theta$$

$$\phi = E - TS - \mu N$$

$$d\phi = -SdT - pdV - Nd\mu$$

$$p = - \left(\frac{\partial \phi}{\partial V} \right)_{T, \mu} = kT \left(\frac{\partial (zV)}{\partial V} \right) = kTz$$

$$N = - \left(\frac{\partial \phi}{\partial \mu} \right)_{T, V} = kT \left(\frac{\partial z}{\partial \mu} \right) V = zV$$

putting those two parts together and eliminating z gives us the familiar ideal gas equation $p = \frac{kTN}{V}$.

(c)

$$\sqrt{\frac{(\delta \rho)^2}{\rho^2}} = \sqrt{\frac{(\delta N)^2}{N^2}} \quad (\text{because } V \text{ fixed})$$

We need to get $\overline{(\delta N)^2} = \overline{N^2} - \overline{N}^2$. Follow the 3-step procedure.

Step 1: Multiply both sides by the partition function

$$\overline{N}\Theta = \Theta = \sum_{N=0}^{\infty} N \frac{q^N}{N!} e^{\beta \mu N}$$

$$\overline{N} \sum_{N=0}^{\infty} \frac{q^N}{N!} e^{\beta \mu N} = \sum_{N=0}^{\infty} N \frac{q^N}{N!} e^{\beta \mu N}$$

Step 2: Get derivative with respect to mechanical variable's conjugate.

$$\left(\frac{\partial \overline{N}}{\partial \mu} \right) \Theta + \overline{N} \left(\sum_{N=0}^{\infty} \beta N \frac{q^N}{N!} e^{\beta \mu N} \right) = \sum_{N=0}^{\infty} \beta N^2 \frac{q^N}{N!} e^{\beta \mu N}$$

$$\left(\frac{\partial \overline{N}}{\partial \mu} \right) \Theta + \beta \overline{N} \cdot \overline{N}\Theta = \beta \overline{N^2} \Theta$$

Step 3: Divide through by the partition function

$$\left(\frac{\partial \overline{N}}{\partial \mu} \right) + \beta \overline{N}^2 = \beta \overline{N^2}$$

$$\overline{N^2} - \overline{N}^2 = kT \left(\frac{\partial \overline{N}}{\partial \mu} \right)$$

from (b) we have that $\overline{N} = zV$ with $z = \frac{e^{\beta \epsilon}}{h^2} \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}}$.

$$\left(\frac{\partial \overline{N}}{\partial \mu} \right) = \left(\frac{\partial z}{\partial \mu} \right) V = \beta z V$$

$$\overline{N^2} - \overline{N}^2 = zV$$

divide by V to get the densities

$$\overline{\rho^2} - \overline{\rho}^2 = \frac{z}{V} = \frac{\overline{N}}{V^2}$$

$$\frac{\overline{\rho^2} - \overline{\rho}^2}{\overline{\rho}^2} = \frac{\overline{N}}{N^2}$$

$$\frac{\sqrt{\overline{\rho^2} - \overline{\rho}^2}}{\overline{\rho}} = \frac{1}{\sqrt{N}} = \sqrt{\frac{kT}{pV}}$$

(d) To second order in δN

$$\ln P(N) = \ln P(\bar{N}) + \frac{1}{2} (\delta N)^2 \left(\frac{\partial^2 \ln P(N)}{\partial N^2} \right)_{N=\bar{N}}$$

assuming a Gaussian distribution around \bar{N} with variance $(\delta N)^2$ we get

$$\frac{P(N)}{P(\bar{N})} = \exp \left[\frac{-10^{-12} \cdot \bar{N}}{2} \right] = e^{-10^7} \quad \text{which is very unlikely.}$$