Problem 1

\[ dE = TdS - pdV + Fdl + \mu dN \]
\[ E = TS - pV + Fl + \mu N \]

But we are told that we are working under a vacuum so \( p = 0 \).

(a) What is the characteristic potential (\( \phi \))?

Our controlling variables are \( T, F, N \) so

\[ \phi = E - TS - Fl \]

or

\[ d\phi = -SdT - ldF + \mu dN \]

Or in terms of a Legendre transform of the entropy:

\[ -\beta \phi = \frac{S}{k} - \beta E + \beta Fl \]

(b) What is the partition function (\( \Lambda \)) for this ensemble?

\[ \Lambda = \sum_j \exp \left[ -\beta E_j + \beta Fl_j \right] \]

and

\[ -\beta \phi = \ln \Lambda \quad \text{or} \quad \phi = -kT \ln \Lambda \]

(c) Write the thermodynamic variables \( l, S, \mu \) and \( E \) as a function of the partition function.

We can start with the equations of state we get from \( \phi \)

\[ l = -\left( \frac{\partial \phi}{\partial F} \right)_{T,N} = kT \left( \frac{\partial \ln \Lambda}{\partial F} \right)_{T,N} \]
\[ S = -\left( \frac{\partial \phi}{\partial T} \right)_{F,N} = k \ln \Lambda + kT \ln \left( \frac{\partial \ln \Lambda}{\partial T} \right)_{F,N} \]
\[ \mu = \left( \frac{\partial \phi}{\partial N} \right)_{T,F} = -kT \left( \frac{\partial \ln \Lambda}{\partial N} \right)_{T,F} \]

and for \( E \) we can do the following

\[ E = \phi + TS + Fl \]
\[ E = -kT \ln \Lambda + kT \ln \Lambda + kT^2 \left( \frac{\partial \ln \Lambda}{\partial T} \right)_{F,N} + kTF \left( \frac{\partial \ln \Lambda}{\partial F} \right)_{T,N} \]
\[ E = kT^2 \left( \frac{\partial \ln \Lambda}{\partial T} \right)_{F,N} + FkT \left( \frac{\partial \ln \Lambda}{\partial F} \right)_{T,N} \]
Problem 2

(a) What is \( \frac{V^2 - \bar{V}^2}{\bar{V}^2} \) at constant \( T, P, N \)?

We are in the isothermal-isobaric ensemble and the partition function is

\[
\Delta = \sum_j \exp \left[ -\frac{E_j}{kT} \right] \exp \left[ -\frac{pV_j}{kT} \right]
\]

Follow the three step procedure:

**Step 1:** Multiply both sides by the partition function

\[
\Delta \bar{V} = \sum_j V_j \exp \left[ -\frac{E_j}{kT} \right] \exp \left[ -\frac{pV_j}{kT} \right]
\]

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

\[
\Delta \frac{\partial \bar{V}}{\partial p} + \bar{V} \frac{\partial \Delta}{\partial p} = \frac{\partial}{\partial p} \left( \sum_j V_j \exp \left[ -\frac{E_j}{kT} \right] \exp \left[ -\frac{pV_j}{kT} \right] \right)
\]

\[
\Delta \frac{\partial \bar{V}}{\partial p} + \bar{V} \left\{ \sum_j \left( -\frac{V_j}{kT} \right) \exp \left[ -\frac{E_j}{kT} \right] \exp \left[ -\frac{pV_j}{kT} \right] \right\} = \sum_j \left( -\frac{V_j^2}{kT} \right) \exp \left[ -\frac{E_j}{kT} \right] \exp \left[ -\frac{pV_j}{kT} \right]
\]

**Step 3:** Divide through by the partition function

\[
\frac{\partial \bar{V}}{\partial p} + \left( \frac{\bar{V}}{kT} \right) \left( \frac{\partial \bar{V}}{\partial p} \right) = -\frac{\bar{V}^2}{kT}
\]

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

\[
\frac{\bar{V}^2 - \bar{V}^2}{\bar{V}^2} = -\frac{kT}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial p} \right) = kT \frac{\bar{V}}{\bar{V}} \kappa
\]

where \( \kappa = -\frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial p} \right) = \text{compressibility} \).

(b) Evaluate this relationship for an ideal gas.

\[
pV = NkT
\]

\[
\kappa = -\frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial p} \right) = \left( -\frac{1}{\bar{V}} \right) \left( -\frac{NkT}{p^2} \right) = \frac{1}{p}
\]

\[
\frac{\bar{V}^2 - \bar{V}^2}{\bar{V}^2} = \frac{kT}{\bar{V}} \left( \frac{1}{p} \right) = \frac{1}{N}
\]

This is a general result for the fluctuation of an extensive variable for an ideal gas. It means the fluctuations are small when \( N \) is large.

(c) When can the volume fluctuations become large?

Near a critical point where \( \kappa = -\frac{1}{\bar{V}} \left( \frac{\partial \bar{V}}{\partial p} \right) \to \infty \).
Problem 3

(a) The degeneracy

\[
\Omega = \frac{M!}{N!(M-N)!}\]

which is the number of ways to distribute \(N\) particles and \((M - N)\) vacancies over \(M\) surface sites.

(b) \(N, V, T\) constant mean the canonical ensemble

\[
Q = \sum_j e^{-\beta E_j} = \sum E \Omega(E) e^{-\beta E}
\]

\(E = -N \varepsilon\) which depends only on \(N\) and not the particular arrangement of the atoms. But since \(N\) is fixed, there is only one energy level.

\[
Q = \frac{M!}{N!(M-N)!} e^{\beta N \varepsilon}
\]

(c) Obtain an expression for the chemical potential of the argon atoms on the surface

\[
\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}
\]

\[
F = -kT \ln Q = -kT \left\{ \ln \left( \frac{\frac{M!}{N!(M-N)!}}{\varepsilon} \right) + \beta N \varepsilon \right\}
\]

\[
F = -kT \left\{ \ln (M!) - N \ln N + N - (M - N) \ln (M - N) + (M - N) \right\} - N \varepsilon
\]

\[
\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -kT \left\{ - \ln N + 1 + \ln (M - N) + 1 - 1 \right\} - \varepsilon
\]

if we let \(x = \frac{N}{M}\) we get

\[
\mu = -\varepsilon + kT \ln \left( \frac{N}{M-N} \right) = -\varepsilon + kT \ln \left( \frac{x}{1-x} \right)
\]

Problem 4

(a) We assumed:

- Boltzmann statistics
- non-interacting particles
- gas particles are indistinguishable
- mono-atomic particles, in which electronic & nuclear excitations are neglected

(b) \(\mu = 0\)

(c) Yes for both Fermions and Bosons but at high \(T\), low density, high mass.

(d) \(P_{AB}\) for a totally random solution is equal to \(2x_A x_B = 0.5\). Hence, a value of \(P_{AB} = 0.25\) represents short-range clustering. This restriction on the number of microstates reduces the entropy. To increase \(S\) we need to increase \(P_{AB}\) towards 0.5.
### Problem 5

<table>
<thead>
<tr>
<th></th>
<th>$S_{\text{tot}}$</th>
<th>$S_{\text{tot}}/2N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>$k \ln 1$ or $k \ln 2$</td>
<td>0</td>
</tr>
<tr>
<td>(b)</td>
<td>$k \ln N$ (N ways to insert atom)</td>
<td>0</td>
</tr>
<tr>
<td>(c)</td>
<td>$-Nk \begin{pmatrix} 0.01 \ln 0.01 + 0.99 \ln 0.99 \ -0.056 \end{pmatrix}$</td>
<td>$-\frac{1}{2}k [0.01 \ln 0.01 + 0.99 \ln 0.99]$</td>
</tr>
<tr>
<td>(d)</td>
<td>There are $\frac{4 \times 2N}{2}$ number of pairs, each can be exchanged $\rightarrow k \ln 4N$</td>
<td>0</td>
</tr>
</tbody>
</table>