1 Systems with Variable Number of Particles

a Employing the fact that energy per particle can depend only on intensive variables $s = S/N$ and $v = V/N$, prove that the chemical potential coincides with the Gibbs thermodynamic potential per particle.

We know that
\[
dG = V dp - SdT + \mu dN
\]
\[
= (\frac{\partial G}{\partial p})_{T,N} dp + (\frac{\partial G}{\partial T})_{p,N} dT + (\frac{\partial G}{\partial N})_{p,T} dN
\]
Therefore, a purely mathematical relation tells us that
\[
(\frac{\partial G}{\partial N})_{p,T} = \mu
\]
Writing $G$ in terms of intensive variables:
\[
dG = N v dp - N s dT + \mu dN
\]
we know that thermodynamic quantities are homogenous of degree one in extensive variables, meaning that
\[
G(N, T, p) = N f(T,p)
\]
where $f(T,p)$ is only intensive and not dependent on $N$. Taking a derivative of this relation yields that
\[
(\frac{\partial G}{\partial N})_{p,T} = f(T,p)
\]
And we just saw that
\[
(\frac{\partial G}{\partial N})_{p,T} = \mu
\]
where of course the chemical potential $\mu$ is purely intensive, and thus comparing the two relations we see that
\[
f(T,p) = \mu
\]
and thus
\[
G(N, T, p) = N f(T,p) = \mu \rightarrow \text{QED}
\]

b The density of particles $n = N/V$ as an intensive value is a function of only intensive variables $p$ and $T$. Employ this fact to prove \[
(\frac{\partial N}{\partial \mu})_{T,V} = -n^2 (\frac{\partial V}{\partial p})_{T,N}.
\]
We just found that $G = \mu N$, so we can write $dG = Nd\mu + \mu dN$ and equate this with our other total differential expression for $G$: $dG = Nd\mu + \mu dN = \mu dN - SdT + Vdp \rightarrow Nd\mu = -SdT + Vdp$. And if we hold temperature fixed,
we see that $N d\mu = V dp$ or equivalently, $\left(\frac{\partial \mu}{\partial p}\right)_T = \frac{V}{N} = \frac{1}{n}$. We can use this relation to help solve our problem.

We want to prove that:

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

$$\frac{1}{n} \left(\frac{\partial N}{\partial \mu}\right)_{T,V} = -\frac{1}{1/n} \left(\frac{\partial V}{\partial p}\right)_{T,N}$$

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

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

$$\left(\frac{\partial \mu}{\partial p}\right)_T \left(\frac{\partial (N,V)}{\partial (p,V)}\right)_T = -\left(\frac{\partial \mu}{\partial p}\right)_T \left(\frac{\partial (V,N)}{\partial (p,V)}\right)_T$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T \left(\frac{\partial (N,V)}{\partial (\mu,N)}\right)_T = 1$$

$$\left(\frac{\partial \mu}{\partial p}\right)_T \left(\frac{\partial N}{\partial V}\right)_p - \left(\frac{\partial \mu}{\partial p}\right)_T \left(\frac{\partial N}{\partial V}\right)_p \left(\frac{\partial \mu}{\partial p}\right)_T \left(\frac{\partial V}{\partial p}\right)_V \right)_T = 1$$

Now $\mu$ is intensive so it cannot depend on any extensive variables, and thus $\frac{\partial \mu}{\partial p} = 0$. We already found an expression for $\left(\frac{\partial \mu}{\partial p}\right)_T$, and we use the definition $N = V n$ to get that $\left(\frac{\partial N}{\partial p}\right)_V = n$, and plugging these in we get that:

$$\left(\frac{1}{n} n - 0\right) = 1$$

$$1 = 1$$

therefore we proved what we set out to.

2 Adiabatic Process in an ideal gas.

a A gas of helium atoms expands adiabatically and its volume increases by a factor of 10. Assuming an ideal gas, how do the temperature, pressure, and entropy change?

For adiabatic processes, heat remains constant, which in turn also means that entropy is unchanged. Thus, $S_2 = S_1$ and therefore $\Delta S = 0$. The equation describing this process is $pV^\gamma = c$, where $c$ is a constant, and so

$$p_1 V_1^\gamma = p_2 V_2^\gamma$$

and we know that $V_2 = 10 V_1$ and so

$$p_2 = p_1 \frac{V_1^\gamma}{10^\gamma V_1^\gamma} \rightarrow p_2 = p_1 \frac{1}{10^\gamma}$$

and thus

$$\Delta p = p_1 (10^{-\gamma} - 1)$$

All that’s left is finding the change in temperature. For this we use the ideal gas equation of state at both initial and final states.

$$p_1 V_1 = N_1 T_1 \quad p_2 V_2 = N_2 T_2$$

$$N_1 = \frac{p_1 V_1}{T_1} \quad N_2 = \frac{p_2 V_2}{T_2}$$
But in this system the number of particles remains constant, \( N_1 = N_2 \), therefore

\[
\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}
\]

and writing everything in terms of \( T_2, T_1, p_1, \) and \( V_1 \):

\[
T_2 = \frac{p_2 V_2 T_1}{p_1 V_1} = \frac{p_1 V_1}{p_1 V_1} 10 V_1 T_1 = 10^{1-\gamma} T_1, \quad \text{and thus}\]

\[
\Delta T = T_1 (10^{1-\gamma} - 1)
\]

This is true for both Helium and Hydrogen molecules, except the factor \( \gamma \) is changed between the two. For Helium, a monatomic gas, we have \( \gamma = \frac{5}{3} \) and our final results are

\[
\Delta S = 0 \\
\Delta p = p_1 (10^{-5/3} - 1) \\
\Delta T = T_1 (10^{-2/3} - 1)
\]

b Answer the same question, but for hydrogen molecules instead of helium.

Therefore, for hydrogen molecules, where we have more degrees of freedom (the molecule can rotate (and at high energies it can vibrate )), we have that \( \gamma = \frac{7}{5} \) and our final results are

\[
\Delta S = 0 \\
\Delta p = p_1 (10^{-7/5} - 1) \\
\Delta T = T_1 (10^{-2/5} - 1)
\]

c Find the adiabatic coefficient of thermal expansion \( \alpha_S = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_S \) for an ideal gas in terms of \( V \) and \( T \). What happens with the temperature during adiabatic expansion?

For adiabatic processes, we know that \( TV\gamma^{-1} = c \), where \( c \) is a constant, or rewriting it \( V = c^{-1/(1-\gamma)} T^{1/(1-\gamma)} \). So

\[
\left( \frac{\partial V}{\partial T} \right)_S = c^{-1/(1-\gamma)} \frac{1}{1-\gamma} T^{1/(1-\gamma)-1}
\]
So,

\[ \alpha_S = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_S \]
\[ = \frac{c^{-1/(1-\gamma)}}{V(1 - \gamma)} T^{\gamma/(1-\gamma)} \]
\[ = \frac{c^{-1/(1-\gamma)}}{V(1 - \gamma)^{1/\gamma}} T^{\gamma/(1-\gamma)} \]
\[ = \frac{T^{-\gamma} (1 - \gamma)^{1/\gamma}}{(1 - \gamma)^{1 - \gamma/(1-\gamma)}} \]
\[ = \frac{T^{-\gamma}}{(1 - \gamma)} \]

\[ \alpha_S = \frac{1}{T(1 - \gamma)} \]

3 The Joule-Thomson Effect

a Find the change of temperature, entropy and volume when \( N \) molecules of an ideal gas from a chamber with temperature \( T_1 \) under pressure \( p_1 \) penetrates through a porous tube into another chamber with controllable pressure \( p_2 < p_1 \). Assume that \( c_p \) doesn’t depend on temperature.

Landau and Lifshitz’s treatment of this topic yields formulas that help us solve the problem. Specifically,

\[ \left( \frac{\partial T}{\partial p} \right)_W = \frac{1}{c_p} \left( T \left( \frac{\partial V}{\partial T} \right)_p - V \right) \]

and

\[ \left( \frac{\partial S}{\partial p} \right)_W = -\frac{V}{T} \]

For an ideal gas, \( pV = NT \). So:

\[ \left( \frac{\partial T}{\partial p} \right)_W = \frac{1}{c_p} \left( T \left( \frac{N}{p} - \frac{NT}{p} \right) \right) \]

\[ = 0 \], and integrating

\[ \Delta T = T_2 - T_1 = 0 \]

We see that the throttling process of an ideal gas is an isothermal process interestingly enough, since the point of this process is to cool gases.

Then,

\[ \left( \frac{\partial S}{\partial p} \right)_W = -\frac{N}{p} \], and integrating

\[ \Delta S = S_2 - S_1 = -N \ln \left( \frac{p_2}{p_1} \right) \]

\[ \Delta S = N \ln \left( \frac{p_1}{p_2} \right) \]

and we indeed can validate the entropy is increasing in this process! (I note that an equivalent way of finding the change in entropy would be to integrate dE/T, where because it’s isothermal dE is given by the work which can be written as pdV).

And then simply the change in volume is given by:

\[ \Delta V = V_2 - V_1 \]

\[ \Delta V = V_1 \left( \frac{p_1}{p_2} - 1 \right) \]
because T is constant and so is N, so from the ideal gas equation of state, \( pV = c \) with c a constant, and so \( p_1V_1 = p_2V_2 \)

b How does the answer change if the gas is slightly non-ideal? The energy of slightly non-ideal gas is \( E = Nc_vT + \frac{gN^2}{2V} \) with g the strength of interaction between particles. \( g > 0 \) corresponds to repulsion, \( g < 0 \) corresponds to attraction. Assume that the interaction is weak, i.e. \( |g|n \ll T \).

The difference here is we need to substitute in a different equation of state for the volume. The equation of state is given by:

\[
p = \frac{NT}{V} \left(1 - \frac{gN}{2V}\right)
\]

We can calculate the change in entropy using

\[
\Delta S = \int \frac{dE}{T} = \int \frac{pdV}{T} = \int \frac{N}{V} \left(1 - \frac{gN}{2V}\right) dV
\]

\[
\Delta S = N \ln \left(\frac{V_2}{V_1}\right) + \frac{gN^2}{2} \left(\frac{1}{V_2} - \frac{1}{V_1}\right)
\]

4 The ideal gas with a variable number of particles

a Find the chemical potential of the ideal gas as a function of pairs of variables \((p, T), (v, T), (T, s), \text{ and } (p, s)\).

For an ideal gas, \( pv = T \). We can use this to switch between these three variables in our final result.

\[
\mu = \frac{G}{N} = \frac{E + pV - ST}{N} = \frac{H - ST}{N} = \frac{F + pV}{N}
\]

To get these quantities, we start with the partition function, which for an ideal gas is given by:

\[
Z = \left(\frac{\gamma VT^3}{2}\right)^N / N!,
\]

with \( \gamma \) a multiplicative factor containing all the rest of the constants. Using Sterling’s approximation:

\[
\ln(Z) = N\zeta + N \ln(VT^{3/2}) - \ln(N!) \approx N\zeta + N \ln(VT^{3/2}) - N \ln(N) + N = N \left(\zeta + 1 - \ln(N) + \ln(VT^{3/2})\right)
\]

and to get this in terms of intensive parameters, we simply write:

\[
\ln(Z) = N \left(\zeta + 1 - \ln\left(\frac{V}{N}\right) + \frac{3}{2} \ln(T)\right) = N \left(\zeta + 1 + \ln(v) + \frac{3}{2} \ln(T)\right)
\]

And then we can find \( F \):

\[
F = -T \ln(Z) = -NT \left(\zeta + 1 + \ln(v) + \frac{3}{2} \ln(T)\right)
\]

And also we will need a relation for entropy, so we find

\[
S = Ns = -\frac{\partial F}{\partial T} = N(\zeta + 1 + \ln(v) + \frac{3}{2}(1 + \ln(T))) \rightarrow s = \zeta + \frac{5}{2} + \ln(v) + \frac{3}{2} \ln(T)
\]

And another relation with entropy which will be useful for us later is

\[
s = \zeta + \frac{5}{2} + \ln(T/p) + \frac{3}{2} \ln(T) = \zeta + \frac{5}{2} + \ln(T) - \ln(p) + \frac{3}{2} \ln(T) = \zeta + \frac{5}{2} - \ln(p) + \frac{5}{2} \ln(T) \rightarrow T = \exp \left(\frac{2}{5} \left(s + \ln(p) - \zeta\right) - 1\right)
\]
or

\[ T = p^2 \exp \left( \frac{2}{5} (s - \zeta) - 1 \right) \]

And so then

\[
\mu = \frac{pV - NT (\zeta + 1 + \ln(v) + \frac{3}{2} \ln(T))}{N}
\]

\[ = pV - T \left( \zeta + 1 + \ln(v) + \frac{3}{2} \ln(T) \right) \]

\[ = -T \left( \zeta + 1 + \ln(v) + \frac{3}{2} \ln(T) \right) \]

\[ = -T \left( \zeta + 3 \ln(T) \right) \]

\[
\mu(v, T) = -T \left( \zeta + \ln(v) + \frac{3}{2} \ln(T) \right)
\]

\[
\mu(p, T) = -T \left( \zeta + \ln \left( \frac{T}{p} \right) + \frac{3}{2} \ln(T) \right)
\]

\[
\mu = -T \left( \zeta + \ln(v) + \frac{3}{2} \ln(T) \right) - \frac{5}{2}
\]

\[
\mu(s, T) = -T \left( s - \frac{5}{2} \right)
\]

\[
\mu(p, s) = - \left( s - \frac{5}{2} \right) p^2 \exp \left( \frac{2}{5} (s - \zeta) - 1 \right)
\]

b Express the potential \( \Omega \) for the ideal gas in terms of its natural variables \( T, V, \mu \).

For a homogenous system,

\[ \Omega = -pV \]

But we know from the last part of the problem that

\[ \mu = -T \left( \zeta + \ln(v) + \frac{3}{2} \ln(T) \right) = -T \left( \zeta + \ln \left( \frac{T}{p} \right) + \frac{3}{2} \ln(T) \right) \]

and solving this for \( p(T, \mu) \) we get that

\[ p(\mu, T) = \exp \left( \frac{\mu}{T} + \frac{5}{2} \ln(T) + \zeta \right) \]

and so we can now easily express \( \Omega \) as a function of \( T, V, \mu \):

\[
\Omega(T, V, \mu) = -V \exp \left( \frac{\mu}{T} + \frac{5}{2} \ln(T) + \zeta \right)
\]