Phys 418 Problem Set #1 Solutions

1) Classical ideal gas

$$S(E,V,N) = \frac{N}{N_0} S_0 + N k_B \ln\left[\left(\frac{E}{E_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right]$$

$S_0,\ E_0,\ V_0,\ N_0$ constants

a) Helmholtz free energy $\quad A = E - TS$

The first step is to invert $S(E)$ to get $E(S)$

$$E = E_0 \left(\frac{V}{V_0}\right)^{-2/3} \left(\frac{N}{N_0}\right)^{5/3} \exp\left[\frac{2}{3}\left(\frac{S}{N} - \frac{S_0}{N_0}\right) / k_B \right]$$

next we find the temperature

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} = \frac{2}{3 N k_B} E \quad \Rightarrow \quad E = \frac{3}{2} N k_B T$$

now substitute this expression for E in terms of T into:

$$A = E - TS$$

$$= \frac{3}{2} N k_B T - T \frac{N}{N_0} S_0 - T N k_B \ln\left[\left(\frac{3 N k_B T}{2 E_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N}{N_0}\right)^{-5/2} \right]$$

$$\boxed{A(T,V,N) = \left(\frac{3}{2} k_B - \frac{S_0}{N_0}\right) N T - N T k_B \ln\left[\left(\frac{3 N_0 k_B T}{2 E_0}\right)^{3/2} \left(\frac{V}{V_0}\right) \left(\frac{N_0}{N}\right) \right]}$$

<u>Gibbs free energy</u> $G = E - TS + pV = A + pV$

The first step is to find the pressure. Use earlier result for A

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = \frac{TNk_B}{V} \Rightarrow \boxed{pV = Nk_B T}$$

this is the familiar equation of state that is asked for in part (b)

$$\Rightarrow V = TNk_B/p$$

Now substitute this expression for V in terms of p into:

$$G = A + pV$$

$$= \left(\frac{3}{2}k_B - \frac{S_0}{N_0}\right)NT - NTk_B \ln\left[\left(\frac{3N_0k_BT}{2E_0}\right)^{3/2}\left(\frac{TNk_B}{pV_0}\right)\left(\frac{N_0}{N}\right)\right] + \overbrace{Nk_BT}^{pV}$$

$$\boxed{G(T,p,N) = \left(\frac{5}{2}k_B - \frac{S_0}{N_0}\right)NT - NTk_B \ln\left[\left(\frac{3N_0k_BT}{2E_0}\right)^{3/2}\left(\frac{TN_0k_B}{pV_0}\right)\right]}$$

<u>Grand Potential</u> $\Phi = E - TS - \mu N = A - \mu N$

The first step is to compute the chemical potential. Use result for A

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = \left(\frac{3}{2}k_B - \frac{S_0}{N_0}\right)T - Tk_B \ln\left[\left(\frac{3N_0k_BT}{2E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N_0}{N}\right)\right]$$

$$+ Tk_B$$

comes from the derivative of the logarithm

$$\mu = \left(\frac{5}{2}k_B - \frac{S_0}{N_0}\right)T - Tk_B \ln\left[\left(\frac{3N_0k_BT}{2E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N_0}{N}\right)\right]$$

Now invert this to find N in terms of μ

$$N = N_0\left(\frac{3N_0k_BT}{2E}\right)^{3/2}\left(\frac{V}{V_0}\right)\exp\left[\frac{\mu}{k_BT} - \frac{5}{2} + \frac{S_0}{N_0k_B}\right]$$

Now substitute this expression for N in terms of μ into

$$\Phi = A - \mu N$$

$$= \left(\frac{3}{2}k_B - \frac{S_0}{N_0}\right)NT - NTk_B \ln\left[\left(\frac{3N_0k_BT}{2E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N_0}{N}\right)\right]$$

$$- \left(\frac{5}{2}k_B - \frac{S_0}{N}\right)TN + NTk_B \ln\left[\left(\frac{3N_0k_BT}{2E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N_0}{N}\right)\right]$$

$$= -Nk_BT$$ substitute in for N

$$\boxed{\Phi(T,V,\mu) = -N_0k_BT\left(\frac{3N_0k_BT}{2E}\right)^{3/2}\left(\frac{V}{V_0}\right)\exp\left[\frac{\mu}{k_BT} - \frac{5}{2} + \frac{S_0}{N_0k_B}\right]}$$

(b) We already found the equation of state $pV = Nk_BT$ in part (a), by taking $p = -\left(\frac{\partial A}{\partial V}\right)_{T,N}$

(c) In part (a) we found

$$G(T,p,N) = N\left\{\frac{5}{2}k_BT - \frac{S_0}{N_0}T - k_BT\ln\left[\left(\frac{3N_0k_BT}{2E_0}\right)^{3/2}\left(\frac{TN_0k_B}{pV_0}\right)\right]\right\}$$

only N dependence is here, as it must be since G is extensive and T and p are intensive variables

$$\Rightarrow \boxed{\mu = \left(\frac{\partial G}{\partial N}\right)_{T,p} = \frac{G}{N}} = \text{Gibbs free energy per particle}$$

(d) In part (a), before the last step in our calculation of Φ, we found

$$\Phi = -Nk_BT$$

combine with equation of state $pV = Nk_BT$

$$\Rightarrow \Phi = -pV \Rightarrow \boxed{p = -\frac{\Phi}{V}}$$ grand potential per unit volume

problem 2

Consider taking the Legendre transform of the energy $E(S, V, N)$ with respect to S, V, and N, to get a new thermodynamic potential $X(T, p, \mu)$.

What can you say about this new potential X? What does X imply about the variables T, p, and μ? Have you seen this before?

The naive answer is as follows: To construct X we take the Legendre transform of E from S to T, from V to p, and from N to μ. This is given by,

$$X = E - TS + pV - \mu N \tag{1}$$

But the Euler relation gives $E = TS - pV + \mu N$. Insert this into the above and you get $X(T, p, \mu) = 0$! What does this mean? It says there is a constraint among the three variables T, p, and μ, such that $X(T, p, \mu)$ is always constrained to be zero. That should remind you of the Gibbs-Duhem relation. And we can then rederive the Gibbs-Duhem relation as follows.

Since $X(T, p, \mu) = 0$, then it must be that $dX = 0$ as we vary the variables T, p, and μ. We therefore have,

$$dX = \left(\frac{\partial X}{\partial T}\right)_{p,\mu} dT + \left(\frac{\partial X}{\partial p}\right)_{T,\mu} dp + \left(\frac{\partial X}{\partial \mu}\right)_{T,p} d\mu = 0 \tag{2}$$

But, by the properties of the Legendre transform, we should have,

$$\left(\frac{\partial X}{\partial T}\right)_{p,\mu} = -S, \qquad \left(\frac{\partial X}{\partial p}\right)_{T,\mu} = V, \qquad \left(\frac{\partial X}{\partial \mu}\right)_{T,p} = -N \tag{3}$$

We then conclude from Eq. (2),

$$dX = \boxed{-SdT + Vdp - Nd\mu = 0} \qquad \text{which is just the Gibbs-Duhem relation.} \tag{4}$$

But upon further reflection, there are some peculiar things about $X(T, p, \mu)$. One can ask, since $X = 0$, does it really exist as a function? From Eqs. (1) and the Euler relation, it would appear that X simply vanishes term by term. Also, since X is a Legendre transform starting from the extensive quantity E, we would expect X to also be extensive. But X depends only on the *intensive* variables T, p, and μ, so how can it provide any information about the overall size of the system as it must if it is extensive?

To address these points, first consider the Legendre transform from E to the Gibbs free energy G. We have for $G(T, p, N)$,

$$G = E - TS + pV \tag{5}$$

From the Euler relation $E = TS - pV + \mu N$ we then get,

$$G = \mu N \qquad \Rightarrow \qquad \mu = \frac{G}{N} = g(T, p) \tag{6}$$

where $g(T, p)$ is the Gibbs free energy per particle, and it depends *only* on T and p. It cannot depend on N because μ and hence G/N is *intensive*. We thus have $G(T, p, N) = Ng(T, p)$.

Now we can take the Legendre transform from G to X,

$$X = G - \mu N \tag{7}$$

Now since $G = \mu N$, if we substitute that into the above we again get the result that $X = 0$. But instead we can write this as,

$$X(T,p,\mu) = Ng(T,p) - N\mu = N[g(T,p) - \mu] = 0 \tag{8}$$

Our expression above, however, still has the variable N. To get rid of N, remember what we are suppose to do. We define $\mu(T,p,N) = \left(\frac{\partial G}{\partial N}\right)_{T,p}$, then try to invert that to get $N(T,p,\mu)$ and insert that into

$$X(T,p,\mu) = G(T,p,N(T,p,\mu)) - \mu N(T,p,\mu) \quad \text{to get } X \text{ as a function of only } T,\ p, \text{ and } \mu. \tag{9}$$

But since $\mu(T,p) = \left(\frac{\partial G}{\partial N}\right)_{T,p} = g(T,p)$ is *independent* of N, there is no way to invert $\mu(T,p,N)$ to get $N(T,p,\mu)$, since μ does not depend on N!

Alternatively, we can define the Legendre transform from G to X as,

$$X(T,p,\mu) = \underset{N}{\text{extremum}}\,[G(T,p,N) - \mu N] = \underset{N}{\text{extremum}}\,[N(g(T,p) - \mu)] \tag{10}$$

But since the function we take the extremum of, $N(g(T,p) - \mu)$, is *linear* in N, there is no real extremal value (except $N = 0$ or $N = \infty$).

So the step of taking the Legendre transform from G to X really fails. This is where we lose the information in X about the extensivity of the system. The Legendre transform of a function is supposed to contain all the same information as the original function. That fails here because we are losing the information contained in N about the extensivity of the system. More generally, Legendre transforms do not work when the function is *linear* in the variable one is transforming on.

Nevertheless, it is still perfectly fine to define the quantity X/N, the X per particle!

$$\frac{X}{N} = g(T,p) - \mu \tag{11}$$

Now $\frac{X}{N}(T,p,\mu)$ depends only on T, p, and μ and is intensive like its arguments.

Also, $\frac{X}{N}(T,p,\mu) = 0$ is the same as $\mu = g(T,p)$ and gives explicitly the constraint among the three variables T, p, and μ.

We can also write,

$$\left(\frac{\partial(X/N)}{\partial T}\right)_{p,\mu} = \left(\frac{\partial g}{\partial T}\right)_p = -s(T,p) \quad \text{and} \quad \left(\frac{\partial(X/N)}{\partial p}\right)_{T,\mu} = \left(\frac{\partial g}{\partial p}\right)_T = v(T,p) \quad \text{and} \quad \left(\frac{\partial(X/N)}{\partial \mu}\right)_{T,p} = -1 \tag{12}$$

where $s = S/N$ and $v = V/N$ are the entropy and volume per particle.

Then we can write,

$$d(X/N) = 0 = \left(\frac{\partial(X/N)}{\partial T}\right)_{p,\mu} dT + \left(\frac{\partial(X/N)}{\partial p}\right)_{T,\mu} dp + \left(\frac{\partial(X/N)}{\partial \mu}\right)_{T,p} d\mu \quad \Rightarrow \quad \boxed{-s dT + v dp - d\mu = 0} \tag{13}$$

This is just the Gibbs-Duhem relation written in terms of intensive quantities!

The original Gibbs-Duhem relation was $-SdT + Vdp - Nd\mu = 0$. Divide each term by N and we get the above.

We could have done the above in a slightly different way.

Suppose we first transform E from S to T and from N to μ to get the Grand Potential,

$$\Phi(T, V, \mu) = E - TS - \mu N \tag{14}$$

From the Euler relation $E = TS - pV + \mu N$ we then get,

$$\Phi = -pV \qquad \Rightarrow \qquad p = -\frac{\Phi}{V} = -\phi(T, \mu) \tag{15}$$

where $\phi(T, \mu)$ is the Grand Potential per volume. This ϕ depends only on T and μ; it cannot depend on V since p and hence Φ/V is *intensive*. We thus have $\Phi(T, V, \mu) = V\phi(T, \mu)$.

We can now take the Legendre transform from Φ to X,

$$X = \Phi + pV = V\phi(T, \mu) + pV = V[\phi(T, \mu) + p] \tag{16}$$

Now since $p = -\Phi/V = -\phi$, we again get $X = 0$. But as we saw before, we cannot really take the Legendre transform from Φ to X because $\Phi(T, V, \mu) = V\phi(T, \mu)$ is linear in the transformation variable V.

But we can define X/V, as the X per volume, and then get,

$$X/V = \phi(T, \mu) + p = 0 \tag{17}$$

which gives the constraint among the three variables T, p, and μ as $p = -\phi(T, \mu)$.

And we could also write,

$$d(X/V) = 0 = \left(\frac{\partial(X/V)}{\partial T}\right)_{p,\mu} dT + \left(\frac{\partial(X/V)}{\partial p}\right)_{T,\mu} dp + \left(\frac{\partial(X/V}{\partial \mu}\right)_{T,p} d\mu \tag{18}$$

$$= \left(\frac{\partial \phi}{\partial T}\right)_{\mu} dT + dp + \left(\frac{\partial \phi}{\partial \mu}\right)_{T} d\mu \tag{19}$$

$$= \frac{1}{V}\left(\frac{\partial \Phi}{\partial T}\right)_{\mu,V} dT + dp + \frac{1}{V}\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} d\mu \tag{20}$$

$$= -\frac{S}{V} dT + dp - \frac{N}{V} d\mu \tag{21}$$

Multiplying each term by V we then get,

$$-SdT + Vdp - Nd\mu = 0 \tag{22}$$

which again is just the Gibbs-Duhem relation!

And, just to be complete, we could also have first transformed E from V to p and from N to μ to get a new potential,

$$\Xi(S, p, \mu) = E + pV - \mu N \tag{23}$$

By the Euler relation $E = TS - pV + \mu N$ we then get,

$$\Xi = TS \qquad \Rightarrow \qquad T = \frac{\Xi}{S} = \xi(p, \mu) \tag{24}$$

where $\xi(p, \mu)$ is the potential Ξ per unit entropy! This ξ depends only on p and μ; it cannot depend on S since T and hence Ξ/S must be an intensive quantity. We thus have $\Xi(S, p, \mu) = S\xi(p, \mu)$.

Now transform from Ξ to X.

$$X = \Xi - TS = S\xi(p, \mu) - TS = S[\xi(p, \mu) - T] \tag{25}$$

Now since $\Xi = TS$, we again get $X = 0$. But, as before, we cannot really take the Legendre transform from Ξ to X because $\Xi(S, p, \mu) = S\xi(p, \mu)$ is linear in the transformation variable S.

But we can define $X/S = \xi(p, \mu) - T = 0$, which then gives the constraint on T, p, and μ as $T = \xi(p, \mu)$.

And we could then write,

$$d(X/S) = 0 = \left(\frac{\partial(X/S)}{\partial T}\right)_{p,\mu} dT + \left(\frac{\partial(X/S)}{\partial p}\right)_{T,\mu} dp + \left(\frac{\partial(X/S)}{\partial \mu}\right)_{T,p} d\mu \tag{26}$$

$$= -dT + \left(\frac{\partial \xi}{\partial p}\right)_{\mu} dp + \left(\frac{\partial xi}{\partial \mu}\right)_{p} d\mu \tag{27}$$

$$= -dT + \frac{1}{S}\left(\frac{\partial \Xi}{\partial p}\right)_{\mu,S} dp + \frac{1}{S}\left(\frac{\partial \Xi}{\partial \mu}\right)_{p,S} d\mu \tag{28}$$

$$= -dT + \frac{V}{S} dp - \frac{N}{S} d\mu \tag{29}$$

Multiply each term by S and we get,

$$-SdT + Vdp - Nd\mu = 0 \tag{30}$$

which again is just the Gibbs-Duhen relation.

To summarize some of the above results, we have,

$$G(T, p, N) = Ng(T, p), \qquad \Phi(T, V, \mu) = V\phi(T, \mu), \qquad \Xi(S, p, \mu) = S\xi(p, \mu) \tag{31}$$

These results lead to some funny conclusions!

Suppose we have a system in contact with a temperature and pressure reservoir, so T, p, and N are fixed. The relevant potential is $G(T, p, N) = Ng(T, p)$. If we now relaxed the constraint holding the number of particles fixed at N, and let N vary as it likes (i.e. we now put the system in contact with a particle reservoir), then the new equilibrium state will be at the value of N that minimizes $G = Ng(T, p)$, i.e. the system goes to $N = 0$. All the particles in the system get absorbed by the particle reservoir!

Suppose we have a system in contact with a temperature and particle reservoir, so T, μ and V are fixed. The relevant potential is $\Phi(T, V, \mu) = V\phi(T, \mu)$. If we now relaxed the constraint holding the volume fixed at V, and let V vary as it likes (i.e. we now put the system in contact with a pressure reservoir), then the new equilibrium state will be at the value of V that minimizes $\Phi = V\phi(T, \mu)$, i.e. the system goes to $V = 0$. All the volume of the system gets absorbed into the pressure reservoir!

Suppose we have a system in contact with a pressure and particle reservoir, so p, μ and S are fixed. The relevant potential is $\Xi(S, p, \mu) = S\xi(p, \mu)$. If we now relaxed the constraint holding the entropy fixed at S, and let S vary as it likes (i.e. we now put the system in contact with a thermal reservoir), then the new equilibrium state will be at the value of S that minimizes $\Xi = S\xi(p, \mu)$, i.e. the system goes to $S = 0$. All the entropy of the system gets absorbed into the thermal reservoir (the system transfers heat to the reservoir until its entropy vanished)!

In each case, as we move to a situation where only the intensive variables of the system are fixed, the system gets totally absorbed by the reservoir it is in contact with! This is perhaps another way to think about the result that $X(T, p, \mu) = 0$.

Let us now reexamine this problem from yet another perspective. Suppose our system has some internal degree of freedom Y that we can control. So now the system is described by $E(S, V, N, Y)$. We can define the variable η

conjugate to Y,

$$\eta(S,V,N,Y) = \left(\frac{\partial E}{\partial Y}\right)_{S,V,N} \tag{32}$$

By arguments similar to how we derived the Euler relation, we can now conclude,

$$E = TS - pV + \mu N + \eta Y \tag{33}$$

We can now transform from S to T, from V to p, and from N to μ, to get

$$X(T,p,\mu,Y) = E - TS + pV - \mu N = \eta Y \tag{34}$$

where

$$\left(\frac{\partial X}{\partial T}\right)_{p,\mu,Y} = -S(T,p,\mu,Y), \quad \left(\frac{\partial X}{\partial p}\right)_{T,\mu,Y} = V(T,p,\mu,Y), \tag{35}$$

$$\left(\frac{\partial X}{\partial \mu}\right)_{T,p,Y} = -N(T,p,\mu,Y), \quad \left(\frac{\partial X}{\partial Y}\right)_{T,p,\mu} = \eta(T,p,\mu,Y) \tag{36}$$

Note, this X does not have any of the problems of our previous X when we did not have the variable Y. This $X(T,p,\mu,Y)$ can be properly extensive since it depends on the extensive variable Y. And this $X = \eta Y \neq 0$.

However, we now note that the quantity $X/Y = \eta$ is the ratio of two extensive quantities and so η must be *intensive*. Since η depends only on T, p, μ, and Y, there is no way to make η intensive unless it does not explicitly depend on Y. So we must have $\eta(T,p,\mu)$ is independent of Y.

[This is similar to when we have $\mu(T,p,N) = (\partial G/\partial N)_{T,p}$. Since μ is intensive, and can depend only on T, p, and N, then it must be independent of N. This is unlike $\mu = (\partial A/\partial N)_{T,V}$. There $\mu(T,V,N)$ can depend on V and N via their ratio $V/N = v$.]

So the conclusion that $\eta(T,p,\mu)$ depends only on T, p, and μ, and *not* on Y, gives a constraint on the four intensive variables T, p, μ and η, i.e. η is a function of the other three. This will give the analog of the Gibbs-Duhen relation, but now involving the new variable η.

Now suppose we relax our constraint on the variable Y, and let it be free to adjust itself. The new equilibrium will be the state in which $X(T,p,\mu,Y) = \eta(T,p,\mu)Y$ is minimized. That will be at $Y = 0$. When $Y = 0$, then $X = \eta Y = 0$, and we return to the situation we started with, $X = 0$.

3) $C_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N}$

We can use $A(T,V,N)$ found in problem set 1

$$A(T,V,N) = \left(\frac{3}{2}k_B - \frac{S_0}{N_0}\right)NT - NTk_B \ln\left[\left(\frac{3N_0 k_B T}{2E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N_0}{N}\right)\right]$$

$$\left(\frac{\partial A}{\partial T}\right)_{V,N} = \left(\frac{3}{2}k_B - \frac{S_0}{N_0}\right)N - Nk_B \ln\left[\left(\frac{3N_0 k_B T}{2E_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{N_0}{N}\right)\right]$$

$$- \frac{3}{2}NTk_B\left(\frac{1}{T}\right) \leftarrow \text{comes from derivative of the logarithm}$$

$$\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} = -\frac{3}{2}Nk_B\left(\frac{1}{T}\right)$$

$$\Rightarrow \boxed{C_V = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{V,N} = \frac{3}{2}Nk_B}$$

$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N}$

We can use $G(T,p,N)$ found in Problem Set 1

$$G(T,p,N) = \left(\frac{5}{2}k_B - \frac{S_0}{N_0}\right)NT - NTk_B \ln\left[\left(\frac{3N_0 k_B T}{2E_0}\right)^{3/2}\left(\frac{TN_0 k_B}{pV_0}\right)\right]$$

$$\left(\frac{\partial G}{\partial T}\right)_{p,N} = \left(\frac{5}{2}k_B - \frac{S_0}{N_0}\right)N - Nk_B \ln\left[\left(\frac{3N_0 k_B T}{2E_0}\right)^{3/2}\left(\frac{TN_0 k_B}{pV_0}\right)\right] - \frac{5}{2}Nk_B T\left(\frac{1}{T}\right)$$

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} = -\frac{5}{2}Nk_B\left(\frac{1}{T}\right)$$

$$\boxed{C_p = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_{p,N} = \frac{5}{2}Nk_B}$$

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N}$$

using $G(T, p, N)$ as before

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = N T k_B \left(\frac{1}{p}\right)$$

$$\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N} = -\frac{N T k_B}{p^2}$$

$$\boxed{\kappa_T = -\frac{1}{V}\left(\frac{\partial^2 G}{\partial p^2}\right)_{T,N} = \frac{N T k_B}{V p^2} = \frac{1}{p}}$$ using $pV = N k_B T$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial p^2}\right)_{S,N}$$

to compute κ_S, we first need to compute $H(S, p, N)$

we need to compute $H = E + pV$

using $E(S, V, N)$ from Problem Set 1

$$E = E_0 \left(\frac{V}{V_0}\right)^{-2/3} \left(\frac{N}{N_0}\right)^{5/3} \exp\left[\frac{2}{3}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)/k_B\right]$$

$$p = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{2}{3}\frac{E}{V} \Rightarrow V = \frac{2}{3}\frac{E}{p}$$

$$H = E + pV = E + \frac{2}{3}p\left(\frac{E}{p}\right) = \frac{5}{3}E$$

we still need to write E as a function of S, p, N

To get that we can use $p(S, V, N) = \frac{2}{3}\frac{E}{V}$

and invert to get $V(S, p, N)$, then substitute

into $E(S, V, N)$.

$$p = \frac{2}{3}\frac{E}{V} = \frac{2}{3} E_0 V^{2/3} V^{-5/3} \left(\frac{N}{N_0}\right)^{5/3} \exp\left[\frac{2}{3}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)/k_B\right]$$

invert

$$V = \left(\frac{2E_0}{3pV_0}\right)^{3/5} V_0 \left(\frac{N}{N_0}\right) \exp\left[\frac{2}{5}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)/k_B\right]$$

Now insert this $V(S,p,N)$ into $E(S,V,N)$ to get

$$H(S,p,N) = \frac{5}{3} E(S, V(S,p,N), N)$$

$$= \frac{5}{3} E_0 \left(\frac{N}{N_0}\right)\left(\frac{2E_0}{3pV_0}\right)^{-2/5} \exp\left[\frac{2}{5}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)/k_B\right]$$

Now we can compute

$$\left(\frac{\partial H}{\partial p}\right)_{S,N} = \frac{2}{5}\frac{H}{p}$$

$$\left(\frac{\partial^2 H}{\partial p^2}\right)_{S,N} = -\frac{2}{5}\frac{H}{p^2} + \frac{2}{5}\frac{1}{p}\left(\frac{\partial H}{\partial p}\right)_{S,N} = -\frac{2}{5}\frac{H}{p^2} + \frac{2}{5}\frac{1}{p}\frac{2}{5}\frac{H}{p}$$

$$= \frac{-6}{25}\frac{H}{p^2}$$

use $V = \frac{2}{3}\frac{E}{p}$ and $H = \frac{5}{3}E$

$$\kappa_S = -\frac{1}{V}\left(\frac{\partial^2 H}{\partial p^2}\right)_{S,N} = \frac{6}{25}\frac{H}{p^2}\frac{1}{V}$$

$$= \frac{6}{25}\frac{1}{p^2}\left(\frac{5}{3}E\right)\left(\frac{3p}{2E}\right) = \frac{3}{5}\frac{1}{p}$$

$$\boxed{\kappa_S = \frac{3}{5p}}$$

We could have done this another way.

Use $E = \frac{3}{2} N k_B T$, $pV = N k_B T \Rightarrow H = E + pV = \frac{5}{2} N k_B T$

we now have to write T in terms of S, p, N to get $H(S, p, N)$

to get that we can use

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,N} = S(T, p, N) \quad \text{and then invert}$$

to get $T(S, p, N)$

Using $G(T, p, N)$ from Problem Set 1. From page 1,

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,N} = -\left(\frac{5}{2} k_B - \frac{S_0}{N_0}\right) N + N k_B \ln\left[\left(\frac{3 N_0 k_B T}{2 E_0}\right)^{3/2} \left(\frac{T N_0 k_B}{p V_0}\right)\right] + \frac{5}{2} N k_B$$

solve for T.

$$\left(\frac{S}{N} - \frac{S_0}{N_0}\right) / k_B = \ln\left[\left(\frac{3 N_0 k_B}{2 E_0}\right)^{3/2} \left(\frac{N_0 k_B}{p V_0}\right) T^{5/2}\right]$$

$$T^{5/2} = \left(\frac{2 E_0}{3 N_0 k_B}\right)^{3/2} \left(\frac{p V_0}{N_0 k_B}\right) e^{\left(\frac{S}{N} - \frac{S_0}{N_0}\right)/k_B}$$

$$T = \left(\frac{2 E_0}{3 N_0 k_B}\right)^{3/5} \left(\frac{p V_0}{N_0 k_B}\right)^{2/5} e^{\frac{2}{5}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)/k_B}$$

$$H = \frac{5}{2} N k_B T = \frac{5}{2} N k_B \left(\frac{2 E_0}{3 N_0 k_B}\right)^{3/5} \left(\frac{p V_0}{N_0 k_B}\right)^{2/5} e^{\frac{2}{5}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)/k_B}$$

$$= \frac{5}{2} \left(\frac{N}{N_0}\right) \left(\frac{2 E_0}{3}\right)^{3/5} \left(p V_0\right)^{2/5} e^{\frac{2}{5}\left(\frac{S}{N} - \frac{S_0}{N_0}\right)/k_B}$$

write $\left(\frac{2}{3}E_0\right)^{3/5} = \left(\frac{2}{3}E_0\right)\left(\frac{2}{3}E_0\right)^{-2/5}$

$$(pV_0)^{2/5} = \frac{1}{(pV_0)^{-2/5}}$$

and we get

$$H = \frac{5}{2}\,\frac{2}{3}E_0\left(\frac{N}{N_0}\right)\left(\frac{2}{3}\frac{E_0}{pV_0}\right)^{-2/5} e^{\frac{2}{5}\left(\frac{S}{N}-\frac{S_0}{N_0}\right)/k_B}$$

$$= \frac{5}{3}E_0\left(\frac{N}{N_0}\right)\left(\frac{2}{3}\frac{E_0}{pV_0}\right)^{-2/5} e^{\frac{2}{5}\left(\frac{S}{N}-\frac{S_0}{N_0}\right)/k_B}$$

This is just the same H as we found before! So from here on the calculation of κ_S proceeds the same as before.

Finally $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{1}{V}\left(\frac{\partial^2 G}{\partial T\partial p}\right)_N$

$$\left(\frac{\partial G}{\partial p}\right)_{T,N} = Nk_B T\left(\frac{1}{p}\right)$$

$$\left(\frac{\partial^2 G}{\partial T\partial p}\right)_{p,N} = \frac{Nk_B}{p}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p,N} = \frac{Nk_B}{Vp} = \frac{1}{T} \quad \text{using } pV = Nk_BT$$

$$\boxed{\alpha = \frac{1}{T}}$$

Now we check the relationships among $C_V, C_p, \kappa_T, \kappa_S, \alpha$

We should have $C_p - C_V = \frac{TV\alpha^2}{\kappa_T}$

using our above results

$$C_p - C_V = \frac{5}{2}Nk_B - \frac{3}{2}Nk_B = Nk_B$$