

Physics 607
Statistical Physics and Thermodynamics
Professor Valery Pokrovsky

Homework #4

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1 Problem #1

(1) Given the fact that energy per particle depends only on the intensive variables

$$s = \frac{S}{N}, \quad \text{and } v = \frac{V}{N}$$

we can show that the Gibbs thermodynamic potential per particle given as

$$d\Phi = VdP - SdT + \mu dN$$

where μ is the chemical potential we note that

$$\mu = \left(\frac{\partial \Phi}{\partial N} \right)_{P,T}.$$

Now if we write $d\Phi$ in terms of the intensive variables we have

$$d\Phi = NvdP - NsdT + \mu dN$$

which implies that we can write Φ as

$$\Phi(T, P) = N\varphi(T, P)$$

where T and P are intensive variables not dependent on N . Then it is easy to see that

$$\begin{aligned} \mu &= \left(\frac{\partial \Phi}{\partial N} \right)_{P,T} = \varphi(T, P) \\ &\Downarrow \\ \mu &= \varphi(T, P) \end{aligned}$$

But by definition we see that

$$\mu = \varphi(T, P) = \frac{\Phi}{N}$$

so the chemical potential is just given by the ratio of Φ with N .

(2) We can introduce the density of particles given by

$$n = \frac{N}{V}$$

as an intensive value that is only a function of intensive variables P and T note that by rearranging to $N = nV$ we see that

$$\frac{\partial N}{\partial V} = n.$$

Also using the result from part (a) which states that

$$\Phi = N\mu \quad \Rightarrow \quad d\Phi = \mu dN + Nd\mu$$

which if we combine with our definition of $d\Phi$ yields

$$\begin{aligned} d\Phi &= \mu dN + Nd\mu = VdP - SdT + \mu dN \\ &\Downarrow \\ Nd\mu &= VdP - SdT \end{aligned}$$

It follows that

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

using the above two identities we see that

$$\begin{aligned} \left(\frac{\partial N}{\partial \mu}\right)_{T,V} &= \frac{\partial N, V}{\partial \mu, V} \\ &= \frac{\partial N, V}{\partial N, P} \frac{\partial N, P}{\partial \mu, V} \\ &= \left(\frac{\partial V}{\partial P}\right)_{T,N} \left(\overset{0}{\cancel{\frac{\partial N}{\partial \mu} \frac{\partial P}{\partial V}}} - \overset{n}{\cancel{\frac{\partial N}{\partial V} \frac{\partial P}{\partial \mu}}} \right) \\ &= -n^2 \left(\frac{\partial V}{\partial P}\right)_{T,N} \end{aligned}$$

Note we explicitly kept T constant throughout the derivation.

2 Problem #2

- (1) For a given gas of Helium atoms expanding adiabatically to a volume ten times its initial volume we and immediately can state that the change in entropy,

$$\Delta S = 0$$

because this is adiabatic expansion. This fact also implies that the change of energy in the system is due to the work of expansion. We note for a mono-atomic gas we have a change in internal energy that is given by

$$dE = \frac{3}{2}NdT$$

where if we use the equation of state for an ideal gas we have

$$d(PV) = NdT$$

where we assume the number of particles is a constant. Using this fact and that the total change in energy is given by the work we have

$$\begin{aligned} dE &= \frac{3}{2}d(PV) = \frac{3}{2}(PdV + VdP) = -PdV \\ &\Downarrow \\ -\left(\frac{3}{2} + 1\right)PdV &= \frac{3}{2}VdP \\ &\Downarrow \\ -\gamma \frac{dV}{V} &= \frac{dP}{P} \\ &\Downarrow \\ -\gamma \int_{V_0}^V \frac{dV}{V} &= \int_{P_0}^P \frac{dP}{P} \\ &\Downarrow \\ P_0 V_0^\gamma &= PV^\gamma \end{aligned}$$

Where we defined γ by the degrees of freedom, d , given by

$$\gamma \equiv \frac{d/2 + 1}{d/2}$$

where we take $d = 3$ for a mono-atomic gas which yields $\gamma = 5/3$. So for $V = 10V_0$ we have

$$P = P_0 \left(\frac{V_0}{10V_0} \right)^{5/3} = \frac{P_0}{10^{5/3}}$$

This implies that the change in pressure is given by

$$\Delta P = P_0 \left(10^{-5/3} - 1 \right)$$

Using this change in pressure and the equation of state for an ideal gas we can find the change in temperature by

$$\begin{aligned} \Delta T &= T - T_0 = \frac{PV}{N} - \frac{P_0 V_0}{N} \\ &= \frac{P_0}{10^{5/3}} \frac{10V_0}{N} - \frac{P_0 V_0}{N} \\ &= \frac{P_0 V_0}{N} \left(10^{-2/3} - 1 \right) \end{aligned}$$

- (2) Repeating this process of a gas of H_2 molecules we note that everything remains the same except for the degrees of freedom change to $d = 5$ to account for the two new rotational degrees of freedom. This implies that $\gamma = 7/5$ so it follows that

$$\begin{aligned}\Delta S &= 0 \\ \Delta P &= P_0 \left(10^{-7/5} - 1 \right) \\ \Delta T &= \frac{P_0 V_0}{N} \left(10^{-2/5} - 1 \right)\end{aligned}$$

- (3) We can calculate the adiabatic coefficient of thermal expansion, α_S , for an ideal gas by noting that T and V are related to a constant, C , given by

$$TV^{\gamma-1} = C$$

when we hold S constant which represents an adiabatic process. This allows us to calculate α_S by

$$\begin{aligned}\alpha_S &= \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_S = \frac{1}{V} \frac{\partial}{\partial T} \left(\frac{C}{T} \right)^{1/\gamma-1} \\ &= \left(\frac{T}{C} \right)^{1/\gamma-1} C^{1/\gamma-1} \left(\frac{-1}{\gamma-1} \right) T^{-\gamma/\gamma-1} \\ &= -\frac{1}{\gamma-1} T^{\frac{-\gamma+1}{\gamma-1}} \\ &= -\frac{1}{\gamma-1} \frac{1}{T}\end{aligned}$$

We note for the minimal degrees of freedom $d = 3$ we have $\gamma > 1$ which implies that α_S is negative. Therefore an ideal gas undergoing adiabatic expansion decrease in temperature at a rate inversely proportional to the temperature.

3 Problem #3

- (1) Given an ideal gas with N molecules in a chamber at temperature, T_1 under the pressure P_1 that is penetrating through a porous tube into another chamber with controllable pressure $P_2 < P_1$ we can find the change in temperature, entropy, and volume for this process. Note we assume that C_P is not dependent on temperature. Noting that the gas is undergoing a *Joule-Thomson* process which in general is governed by the equations

$$\left(\frac{\partial T}{\partial P}\right)_W = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right] \quad (3.1)$$

where we apply the equation of state for an ideal gas which states

$$V = \frac{NT}{P} \quad \Rightarrow \quad \frac{\partial V}{\partial T} = \frac{N}{P}$$

Therefore equation 3.1 becomes

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_W &= \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right] \\ &\Downarrow \\ \left(\frac{\partial T}{\partial P}\right)_W &= \frac{1}{C_P} \left[T \frac{N}{P} - \frac{NT}{P} \right] = 0 \end{aligned}$$

So for any change in pressure we have no change in temperature so

$$\Delta T = 0$$

This implies that by the equation of state the change in volume is directly related to the change in pressure as T and N are constant. So we see

$$\begin{aligned} \Delta V = V_2 - V_1 &= \frac{NT}{P_2} - \frac{NT}{P_1} \\ &= NT \left(\frac{1}{P_2} - \frac{1}{P_1} \right) \end{aligned}$$

Now, if use the relation

$$dW = TdS + VdP \quad \Rightarrow \quad dS = \frac{dW}{T} - \frac{V}{T}dP$$

we can write the change in entropy as

$$\begin{aligned} \left(\frac{\partial S}{\partial P}\right)_W &= -\frac{V}{T} = -\frac{N}{P} \\ &\Downarrow \\ \int_{S_1}^{S_2} dS &= -N \int_{P_1}^{P_2} \frac{dP}{P} \\ \Delta S &= N \ln \left(\frac{P_1}{P_2} \right) \end{aligned}$$

Note that $P_1 > P_2$ so as expected $\Delta S > 0$.

(2) Now, if we take the gas as slightly non-ideal with an energy given as

$$E = NC_V T + \frac{gN^2}{2V}$$

where g is the strength of interaction between particles. A positive g corresponds to repulsion, negative to attraction. We assume that the interaction is weak or $|g|n \ll T$. So we take the equation of state to be a first order correction given as

$$V = \frac{NT}{P} + \frac{gN^2}{2}.$$

Using this new equation of state we can apply equation 3.1 to find the change in temperature

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_W &= \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right] \\ &\Downarrow \\ \left(\frac{\partial T}{\partial P}\right)_W &= \frac{1}{C_P} \left[T \frac{N}{P} - \frac{NT}{P} + \frac{gN^2}{2} \right] \\ &= \frac{1}{C_P} \frac{gN^2}{2} \end{aligned}$$

Note the interaction term allows for the change in temperature to be non-zero given by an integration of a constant. This yields

$$\Delta T = \frac{P_2 - P_1}{C_P} \frac{gN^2}{2}$$

And we find the change in entropy by

$$\begin{aligned} \left(\frac{\partial S}{\partial P}\right)_W &= -\frac{V}{T} = -\frac{N}{P} - \frac{gN^2}{2T} \\ &\Downarrow \\ \int_{S_1}^{S_2} dS &= -N \int_{P_1}^{P_2} \frac{dP}{P} - \frac{gN^2}{2T} (P_2 - P_1) \\ \Delta S &= N \ln \left(\frac{P_1}{P_2} \right) - \frac{gN^2}{2T} (P_2 - P_1) \end{aligned}$$

Note we assume that $|g|n \ll T$ so the term we are correcting lowers the change in entropy from the ideal case but the correction is small so that the total change in entropy remains positive.

4 Problem #4

- (1) We can find the chemical potential of an ideal gas as a function of variable pairs. First we start with the partition function for an ideal gas

$$Z = \frac{(CVT^{3/2})^N}{N!}$$

where we take the log assuming N is large with yields

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

So we can calculate F as

$$F = -T \ln(Z) = -NT \left(\zeta + 1 - \ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln(T) \right)$$

which yields the entropy by

$$S = -\frac{\partial F}{\partial T} = N \left(\zeta + 1 + \ln \left(\frac{V}{N} \right) + \frac{3}{2} (1 + \ln(T)) \right)$$

So we can calculate the chemical potential by

$$\begin{aligned} \mu &= \frac{\Phi}{N} = \frac{PV + F}{N} = P \frac{V}{N} - T \left(\zeta + 1 - \ln \left(\frac{V}{N} \right) + \frac{3}{2} \ln(T) \right) \\ &\Downarrow \\ \mu(V, T) &= -T \left(\zeta + \ln(V/N) + \frac{3}{2} \ln(T) \right) \end{aligned}$$

Using the relation defined by the entropy we have

$$\begin{aligned} \mu(P, T) &= -T \left(\zeta + \ln(T/P) + \frac{3}{2} \ln(T) \right) \\ \mu(S, T) &= -T \left(\frac{S}{N} - \frac{5}{2} \right) \\ \mu(P, S) &= - \left(\frac{S}{N} - \frac{5}{2} \right) P^{2/5} \exp \left(\frac{2}{5} \left(\frac{S}{N} - \zeta \right) - 1 \right) \end{aligned}$$

- (2) We note that for an ideal gas we have the potential, Ω , given as

$$\Omega = -PV$$

Note the result from part (1) for the chemical potential

$$\begin{aligned} \mu(P, T) &= -T \left(\zeta + \ln(T/P) + \frac{3}{2} \ln(T) \right) \\ &\Downarrow \\ P(\mu, T) &= \exp \left(\frac{\mu}{T} + \frac{5}{2} \ln(T) + \zeta \right) \end{aligned}$$

Replacing we have

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