PHYS 521: Statistical Mechanics

Homework #1

Prakash Gautam

April 17, 2018

1. A particular system obeys two equations of state

$$T = \frac{3As^2}{v} \qquad \text{(thermal equation of state)}, \qquad P = \frac{As^3}{v^2} \qquad \text{(mechanical equation of state)}.$$

Where A is a constant.

(a) Find μ as a function of s and v, and then find the fundamental equation.
Solution:
Given P and T the differential of each of them can be calculated as

$$\begin{aligned} dT &= \frac{6As}{v}ds - \frac{3As^2}{v^2}dv \qquad \Rightarrow \qquad sdT = \frac{6As^2}{v}ds - \frac{3As^3}{v^2}dv \\ dP &= \frac{3As^2}{v^2}ds - \frac{2As^3}{v^3}dv \qquad \Rightarrow \qquad vdP = \frac{3As^2}{v}ds - \frac{2As^3}{v^2}dv \end{aligned}$$

The Gibbs-Duhem relation in energy representation allows to calculate the value of μ.

$$\begin{aligned} d\mu &= vdP - sdT \\ &= \frac{3As^2}{v}ds - \frac{2As^3}{v^2}dv - \frac{6As^2}{v}ds + \frac{3As^3}{v^2}dv \\ &= -\left[\frac{3As^2}{v}ds - \frac{As^3}{v^2}dv\right] = -d\left(\frac{As^3}{v}\right) \end{aligned}$$

This can be identified as the total derivative of $\frac{As^3}{v}$ so the rel

$$d\mu = -d\left(\frac{As^3}{v}\right) \qquad \Rightarrow \qquad \mu = -\frac{As^3}{v} + k$$

Where k is arbitrary constant. We can plug this back to Euler relation to find the fundamental equation as.

$$\begin{aligned} u &= Ts - Pv + \mu \\ &= \frac{3As^3}{v} - \frac{As^3}{v} - \frac{As^3}{v} + k = \frac{As^3}{v} + k \end{aligned}$$

So the fundamental equation of the system is $\frac{As^3}{v} + k$. □

(b) Find the fundamental equation of this system by direct integration of the molar form of the equation.
Solution:
The differential form of internal energy is

$$\begin{aligned} du &= Tds - Pdv \\ &= \frac{3As^2}{v}ds - \frac{As^3}{v^2}dv \end{aligned}$$

As before this is just the total differential of $\frac{As^3}{v}$ so the relation leads to

$$du = d\left(\frac{As^3}{v^2}\right) \qquad \Rightarrow \qquad u = \frac{As^3}{v} + k$$

This k should be the same arbitrary constant that we got in the previous problem. ☐

2. The fundamental equation of system A is

$$S = C(NVE)^{1/3},$$

and similarly for system B. The two system are separated by rigid, impermeable, adiabatic wall. System A has a volume of $9 \times 10^{-6} m^3$ and a molenumber of 3 moles. System B has volume of $4 \times 10^{-6} m^3$ and a mole number of 2 moles. The total energy of the composite system is $80J$.

(a) Plot the entropy as a function of $E_A/(E_A + E_B)$.

Solution:

Since the total energy of the system is $80J$ the sum $E_A + E_B = 80J$. The total entropy of system can be written as

$$S = C\left[\left\{N_1 V_1 \cdot 80 \cdot \left(\frac{E_A}{E_A + E_B}\right)\right\}^{\frac{1}{3}} + \left\{N_2 V_2 \cdot 80 \cdot \left(1 - \frac{E_A}{E_A + E_B}\right)\right\}^{\frac{1}{3}}\right]$$

The graph of Entropy S vs the energy fraction is shown in Figure 1. ☐

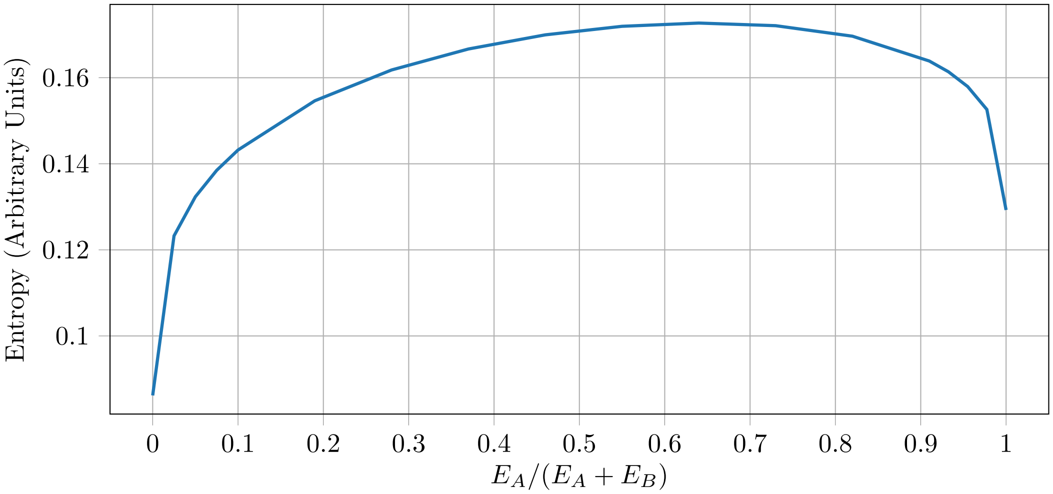

Figure 1: Plot of Entropy vs energy fraction.

(b) If the internal wall is now made diathermal and the system is allowed to come to equilibrium, what are the internal energies of each of the individual systems?

Solution:

If the wall is made diathermal and the energy can flow the total energy of the remains constant $E = E_A + E_B$. Taking differential on both sides we get $dE = dE_A + dE_B = 0$. Since there is no change in volume or the number of molecules $dV = 0$ and $dN = 0$. Thus the differential relation of entropy reduces to $dS = \frac{1}{T}dE$. The additive property allows us to write

$$dS = dS_A + dS_B = \frac{1}{T_A}dE_A + \frac{1}{T_B}dE_B \qquad \Rightarrow \frac{dE_A}{T_A} = -\frac{dE_B}{T_B} \qquad \Rightarrow \quad \frac{1}{T_A} = \frac{1}{T_B}$$

The quantities T_A and T_B for each systems can be from the fundamental equation thus

$$\frac{1}{T_A} = \left(\frac{\partial S_A}{\partial E_A}\right) = \frac{C}{3}\left(\frac{N_A V_A}{E_A^2}\right)^{1/3} \qquad \frac{1}{T_B} = \left(\frac{\partial S_B}{\partial E_B}\right) = \frac{C}{3}\left(\frac{N_B V_B}{E_B^2}\right)^{1/3}$$

These expressions can be simplified down to get and noting $E_A + E_B = 80J$ we have two linear expressions

$$E_B = \sqrt{\frac{N_B V_B}{N_A V_A}} E_A \qquad E_A + E_B = 80 \qquad \Rightarrow \qquad E_A = 51.93J \qquad E_B = 28.07J$$

So the after equilibrium the internal energy of system A is $E_A = 51.93J$ and for system B it is $E_B = 28.07J$. ☐

(c) Comment on the relation between these two results.
Solution:
The graph of S vs $E_A/(E_A+E_B)$ is skewed to the right and its maximum is at $E_A/(E_A+E_B) = 0.64$. The final energy of system A is 51.93 which is $0.64 \cdot 80$. Thus the final final energies are such that the total final entropy is maximum. ☐

3. An impermeable, diathermal, and rigid partition divides a container into two subvolumes, of volume nV_0 and mV_0. The subvolumes contain respectively, n moles of H_2 and m moles of Ne, each to be considered as a simple ideal gas. The system is maintained at a constant temperature T. The partition is suddenly ruptured and equilibrium is allowed to re-establish. Find the change in entropy of the system. How is the result related to the "entropy of mixing"?
Solution:
The fundamental equation of ideal gas can be written as $U = cNRT$ and equivalently as $PV = NRT$ thus the quantities

$$\begin{aligned} U = cNRT \qquad &\Rightarrow \qquad \frac{1}{T} = cR\frac{N}{U} = \frac{cR}{u} \\ PV = NRT \qquad &\Rightarrow \qquad \frac{P}{T} = R\frac{N}{V} = \frac{R}{v} \end{aligned}$$

Sine it is true for each of these systems we can write

$$ds = \frac{1}{T}du + \frac{P}{T}dv \quad \Rightarrow \quad ds = \frac{cR}{u}du + \frac{R}{v}dv \quad \Rightarrow \quad s = s_0 + cR\ln\left(\frac{u_f}{u_i}\right) + R\ln\left(\frac{v_f}{v_i}\right)$$

The initial and final molar volume for each of the gases is

$$\begin{aligned} v_{ih} &= \frac{nV_0}{n} = V_0 \qquad & v_{in} &= \frac{mV_0}{m} = V_0 \\ v_{fh} &= \frac{(m+n)V_0}{n} = \left(1 + \frac{m}{n}\right)V_0 \qquad & v_{fn} &= \frac{(m+n)V_0}{m} = \left(1 + \frac{n}{m}\right)V_0 \end{aligned}$$

Also since the temperature of system is constant and that no heat flows in or out of the composite system the change in internal energy is zero thus $u_i = u_f$ for both thus the total final entropy become

$$s_h = s_{0h} + cR\ln\left(\frac{u_{fh}}{u_{ih}}\right) + R\ln\left(\frac{v_{fh}}{v_{ih}}\right) = s_{0h} + R\ln\left(1 + \frac{m}{n}\right)$$

Similarly for Ne the final entropy of system is

$$s_n = s_{0n} + R\ln\left(1 + \frac{n}{m}\right)$$

The total change in entropy is

$$\begin{aligned} \Delta S &= ms_n + ns_h - (ms_{0n} + ns_{0h}) \\ &= mR\ln\left(1 + \frac{n}{m}\right) + ms_{n0} + nR\ln\left(1 + \frac{m}{n}\right) + ns_{h0} - (ms_{0n} + ns_{0h}) \\ &= n\ln\left(1 + \frac{m}{n}\right) + m\ln\left(1 + \frac{n}{m}\right) \end{aligned}$$

This is exactly equal to the Entropy of mixing. ☐

4. The entropy of blackbody radiation is given by the formula

$$S = \frac{4}{3}\sigma V^{1/4}E^{3/4},$$

where σ is a constant.

(a) Show that S is an extensive parameter.

(b) Determine the temperature and the pressure of the radiation.

Solution:

The Entropy relation can be inverted to get

$$E = \left(\frac{81S^4}{256\sigma^4 V}\right)^{1/3}$$

Differentiating this with repsect to V to get the pressure gives

$$P = -\left(\frac{\partial E}{\partial V}\right) = \frac{\sqrt[3]{6}S^{\frac{4}{3}}}{8V^{\frac{4}{3}}\sigma^{\frac{4}{3}}}$$

The temperature similarly is

$$T = \left(\frac{\partial E}{\partial S}\right) = \frac{\sqrt[3]{6}\sqrt[3]{S}}{2\sqrt[3]{V}\sigma^{\frac{4}{3}}}$$

Thus the temperature and pressure are determined. □

(c) Prove that

$$PV = \frac{E}{3}$$

Solution:

Substuting $S = \frac{4}{3}\sigma V^{1/4}E^{3/4}$ into the pressure expression

$$P = \frac{\sqrt[3]{6}S^{\frac{4}{3}}}{8V^{\frac{4}{3}}\sigma^{\frac{4}{3}}} = \frac{\sqrt[3]{6}\left(\frac{4}{3}\sigma V^{1/4}E^{3/4},\right)^{\frac{4}{3}}}{8V^{\frac{4}{3}}\sigma^{\frac{4}{3}}} = \frac{E}{3V} \qquad \Rightarrow PV = \frac{E}{3}$$

Thus $PV = \frac{E}{3}$ is proved as required. □

5. For a particular system, it is found that $e = (3/2)Pv$ and $P = AvT^4$. Find the molar Gibbs potential and molar Helmholtz potential for the system.

Solution:

Since there are two equations of state we can modify them to express the intensive parameters as

$$P = \frac{2e}{3v} \qquad T = \left(\frac{P}{Av}\right)^{1/4} = \left(\frac{2u}{3Av^2}\right)^{1/4}$$

These can be used in Entropy differential equation to get

$$\begin{aligned} ds &= \frac{1}{T}de + \frac{P}{T}dv \\ &= \left(\frac{3A}{2}\frac{v^2}{e}\right)^{1/4} de + \left(\frac{8A}{27}\frac{e^3}{v^2}\right)^{1/4} dv \end{aligned}$$

The above expression can be recocnized as the total differential of $\left(\frac{128Av^2e^3}{27}\right)^{1/4}$

$$ds = d\left(\frac{128Av^2e^3}{27}\right)^{1/4} \qquad \Rightarrow \qquad s = \left(\frac{128Av^2e^3}{27}\right)^{1/4} + s_0$$

Multiplying thourgh by N to get the non molar quantities we get

$$S = \left(\frac{128A}{27} \frac{V^2 E^3}{N} \right)^{1/4} + S_0$$

This above relation can be inverted to get the fundamental energy representation. So we get

$$E = \left[\frac{27}{128A} \frac{N}{V^2} (S - S_0)^4 \right]^{1/3}$$

This serves as the fundamental Energy relation which can be used to find the Gibbs and Helmholtz potential. We can now find the intensive parameters T and P in terms of the extensive parameters as

$$T = \left(\frac{\partial E}{\partial S} \right) = \frac{\partial}{\partial S} \left[\frac{27}{128A} \frac{N}{V^2} (S - S_0)^4 \right]^{1/3} = \frac{1}{\sqrt[3]{2A}} \left(\frac{N}{V^2} \right)^{1/3} (S - S_0)^{1/3}$$

We can invert to find S as a function of T so

$$S = S_0 + \frac{2AV^2}{N} T^3$$

Similarly we can find the intensive parameter P as

$$P = -\left(\frac{\partial E}{\partial V} \right) = \frac{1}{2\sqrt[3]{2A}} N^{1/3} \left(\frac{S - S_0}{V^5} \right)^{1/3}$$

This can again be inverted to get V as a function of P

$$V = \left[\frac{1}{16A} \frac{N(S - S_0)^4}{P^3} \right]^{1/5}$$

Equipped with these functions we can now find the Gibbs potential as

$$\begin{aligned} G &= E - TS + PV \\ &= \left[\frac{27}{128A} \frac{N}{V^2} (S - S_0)^4 \right]^{1/3} - T \cdot \left(S_0 + \frac{2AV^2}{N} T^3 \right) + P \cdot \left[\frac{1}{16A} \frac{N(S - S_0)^4}{P^3} \right]^{1/5} \\ &= \left(\frac{A^3 P^2}{N^3} T^{12} V^8 \right)^{1/5} - \frac{AT^4 V^2}{2N} \end{aligned}$$

This gives the Gibbs Potential now the Helmholtz potential can be similarly found as

$$\begin{aligned} F &= E - TS \\ &= \left[\frac{27}{128A} \frac{N}{V^2} (S - S_0)^4 \right]^{1/3} - T \cdot \left(S_0 + \frac{2AV^2}{N} T^3 \right) \\ &= -\frac{AT^4 V^2}{2N} \end{aligned}$$

Thus the Helmholtz potential is $-\frac{AT^4V^2}{2N}$. □