Homework Advanced Statistical Mechanics #1

Kenneth Goodenough

2 a)

Let $PV = \phi(T)$ hold. Rewriting and differentiating with respect to T at fixed V we find:

$$PV = \phi(T)$$
$$P = \frac{\phi(T)}{V}$$
$$\left.\frac{\partial P}{\partial T}\right|_V = \frac{\phi'(T)}{V}$$

Now, the internal energy is independent of volume at constant temperature. At constant temperature then:

$$dE = dQ - dW = 0$$
$$dQ = dW$$
$$TdS = PdV$$

It is important to note that this only holds at fixed T, and so:

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{P}{T}$$

Using the Maxwell relation $\frac{\partial P}{\partial T}\big|_V = \frac{\partial S}{\partial V}\big|_T$, we see that

$$\frac{P}{T} = \frac{\phi'(T)}{V}$$
$$PV = T\phi'(T) = \phi(T)$$

This relation obviously only holds if $\phi(T)$ is linear in T, and so $\phi(T) = cT$ for some constant c.

b)

We have that $PV = RT$, $R = C_P - C_V$, $C_V = \frac{L}{2}R$ and $R\left(1 + \frac{L}{2}\right) = C_P$.

We know that

$$C_V dT = T\left.\frac{\partial S}{\partial T}\right|_V dT$$
$$C_P dT = T\left.\frac{\partial S}{\partial T}\right|_P dT$$

Where C_V and C_P are the heat capacities at constant volume and constant pressure, respectively. Now let S be $S(V,T)$, then

$$\Delta S = \int_{S_0}^{S} dS = \int_{T_0}^{T} \frac{C_V}{T} dT$$
$$\Delta S = C_P \ln\left(\frac{T}{T_0}\right)$$
$$\Delta S = \left(1 + \frac{L}{2}\right) \ln\left(\frac{\frac{PV}{R}}{\frac{P_0V_0}{R}}\right)$$
$$\Delta S = R\left(1 + \frac{L}{2}\right) \ln\left(\frac{PV}{P_0V_0}\right)$$

But since $S = S(P,T)$, the $\frac{V}{V_0}$ falls out:

$$\Delta S = R\left(1 + \frac{L}{2}\right) \ln\left(\frac{P}{P_0}\right)$$

Now let S be $S(P,T)$, then:

$$\Delta S = \int_{S_0}^{S} dS = \int_{T_0}^{T} \frac{C_V}{T} dT$$
$$\Delta S = C_V \ln\left(\frac{T}{T_0}\right)$$
$$\Delta S = R\left(\frac{L}{2}\right) \ln\left(\frac{PV}{P_0V_0}\right)$$

But since $S = S(V,T)$, the $\frac{P}{P_0}$ falls out:

$$\Delta S = R\frac{L}{2} \ln\left(\frac{V}{V_0}\right)$$

c)
First law of thermodynamics for adiabatic process:

$$\mathrm{d}E = C_v \mathrm{d}T = \mathrm{d}Q - \mathrm{d}W$$
$$C_v \mathrm{d}T = -p\mathrm{d}V = -\frac{RT}{V}\mathrm{d}V$$

Rewriting gives us:

$$\frac{1}{T}\mathrm{d}T = -\frac{R}{C_v}\frac{1}{V}\mathrm{d}V = -\frac{C_P - C_V}{C_V}\frac{1}{V}\mathrm{d}V$$

$$\frac{1}{T}\mathrm{d}T = (1-\gamma)\,\frac{1}{V}\mathrm{d}V$$

Then:

$$\begin{aligned}\int \frac{1}{T}\mathrm{d}T &= \int (1-\gamma)\,\frac{1}{V}\mathrm{d}V\\ \ln(T) &= (1-\gamma)\ln(V) + C\\ T &= CV^{1-\gamma}\\ TV^{\gamma-1} &= C\end{aligned}$$

Where C is some constant.

Now using that $T = \frac{PV}{R}$, gives:

$$\begin{aligned}TV^{\gamma-1} = \frac{PV}{R}V^{\gamma-1} &= C\\ PV^{\gamma} &= C\end{aligned}$$

Note that C is now a different constant then the one used before, i.e. $TV^{\gamma-1} \neq PV^{\gamma}$. Now using that $V = \frac{RT}{P}$:

$$\begin{aligned}TV^{\gamma-1} = T\left(\frac{RT}{P}\right)^{\gamma-1} &= C\\ \frac{T^{\gamma}}{P^{\gamma-1}} = T^{\gamma}P^{1-\gamma} &= C\\ TP^{\frac{1-\gamma}{\gamma}} &= C\end{aligned}$$

d)
We know that for adiabatic processes $P = cV^{-\gamma}$, where c is some constant and that for an ideal gas $PV = RT$. Then:

$$\begin{aligned}P = \frac{RT}{V} &= cV^{-\gamma}\\ c = RTV^{\gamma-1} &= RT_fV_f^{\gamma-1} = RT_iV_i^{\gamma-1}\end{aligned}$$

Then the work done is

$$W = \int_{V_i}^{V_f} PdV = c\int_{V_i}^{V_f} V^{-\gamma} dV$$
$$W = \frac{c}{1-\gamma}\left[V_f^{1-\gamma} - V_i^{1-\gamma}\right]$$
$$W = \frac{R}{1-\frac{C_p}{C_v}}\left[T_f V_f^{\gamma-1} V_f^{1-\gamma} - T_i V_i^{\gamma-1} V_i^{1-\gamma}\right]$$
$$W = C_v\left(T_f - T_i\right)$$

e)

$$\mathrm{d}E = C_v\mathrm{d}T = \mathrm{d}Q - \mathrm{d}W = -P\mathrm{d}V$$
$$C_v\int_{T_i}^{T_f}\mathrm{d}T = -\int_{V_i}^{V_f} P\mathrm{d}V$$
$$C_v\left(T_f - T_i\right) = -P_{ext}\left(V_f - V_i\right)$$

Where P_{ext} is taken to be constant.

$$C_v\left(T_f - T_i\right) = -P_{ext}\left(V_f - V_i\right)$$
$$T_f = -\frac{P_{ext}}{C_v}\left(V_f - V_i\right) + T_i$$
$$T_f = -\frac{P_f}{C_v}\left(V_f - \frac{RT_i}{P_i}\right) + T_i$$
$$T_f = \left(1-\gamma\right)T_f - \left(1-\gamma\right)\frac{T_i P_f}{P_i} + T_i$$
$$T_f - \left(1-\gamma\right)T_f = -T_i\left(1-\gamma\right)\frac{P_f + P_i}{P_i}$$
$$\gamma T_f = -T_i\left(1-\gamma\right)\frac{P_f + P_i}{P_i}$$
$$T_f = T_i\left(1-\gamma^{-1}\right)\frac{P_f + P_i}{P_i}$$
$$T_f = T_i\left(1-\gamma^{-1}\right)\left(\frac{P_f}{P_i} + 1\right)$$

f)

No. Both are adiabatic processes

g)

3)

a)

$$\mathrm{d}E = T\mathrm{d}S - \mathrm{d}W = T\mathrm{d}S + \sigma l \mathrm{d}x$$

$$\mathrm{d}A = -S\mathrm{d}T + \sigma l \mathrm{d}x$$

b)

$$\begin{gathered}\mathrm{d}E = T\mathrm{d}S - \sigma l \mathrm{d}x \\ \frac{\partial E}{\partial x} = T\frac{\partial S}{\partial x} - \sigma l \\ \frac{\partial E}{\partial x} = T\frac{\partial S}{\partial x} - \sigma l\end{gathered}$$

$$\begin{gathered}\mathrm{d}E = T\mathrm{d}S - \sigma l \mathrm{d}x \\ \frac{\partial E}{\partial T}\mid_x = T\frac{\partial S}{\partial T}\mid_x - l\frac{\partial \sigma}{\partial T}\mid_x\end{gathered}$$

b)

4)

For an adiabatic process $TP^{\frac{1-\gamma}{\gamma}}$ is constant, and so $T^{\frac{\gamma}{\gamma-1}} = C \cdot P$.

$$T^{\frac{\gamma}{\gamma-1}} = C \cdot P$$
$$\frac{\gamma}{\gamma-1}\ln(T) = \ln(P) + C$$

Differentiating gives us:

$$\frac{\gamma}{\gamma-1}\frac{1}{T}\mathrm{d}T = \frac{1}{P}\mathrm{d}P$$

Rewriting the given equation with $V = \frac{Nk_bT}{P}$ and rewriting gives:

$$\frac{\partial P}{\partial z} = -m_{mol}g\frac{N}{V} = -m_{mol}g\frac{P}{k_bT}$$
$$\frac{1}{P}\mathrm{d}P = -m_{mol}g\frac{1}{k_bT}\mathrm{d}z$$

And so:

$$-m_{mol}g\frac{1}{k_bT}\mathrm{d}z = \frac{\gamma}{\gamma-1}\frac{1}{T}\mathrm{d}T$$
$$\frac{\partial T}{\partial z} = -m_{mol}g\frac{T}{k_bT} \cdot \frac{\gamma-1}{\gamma}$$
$$\frac{\partial T}{\partial z} = -\frac{m_{mol}g}{k_b}\left(1-\gamma^{-1}\right)$$

And since this only holds for processes at fixed entropy:

$$\left.\frac{\partial T}{\partial z}\right|_S = -\frac{m_{mol}g}{k_b}\left(1-\gamma^{-1}\right)$$