E & E Homework # 6

Blake Evans

① Hot Metal Cube (assumed Isochoric)

a) The entropy of the metal decreases.

$$\Delta S = \int \frac{Q}{T} \rightarrow Q = \Delta U - \underset{W=0 \text{ (No force)}}{W} \rightarrow Q = \Delta U \rightarrow Q = (-)$$

$(\downarrow T)$ decreasing

$$\Delta S = \int \frac{(-Q)}{\underset{\text{decreasing}}{T}} \rightarrow \Delta S = -\int \frac{Q}{T} \rightarrow \Delta S = -(\Delta S) \rightarrow \boxed{\text{Negative (decreasing)}}$$

b) The entropy of the ocean increases

$$\Delta S = \int \frac{Q}{T} \rightarrow Q = \Delta U - \underset{W=0 \text{ (No force)}}{W} \rightarrow Q = \Delta U \rightarrow Q = (+)$$

$(\uparrow T)$ Increasing

$$\Delta S_w = \int \frac{(+Q)}{\underset{\text{Increasing}}{T}} \rightarrow \Delta S_w = +\int \frac{Q}{T} \rightarrow \Delta S_w = +(\Delta S) \rightarrow \boxed{\text{Positive (Increasing)}}$$

① Hot Metal Cube

c) $\Delta S_{univ} = \Delta S_{system} + \Delta S_{surr} = \Delta S_{metal} + \Delta S_{ocean}$

we know that $\Delta S_{metal} = (-)\Delta S$ and that $\Delta S_{ocean} = (+)\Delta S$.

Thus,

ΔQ's are the same

$$\Delta S_{universe} = \Delta S_{metal} + \Delta S_{water} = \left(-\int \frac{\Delta Q}{T_M}\right) + \left(\int \frac{\Delta Q}{T_w}\right) = \boxed{\begin{array}{c}\Delta S = (+) \\ \text{Increases}\end{array}}$$

$T_M > T_W \rightarrow \Delta S_M < \Delta S_W$

① Hot Metal Cube

> **Tom (He/Him)** Yesterday at 4:40 PM
> Blake - word of warning, Dustin doesn't want to see `Delta S = int Q/T` - its not a safe assumption
> you don't need to show any math for Q1, just do sensemaking about what you expect - logic is good

a) The entropy of the metal cube decreases. This is because the initial state of the cube is hot and therefore is expanded from what it would be cold. So, when it is thrown into the ocean, the metal will compress (due to the drop in temperature) and therefore (since the cube is decreasing in heat and volume) it's entropy is negative.

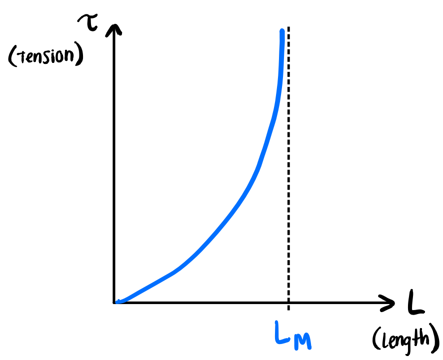
b) The entropy of the ocean increases. The water around the cube will expand due to its increase in temperature. Therefore, since its volume and heat is expanding, the entropy of the ocean must increase.

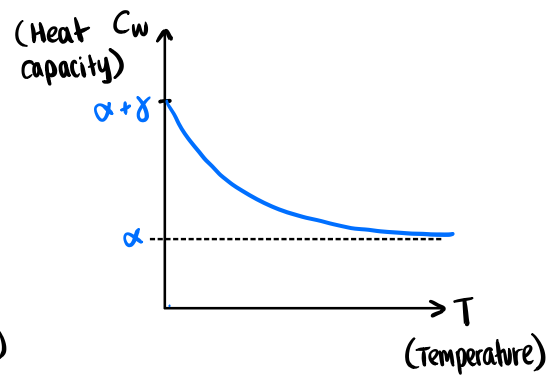
c) The entropy of both systems combined, increases. This is because of two reasons. First, the Second Law tells us that the entropy of any combined real world process will always be positive ($\Delta S_{uni} = +$). Second, since water has more degrees of freedom than the metal, increasing it's temperature will increase the number of microstates more than it will decrease in the cube. Hence, $\Delta S_{universe} = \Delta S_{metal} + \Delta S_{ocean} = (+)$

② Bungee

$$\tau = \left(a - be^{-\frac{T}{T_1}}\right)\tan\left(\frac{\pi L}{2L_M}\right) \;;\; C_L = \alpha + \gamma e^{-\frac{T}{T_1}} \;;\; F = U - TS$$

a)





$$dU = TdS + \tau\, dL \qquad\qquad C_L = \alpha + \gamma e^{-\frac{T}{T_1}}$$

b) $\Delta F = F(T,L) - F(T, \frac{1}{2}L_M)$; $\tau = \left(a - be^{\frac{T}{T_1}}\right)\tan\left(\frac{L}{2L_M}\right)$

Using Helmholtz, we can plug in dU and solve.

$$F(T,L) = U - TS \rightarrow F = \left(\int TdS + \int \tau\, dL\right) - TS$$

$$F(T,L) = \int_0^T TdS + \int_0^L \left(a - be^{-\frac{T}{T_1}}\right)\tan\left(\frac{\pi L}{2L_M}\right) dL - TS$$

$$F(T,L) = \int_0^T TdS + \left(a - be^{-\frac{T}{T_1}}\right)\int_0^L \tan\left(\frac{\pi L}{2L_M}\right) dL - TS$$

$$F(T,L) = \int_0^T TdS + \left(a - be^{\frac{T}{T_1}}\right)\left[\left(\frac{-1}{\pi}\right)\left(2L_M \ln\left(\cos\left(\frac{\pi L}{2L_M}\right)\right)\right)\right]_0^L - TS$$

② Bungee cont.)

Since $C_L = \alpha + \gamma e^{-\frac{T}{T_1}}$; we can let $\gamma = -b$ and $a = \alpha$ to get

$$F(T,L) = (TS) - (TS) - \frac{C_L}{\pi}\left[2L_M \ln\left(\cos\left(\frac{\pi}{2}\cdot\frac{L}{L_M}\right)\right)\right]$$

$$F(T,L) = -\frac{C_L}{\pi}\left[2L_M \ln\left(\cos\left(\frac{\pi}{2}\cdot\frac{L}{L_M}\right)\right)\right]$$

Now for $F(T, \frac{1}{2}L_M)$

$$F(T,\tfrac{1}{2}L_M) = \int_0^T T\,dS + \int_0^{\frac{L_M}{2}} \left(C_L\left(\tan\left(\frac{\pi L}{2L_M}\right)\right)\right) dL - TS$$

$$F(T,L) = \int T\,dS + \left(a - be^{\frac{T}{T_1}}\right)\left[\left(\frac{-1}{\pi}\right)\left(2L_M \ln\left(\cos\left(\frac{\pi L}{2L_M}\right)\right)\right)\right]_0^{\frac{L_M}{2}} - TS$$

$$F(T,L) = \cancel{(TS)} - \cancel{(TS)} - \frac{C_L}{\pi}\left[2L_M \ln\left(\cos\left(\frac{\pi(\frac{1}{2}\cancel{L_M})}{2\cancel{L_M}}\right)\right)\right]$$

$$F(T,L) = -\frac{C_L}{\pi}\left[2L_M \ln\left(\cos\left(\frac{\pi}{4}\right)\right)\right]$$

Now we can find ΔF using $F(T,L)$ and $F(T,L_M)$

$$\Delta F = \left[-\frac{C_L}{\pi}\left[2L_M \ln\left(\cos\left(\frac{\pi}{2}\cdot\frac{L}{L_M}\right)\right)\right]\right] - \left[-\frac{C_L}{\pi}\left[2L_M \ln\left(\cos\left(\frac{\pi}{4}\right)\right)\right]\right]$$

② Bungee Cont.)

$$\Delta F = -\frac{C_L}{\pi} 2L_m \left(\ln\left(\cos\left(\frac{\pi L}{2L_M}\right)\right) - \ln\left(\cos\left(\frac{\pi}{4}\right)\right)\right)$$

$$\Delta F = -\frac{C_L}{\pi}(2L_M)\left(\ln\left(\frac{\cos\left(\frac{\pi L}{2L_M}\right)}{\cos\left(\frac{\pi}{4}\right)}\right)\right)$$

$$\boxed{\Delta F = -\frac{C_L(2L_M)}{\pi}\left[\ln\left(\frac{\sqrt{2}}{1}\cos\left(\frac{\pi L}{2L_M}\right)\right)\right]}$$

c) Solve for change in entropy $S(T,L) - S(T,\frac{1}{2}L_M)$

$$\Delta S = S(T,L) - S(T,\tfrac{1}{2}L_M)$$

$$dS = \left[\cancel{\left(\frac{dS}{dT}\right)_L dT} + \left(\frac{dS}{dL}\right)_T dL\right] - \left[\cancel{\left(\frac{dS}{dT}\right)_L dT} + \cancel{\left(\frac{dS}{dL_M}\right)_T dL_M}\right]$$

Constant Temperature

Constant Temperature

Constant Length

$$dS = \left(\frac{dS}{dL}\right)_T dL \longrightarrow \int_{S_i}^{S_f} dS = \int \left(\frac{dS}{dT}\right)_T dL$$

Now Let's Look to our Savior Helmholtz for a clutch dS formula.

② Bungee Cont.)

Helmholtz: $F = U - TS \rightarrow dF = dU - TdS - SdT$

Plug in our dU equation $\rightarrow$ $dU = TdS + \tau dL$

$$dF = (\cancel{TdS} + \tau dL) - \cancel{TdS} - SdT \rightarrow dF = \tau dL - SdT$$

Now we can use Maxwell's relations to rewrite

$$\left[\frac{d}{dL}\left(\frac{dF}{dT}\right)_L\right]_T = \left[\frac{d}{dT}\left(\frac{dF}{dL}\right)_T\right]_L \longrightarrow -\left(\frac{dS}{dL}\right)_T = \left(\frac{d\tau}{dT}\right)_L$$

Then our entropy equation is

$$\int_{S_i}^{S_f} dS = -\int \left(\frac{d\tau}{dT}\right)_L dL \leftarrow \text{and we know what } \tau \text{ is}$$

$$\frac{d}{dT}(\tau) = \frac{d}{dT}\left[\left(a - be^{\frac{T}{T_1}}\right)\tan\left(\frac{\pi L}{2L_M}\right)\right]$$

$$\left(\frac{d\tau}{dT}\right)_L = \tan\left(\frac{\pi L}{2L_M}\right)\left(-\frac{b}{T_1}e^{\frac{T}{T_1}}\right) \rightarrow \left(\frac{d\tau}{dT}\right)_L = \frac{b}{T_1}e^{-\frac{T}{T_1}}\tan\left(\frac{\pi L}{2L_M}\right)$$

(2) Bungie Cont.)

Plug back into ΔS $\left(\int_{S_i}^{S_f} dS = \Delta S\right)$

$$\Delta S = \int_{\frac{1}{2}L_M}^{L} \left(\frac{b}{T_1} e^{\frac{T}{T_1}} \tan\left(\frac{\pi L}{2L_M}\right)\right) dL$$

$$\Delta S = \frac{b}{T_1} e^{-\frac{T}{T_1}} \left(\frac{2L_M}{\pi}\right)\left[-\ln\left(\cos\left(\frac{\pi L}{2L_M}\right)\right)\right]_{\frac{L_M}{2}}^{L}$$

$$\Delta S = \frac{b}{T_1} e^{-\frac{T}{T_1}} \left(-\frac{2L_M}{\pi}\right)\left[\ln\left(\frac{\cos\left(\frac{\pi L}{2L_M}\right)}{\cos\left(\frac{\pi (L_M/2)}{2L_M}\right)}\right)\right]$$

$$\Delta S = -\frac{b}{T_1} e^{-\frac{T}{T_1}} \left(\frac{2L_M}{\pi}\right) \ln\left(\frac{\cos\left(\frac{\pi L}{2L_M}\right)}{\cos\left(\frac{\pi}{4}\right)}\right)$$

And finally, we get

$$\boxed{\Delta S = -\frac{b}{T_1} e^{-\frac{T}{T_1}} \left(\frac{2L_M}{\pi}\right) \ln\left(\frac{\sqrt{2}}{1} \cos\left(\frac{\pi L}{2L_M}\right)\right)}$$

Or, if you will, $\Delta S = \left(-\frac{b}{T_1} e^{-\frac{T}{T_1}}\right) \frac{\Delta F}{C_M}$

(2) Bungee Cont.)

d) Solve for the change in $\Delta U = U(T,L) - U(T, \frac{1}{2}L_M)$

using the Thermodynamic identity $dU = TdS + \tau dL$ and Helmholtz $F = U - TS$, we can say

$$\Delta F = \Delta U - T\Delta S \rightarrow \Delta U = \Delta F + T\Delta S$$

$$\Delta U = \left[-\frac{C_L(2L_M)}{\pi} \left[\ln\left(\frac{\sqrt{2}}{1} \cos\left(\frac{\pi L}{2L_M} \right) \right) \right] \right]$$

$$+ T\left[-\frac{b}{T_1} e^{-\frac{T}{T_1}} \left(\frac{2L_M}{\pi} \right) \ln\left(\frac{\sqrt{2}}{1} \cos\left(\frac{\pi L}{2L_M} \right) \right) \right]$$

$$\Delta U = \left(\frac{2L_M}{\pi} \right) \ln\left(\frac{\sqrt{2}}{1} \cos\left(\frac{\pi L}{2L_M} \right) \right) \left[a - be^{-\frac{T}{T_1}} + \frac{T}{T_1} b e^{-\frac{T}{T_1}} \right]$$

$$\boxed{\Delta U = \left(\frac{2L_M}{\pi} \right) \ln\left(\frac{\sqrt{2}}{1} \cos\left(\frac{\pi L}{2L_M} \right) \right) \left[a - be^{-\frac{T}{T_1}} \left(1 - \frac{T}{T_1} \right) \right]}$$

③ Plastic Rod

a) Using a Maxwell relation, we can say that

$$\boxed{U = U(T,L) \rightarrow dU = \left[\left(\frac{dU}{dT}\right)_L dT + \left(\frac{dU}{dL}\right)_T dL\right]}$$

b) Show that $\left(\frac{\partial U}{\partial L}\right)_T = -aT^2(L-L_0)$

From Helmholtz, we know that $F = U - TS$ and therefore $dF = dU - TdS - SdT$. We can plug our equation $dU = TdS + \tau dL$ and simplify.

$$dF = dU - TdS - SdT \rightarrow dF = (\cancel{TdS} + \tau dL) - \cancel{TdS} - SdT$$

$$dF = \tau dL - SdT \rightarrow dF = \tau dL - \cancel{SdT}$$

$$\tau = \left(\frac{\partial F}{\partial L}\right)_T \rightarrow \tau = \frac{d}{dL}(U - TS) \rightarrow \tau = \frac{dU}{dL} - \frac{dS}{dL}(T)$$

$$\tau = aT^2(L-L_0) = \frac{dU}{dL} - T\frac{dS}{dL}$$

Now we need to derive a maxwell relation

③ Plastic Rod Cont.)

we know from $dF = \tau dL - SdT = \left(\frac{\partial F}{\partial T}\right)_L dT + \left(\frac{\partial F}{\partial L}\right)_T dL$
that

$$S = -\left(\frac{\partial F}{\partial T}\right)_L = \left(-\frac{d}{dL}\left(\frac{\partial F}{\partial T}\right)_L\right)_T = -\left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial L}\right)_T\right)_L = -\left(\frac{\partial \tau}{\partial T}\right)_L$$

we can then plug this back into our equation

$$a\,T^2(L-L_0) = \frac{dy}{dL} - T\left(-\frac{\partial \tau}{\partial T}\right)_L$$

$$a\,T^2(L-L_0) = \left(\frac{\partial u}{\partial L}\right)_T + (T)\frac{\partial}{\partial T}\left(a\,T^2(L-L_0)\right)$$

$$aT^2(L-L_0) = \left(\frac{\partial y}{\partial L}\right)_T + \left(2aT^2(L-L_0)\right)$$

$$\left(\frac{\partial u}{\partial L}\right)_T = aT^2(L-L_0) - 2aT^2(L-L_0)$$

$$\boxed{\left(\frac{\partial y}{\partial L}\right)_T = -aT^2(L-L_0)}$$

Hence, shown.

3 Plastic Rod

c) Using the thermodynamic Identity, we get

$$dU = \underbrace{TdS}_{\text{Internal Energy}} + \underbrace{\tau dL}_{\text{Work}} \longleftrightarrow U(T,L) = \left(\frac{\partial U}{\partial T}\right)_L dT + \left(\frac{\partial U}{\partial L}\right)_T dL$$

we know that $C_L T = Q$ and $\tau d\ell = W$

$$dU = (C_L \cdot dT) - (\tau dL) \rightarrow \Delta U = \int_{T_0}^{T} (b \cdot T) \cdot dT - \int_{L_0}^{L} \tau \, dL$$

$$\Delta U = \frac{b}{2}(T - T_0)^2 - \left[\left(\frac{aT^2L^2}{2} - LL_0\right) - \left(\frac{aT^2L_0^2}{2} - L_0^2\right)\right]$$

$$\boxed{\Delta U = \frac{b}{2}(T-T_0)^2 - \left[aT^2\left(\frac{L^2}{2} - L_0 L + \frac{L_0^2}{2}\right)\right]}$$

④ Using Gibbs Free Energy

$$G = -kTN \ln\left(\frac{aT^{\frac{5}{2}}}{p}\right) = \Delta H - T\Delta S \quad ; \quad \Delta H = U + PV$$

We can write Gibbs in the following way

$$dG = -SdT + VdP = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

From this, we can see that $S = -\left(\frac{\partial G}{\partial T}\right)_p$

Thus, $S = \frac{d}{dT}\left(kTN \ln\left(\frac{aT^{5/2}}{p}\right)\right)_p$

Finally, plugging into wolfram, we get

$$\boxed{S = kN \ln\left(\frac{aT^{\frac{5}{2}}}{p}\right) + \frac{5}{2}}$$

6) Find Heat Capacity at Constant pressure.

Using the equations given, we know that

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\left[kN\frac{\partial}{\partial T}\left(\ln\left(\frac{aT^{\frac{5}{2}}}{p}\right) + \frac{5}{2}\right)_p\right]$$

④ Using Gibbs Free Energy

$$C_p = Tk_B N + \frac{\partial}{\partial T}\left(\frac{5}{2} \ln\left(\frac{T}{P}\right)\right)_P \rightarrow C_p = \frac{(\cancel{T}k_B N)}{\cancel{T}}\left(\frac{5}{2}\right)$$

$$\boxed{C_p = \frac{5k_B N}{2}}$$

c) Stating from $dG = VdP - SdT$ again, we can say

$$V = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{holding } T \text{ constant where } dT = 0$$

Thus,

$$V = \frac{d}{dP}\left[-k_B TN \ln\left(\frac{aT^{\frac{5}{2}}}{P}\right)\right]$$

$$V = -k_B TN\left(\frac{\cancel{P}}{\cancel{aT^{\frac{5}{2}}}}\right)\left(-\frac{\cancel{aT^{\frac{5}{2}}}}{\cancel{P^2}}\right) \rightarrow \boxed{V = \frac{k_B TN}{P}}$$

d) Starting from $G = U - TS - PV$. Rearranging, we get.

$$U = G + TS + PV$$

(4) Using Gibbs Free Energy

$$U = \left(-k_B T N \ln\left(\frac{aT^{\frac{5}{2}}}{P}\right)\right) + T\left(k_B N\left(\frac{5}{2} + \ln\left(\frac{aT^{\frac{5}{2}}}{P}\right)\right)\right) + \cancel{P}\left(\frac{k_B T N}{\cancel{P}}\right)$$

$$U = -k_B T N \ln\left(\frac{aT^{\frac{5}{2}}}{P}\right) + \frac{5}{2} T k_B N + T k_B N \ln\left(\frac{aT^{\frac{5}{2}}}{P}\right) + k_B T N$$

$$\boxed{U = \frac{7}{5} N k_B T}$$

⑤ Non-Ideal Gas

Find $\left(\frac{\partial U}{\partial V}\right)_T$ and determine its sign.

Effectively, show $\left(\frac{\partial U}{\partial V}\right)_T = \frac{Nk_BT}{V}\left(1 + \frac{NB_2(T)}{V}\right)$

using $dU = TdS - PdV$ and Helmholtz, we can say

$$dU = TdS - PdV \rightarrow dF = -PdV - \overset{\text{const}}{\cancel{SdT}} \rightarrow -P = \left(\frac{dF}{dV}\right)_T$$

$$-P = \frac{d}{dV}(U - TS)_T \rightarrow -P = \left(\frac{dU}{dV}\right)_T - T\left(\frac{dS}{dV}\right)_T$$

we know from $dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV$ that

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \left(-\frac{d}{dV}\left(\frac{\partial F}{\partial T}\right)_V\right)_T = -\left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right)_V = -\left(\frac{\partial S}{\partial V}\right)_V$$

So, plugging back in, we get

$$-P = \left(\frac{\partial U}{\partial V}\right)_T - T\left(-\frac{\partial S}{\partial V}\right)_V \rightarrow \left(\frac{\partial U}{\partial V}\right)_T = -\left(\frac{Nk_BT}{V}\right) - T\left(\frac{\partial S}{\partial V}\right)_V$$

5 Non-Ideal Gas

From our S derivation, we saw

$$\left(-\frac{d}{dV}\left(\frac{\partial F}{\partial T}\right)_V\right)_T = -\left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right)_V = \left(\frac{\partial S}{\partial V}\right)_V$$

$$\left(-\frac{d}{dT}\left(\frac{\partial F}{\partial V}\right)_T\right)_V = \left(\frac{\partial S}{\partial V}\right)_V$$

$$\left(-\frac{d}{dT}(-P)_T\right)_V = \left(\frac{\partial S}{\partial V}\right)_V \quad \text{where } -P = \left(\frac{dF}{dV}\right)_T$$

Therefore, we can say

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{Nk_BT}{V} + \left[\frac{d}{dT}\left(\frac{Nk_BT}{V}\right)\right]$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{Nk_BT}{V} + \frac{N^2k_B}{V^2}\left(\frac{dB}{dT} + B\right)$$

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{Nk_B}{V}\left[1 + \frac{N}{V}\left(\frac{\partial B}{\partial T} + B\right)\right]$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{Nk_BT}{V}\left(1 + \frac{NB(T)}{V}\right)}$$

Hence, Shown