PHY 831: Statistical Mechanics
Homework 1

Due September 14th, 2020

1. Starting with
$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$$
show that the entropy can be derived from the Helmholtz free energy, defined as $F \equiv E - TS$, to be
$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}$$

2. Consider a system in which the entropy $S(N, V, E)$ is an extensive quantity.

   (a) Show that
$$S = \left(\frac{\partial S}{\partial N}\right)_{V,E} N + \left(\frac{\partial S}{\partial V}\right)_{N,E} V + \left(\frac{\partial S}{\partial E}\right)_{N,V} E$$

   (b) Show that this in turn results in
$$E = TS - PV + \mu N$$

3. Derive the Maxwell relations
$$\left(\frac{\partial T}{\partial \mu}\right)_{N,P} = -\left(\frac{\partial N}{\partial S}\right)_{T,P}$$
and
$$\left(\frac{\partial P}{\partial T}\right)_{S,N} = \left(\frac{\partial S}{\partial V}\right)_{P,N}$$

4. A substance has the following properties:

   (i) At constant temperature T_0 the work done by it expanding from V_0 to V is
$$W = T_0 \ln \frac{V}{V_0} \tag{1}$$

   (ii) The entropy of the substance is give by
$$S = \frac{V}{V_0}\left(\frac{T}{T_0}\right)^a \tag{2}$$

   where V_0, T_0, and a are fixed constants.

1. From $F = E - TS$ follows $dF = dE - TdS - SdT$

and we have $dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$ $\Rightarrow$ $dE = TdS - PdV + \mu dN$

$$\Rightarrow dF = -SdT - PdV + \mu dN$$
$$= \left(\frac{\partial F}{\partial T}\right)_{N,V} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

$$\boxed{\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}}$$

2. S is extensive: $\lambda S(E,V,N) = S(\lambda E, \lambda V, \lambda N)$

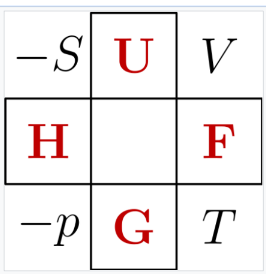
Take derivative: $\frac{\partial}{\partial \lambda}[\lambda S] = S = \left(\frac{\partial S}{\partial(\lambda E)}\right)_{\lambda V, \lambda N} E + \left(\frac{\partial S}{\partial(\lambda V)}\right)_{\lambda E, \lambda N} V + \left(\frac{\partial S}{\partial(\lambda N)}\right)_{\lambda E, \lambda V} N$

Since this has to hold for any λ and the choice of λ is arbitrary, set $\lambda = 1$.

$$\Rightarrow \boxed{S = \underbrace{\left(\frac{\partial S}{\partial E}\right)_{V,N}}_{1/T} E + \underbrace{\left(\frac{\partial S}{\partial V}\right)_{E,N}}_{P/T} V + \underbrace{\left(\frac{\partial S}{\partial N}\right)_{E,V}}_{-\mu/T} N} \quad (a)$$

$$= \frac{E}{T} + \frac{VP}{T} - \frac{\mu N}{T} \Rightarrow \boxed{E = TS - PV + \mu N} \quad b)$$

3.



The thermodynamic square with potentials highlighted in red.

Schwarz' theorem (general)

$$\frac{\partial}{\partial x_j}\left(\frac{\partial \Phi}{\partial x_i}\right) = \frac{\partial}{\partial x_i}\left(\frac{\partial \Phi}{\partial x_j}\right)$$

Helmholtz free energy: $dF = -p\,dV - S\,dT + \mu\,dN$

$$\Rightarrow -S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \text{ and } -p = \left(\frac{\partial F}{\partial V}\right)_{T,N}$$

Symmetry of second derivatives (Schwarz' theorem):

$$\left(\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_{V,N}\right)_{P,N} = \left(\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_{T,N}\right)_{S,N} \Rightarrow \left(\frac{\partial}{\partial V}(-S)\right)_{P,N} = \left(\frac{\partial}{\partial T}(-p)\right)_{S,N}$$

$$\Leftrightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_{P,N} = \left(\frac{\partial p}{\partial T}\right)_{S,N}}$$

For the other one we use Gibbs' function: $dG = -S\,dT + V\,dp + \mu\,dN$

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

Again, using Schwarz' theorem: $\left(\frac{\partial}{\partial N}\left(\frac{\partial G}{\partial T}\right)_{p,N}\right)_{T,p} = \left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial N}\right)_{T,p}\right)_{N,p}$

$$\Rightarrow -\left(\frac{\partial S}{\partial N}\right)_{T,p} = \left(\frac{\partial \mu}{\partial T}\right)_{N,p}$$

Take reciprocal: $\Rightarrow \boxed{-\left(\frac{\partial N}{\partial S}\right)_{T,p} = \left(\frac{\partial T}{\partial \mu}\right)_{N,p}}$

(a) Calculate the Helmholtz free energy (relative to the Helmholtz free energy at (V_0, T_0)).

(b) Find the equation of state.

(c) Find the work done by an arbitrary expansion at an arbitrary constant temperature.

5. Consider a Carnot cycle where the working substance is an ideal gas with the equation of state $PV = NT$, energy $E = NT/(\gamma - 1)$, and entropy given by

$$S = N \ln \left[\left(\frac{E}{E_0} \right)^{\frac{1}{\gamma-1}} \frac{V}{V_0} \right] + N\mathcal{S}(N), \tag{3}$$

where γ is a constant. The cycle operates between temperatures T_1 and T_2 ($T_1 > T_2$) and decompresses at T_1 from volume V_a to volume V_b.

(a) Explicitly calculate the work done and heat gained or lost in each step of the cycle.

(b) Explicitly show this cycle has an efficiency

$$\eta = 1 - \frac{T_2}{T_1}$$

4.

4. A substance has the following properties:

(i) At constant temperature T_0 the work done by it expanding from V_0 to V is

$$W = T_0 \ln \frac{V}{V_0} \quad \cdot R \text{ missing!} \tag{1}$$

(ii) The entropy of the substance is give by

$$S = \frac{V}{V_0}\left(\frac{T}{T_0}\right)^a \tag{2}$$

where V_0, T_0, and a are fixed constants.

(a) We have $dF = -PdV - SdT$ (N constant) $\Rightarrow$ $P = -\left(\frac{\partial F}{\partial V}\right)_T$, $S = -\left(\frac{\partial F}{\partial T}\right)_V$

We can integrate along isotherms: $F(V,T_0) = -\int_{V_0}^{V} P\,dV = -\Delta Q = -\Delta W = -RT_0 \ln \frac{V}{V_0}$

And with that for any temperature it follows:

$$F(V,T) = -\int_{T_0}^{T} S(V,T)\,dT + F(V,T_0) = -\int_{T_0}^{T} R\frac{V}{V_0}\left(\frac{T}{T_0}\right)^a dT + F(V,T_0)$$

$$= -RT_0 \ln\frac{V}{V_0} - R\frac{V}{V_0} T_0^{-a} \left.\frac{T^{a+1}}{a+1}\right|_{T_0}^{T}$$

$$= \boxed{-RT_0 \ln\frac{V}{V_0} + \frac{RVT_0}{V_0(a+1)}\left(1-\left(\frac{T}{T_0}\right)^{a+1}\right) = F}$$

(b) Using the result from (a) and the Maxwell relation $P = -\left(\frac{\partial F}{\partial V}\right)_T$

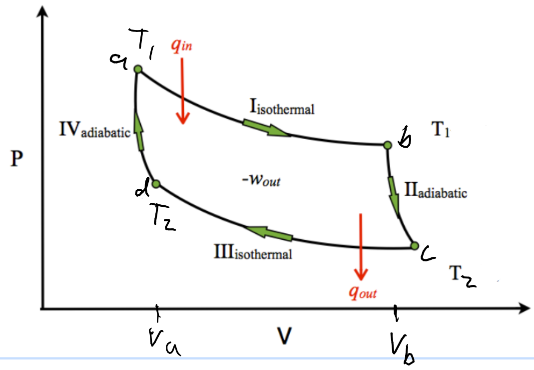
$$\Rightarrow \boxed{P = \frac{RT_0}{V} - \frac{RT_0}{V_0(a+1)}\left(1-\left(\frac{T}{T_0}\right)^{a+1}\right)}$$

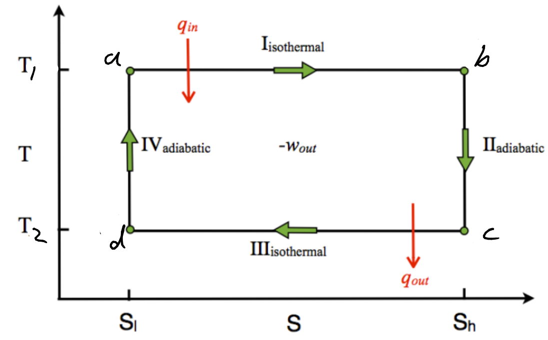
(c)

$$W = \int_{V_0}^{V} P\,dV = RT_0 \ln\frac{V}{V_0} - \frac{RT_0}{V_0(a+1)}\left(1-\left(\frac{T}{T_0}\right)^{a+1}\right)(V-V_0)$$

$$\boxed{W = RT_0 \ln\frac{V}{V_0} - \frac{RT_0}{a+1}\left(1-\left(\frac{T}{T_0}\right)^{a+1}\right)\left(\frac{V}{V_0}-1\right)}$$

5.





(a)

$a \to b$: isothermal $\quad T = T_1 \Rightarrow W_{ab} = \int_{V_a}^{V_b} P\,dV \overset{PV=NT}{=} NT_1 \int_{V_a}^{V_b} \frac{dV}{V} = NT_1 \ln \frac{V_b}{V_a}$

$\Delta E = \Delta Q - \Delta W = q_{in} - W_{ab} = 0 = \frac{N(T_1 - T_1)}{\gamma - 1}$ so $\boxed{W_{ab} = q_{ab} = q_{in} = NT_1 \ln \frac{V_b}{V_a}}$

$b \to c$: adiabatic $\boxed{q_{bc} = 0}$ and $P(V) = P_b \left(\frac{V_b}{V}\right)^{\gamma} = \frac{NT_1}{V_b}\left(\frac{V_b}{V}\right)^{\gamma}$

so $W_{bc} = \int_{V_b}^{V_c} P\,dV = \frac{NT_1 V_b^{\gamma-1}}{\gamma-1}\left(V_c^{1-\gamma} - V_b^{1-\gamma}\right) = \frac{NT_1}{\gamma-1}\left(1 - \left(\frac{V_c}{V_b}\right)^{1-\gamma}\right)$

with $P_c = \frac{NT_2}{V_c} = \frac{NT_1}{V_b}\left(\frac{V_b}{V_c}\right)^{\gamma}$ follows $\frac{V_b}{V_c} = \left(\frac{T_2}{T_1}\right)^{\frac{1}{\gamma-1}}$

and therefore $\boxed{W_{bc} = \frac{NT_1}{\gamma-1}\left(1 - \frac{T_2}{T_1}\right) = \frac{N}{\gamma-1}(T_1 - T_2)}$

$c \to d$: isothermal so same as $a \to b$ just substitute T_1 for T_2
V_a for V_c
and V_b for V_d

$\boxed{q_{out} = q_{cd} = W_{cd} = NT_2 \ln\left(\frac{V_d}{V_c}\right)}$

$d \to$ adiabatic same as $b \to c$ with $T_1 \leftrightarrow T_2$, $V_b \to V_d$, $V_c \to V_a$

$\boxed{q_{da} = 0}$

$\boxed{W_{da} = \frac{N}{\gamma-1}(T_2 - T_1) = -W_{bc}}$

(b) $W = W_{ab} + \cancel{W_{bc}} + W_{cd} + \cancel{W_{da}} = W_{ab} + W_{cd}$

because $\frac{V_d}{V_a} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{\gamma-1}} = \frac{V_c}{V_b}$

$\Rightarrow \frac{V_d}{V_c} = \frac{V_a}{V_b}$

$= NT_1 \ln \frac{V_b}{V_a} + NT_2 \ln \frac{V_d}{V_c} = N(T_1 - T_2)\ln \frac{V_b}{V_c}$

$\Rightarrow \eta = \frac{W}{\underbrace{q_{in}}_{= W_{ab}}} = \frac{\cancel{N}(T_1 - T_2)\cancel{\ln \frac{V_b}{V_a}}}{\cancel{N}\, T_1 \cancel{\ln \frac{V_b}{V_a}}} = \frac{T_1 - T_2}{T_1} = \boxed{1 - \frac{T_2}{T_1} = \eta}$