MAU34405: Statistical Physics I
Homework 2 due 08/11/2021

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Exercise 1

$$\begin{aligned} dE &= \frac{\partial E}{\partial X_1}\,dX_1 + \frac{\partial E}{\partial X_2}\,dX_2 \\ &= P_1\,dX_1 + P_2\,dX_2 \\ \implies P_i &= \frac{\partial E}{\partial X_i}, \qquad i = 1,2 \end{aligned}$$

$$\begin{aligned} \text{Consider } d\Phi_i &\equiv d(E - P_i\,X_i) \\ &= P_1\,dX_1 + P_2\,dX_2 - X_i\,dP_i - P_i\,dX_i \\ &= -X_i\,dP_i + P_j\,dX_j, \qquad i,j = 1,2,\ i \neq j \\ \implies \Phi_i &= \Phi_i(P_i, X_j) \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 \Phi_i}{\partial P_i^2} &= \frac{\partial(-X_i)}{\partial P_i} \\ &= -\left(\frac{\partial P_i}{\partial X_i}\right)^{-1} \\ &= -\left(\frac{\partial^2 E}{\partial X_i^2}\right)^{-1} \\ &\leq 0 \implies \Phi_i \text{ concave function of } P_i \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 \Phi_i}{\partial X_j^2} &= \frac{\partial P_j}{\partial X_j} \\ &= \frac{\partial^2 E}{\partial X_j^2} \\ &\geq 0 \implies \Phi_i \text{ convex function of } X_j \end{aligned}$$

$$\begin{aligned} \text{Consider } d\Psi &\equiv d(E - P_1\,X_1 - P_2\,X_2) \\ &= P_1\,dX_1 + P_2\,dX_2 - X_1\,dP_1 - P_1\,dX_1 - X_2\,dP_2 - P_2\,dX_2 \\ &= -X_1\,dP_1 - X_2\,dP_2 \\ \implies \Psi &= \Psi(P_1, P_2) \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 \Psi}{\partial P_i^2} &= \frac{\partial(-X_i)}{\partial P_i} \\ &= -\left(\frac{\partial P_i}{\partial X_i}\right)^{-1} \\ &= -\left(\frac{\partial^2 E}{\partial X_i^2}\right)^{-1} \\ &\leq 0 \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 \Psi}{\partial P_1^2}\,\frac{\partial^2 \Psi}{\partial P_2^2} - \left(\frac{\partial^2 \Psi}{\partial P_1 \partial P_2}\right)^2 &= \frac{\partial(-X_1)}{\partial P_1}\,\frac{\partial(-X_2)}{\partial P_2} - \left(\frac{\partial(-X_2)}{\partial P_1}\right)^2 \\ &= \left(\frac{\partial P_1}{\partial X_1}\,\frac{\partial P_2}{\partial X_2}\right)^{-1} - \left(\frac{\partial P_1}{\partial X_2}\right)^{-2} \\ &= \left(\frac{\partial^2 E}{\partial X_1^2}\,\frac{\partial^2 E}{\partial X_2^2}\right)^{-1} - \left(\frac{\partial^2 E}{\partial X_2\,\partial X_1}\right)^{-2} \end{aligned}$$

$$\begin{aligned} \frac{\partial^2 E}{\partial X_1^2}\,\frac{\partial^2 E}{\partial X_2^2} - \left(\frac{\partial^2 E}{\partial X_2\,\partial X_1}\right)^2 \geq 0 &\implies \left(\frac{\partial^2 E}{\partial X_1^2}\,\frac{\partial^2 E}{\partial X_2^2}\right)^{-1} - \left(\frac{\partial^2 E}{\partial X_2\,\partial X_1}\right)^{-2} \leq 0 \\ \implies \frac{\partial^2 \Psi}{\partial P_1^2}\,\frac{\partial^2 \Psi}{\partial P_2^2} - \left(\frac{\partial^2 \Psi}{\partial P_1 \partial P_2}\right)^2 &\leq 0 \end{aligned}$$

Thus any Legendre transform of E, whether it has one or two intensive variables, will be a convex function of its extensive variables and a concave function of its intensive parameters.

Exercise 2

1.

First: derive the adiabatic process equations.

$$
\begin{aligned}
\text{Ideal gas, reversible process} \implies C_V &\equiv \left(\frac{\partial E}{\partial T}\right)_V = \frac{dE}{dT} \\
\implies dE &= C_V\, dT \\
đQ &= dE - đW \\
&= C_V\, dT + P\, dV \\
C_P &\equiv \frac{đQ_P}{dT} \\
&= \left(\frac{\partial}{\partial T}\right)_P đQ \\
&= C_V + P\left(\frac{\partial V}{\partial T}\right)_P
\end{aligned}
$$

$$
\begin{aligned}
P\,V &= k\,N\,T \\
\implies \left(\frac{\partial}{\partial T}\right)_P (P\,V) &= \left(\frac{\partial}{\partial T}\right)_P (k\,N\,T) \\
\implies P\left(\frac{\partial V}{\partial T}\right)_P &= k\,N \\
\implies C_P &= C_V + k\,N \\
\implies \frac{k\,N}{C_V} &= \gamma - 1, \qquad \gamma \equiv \frac{C_P}{C_V}
\end{aligned}
$$

$$
\begin{aligned}
\text{Adiabatic} \implies 0 &= đQ \\
&= dE + P\, dV \\
&= C_V\, dT + \frac{k\,N\,T}{V}\, dV \\
\implies C_V \frac{dT}{T} &= C_V\,(1-\gamma)\frac{dV}{V} \\
\implies \ln T &= (1-\gamma)\ln V + \alpha \\
\implies T &= e^\alpha\, V^{1-\gamma} \\
\implies T\,V^{\gamma-1} &= e^\alpha
\end{aligned}
$$

$$
T = \frac{P\,V}{k\,N} \implies \frac{P\,V}{k\,N} V^{\gamma-1} = e^\alpha \qquad\qquad V = \frac{k\,N\,T}{P} \implies T\left(\frac{k\,N\,T}{P}\right)^{\gamma-1} = e^\alpha
$$

$$
\implies P\,V^\gamma = k\,N\,e^\alpha \qquad\qquad \implies T^\gamma\,P^{1-\gamma} = \frac{e^\alpha}{(k\,N)^{\gamma-1}}
$$

$$
\implies P\,T^{\frac{\gamma}{1-\gamma}} = \left(\frac{e^\alpha}{(k\,N)^{\gamma-1}}\right)^{\frac{1}{1-\gamma}}
$$

$$
e, \alpha, k, N, \gamma \text{ constants} \implies P\,V^\gamma = \text{constant} \qquad T\,V^{\gamma-1} = \text{constant} \qquad P\,T^{\frac{\gamma}{1-\gamma}} = \text{constant}
$$

As is clear from the figure, the system attains its minimum volume V_1 at point B, its maximum volume V_2 at points A and D, its minimum pressure P_1 at point A, and its maximum pressure P_2 at points B and C.

From investigating the figure, we can see that $V_B < V_C$ and $P_B = P_C$, and $V_A = V_D$ and $P_A < P_D$. From $P\,V = k\,N\,T$, we can deduce that the minimum temperature T_1 must occur at either A or B, and the maximum temperature T_2 at C or D.

$$\begin{aligned} T_A\,V_A^{\gamma-1} &= T_B\,V_B^{\gamma-1} \\ T_A\,V_2^{\gamma-1} &= T_B\,V_1^{\gamma-1} \\ \frac{T_A}{T_B} &= \left(\frac{V_1}{V_2}\right)^{\gamma-1} \\ V_1 < V_2 \implies T_A &< T_B \\ \implies T_A &= T_1 \end{aligned}$$

$$\begin{aligned} T_C\,V_C^{\gamma-1} &= T_D\,V_D^{\gamma-1} \\ T_C\,V_C^{\gamma-1} &= T_D\,V_2^{\gamma-1} \\ \frac{T_C}{T_D} &= \left(\frac{V_2}{V_C}\right)^{\gamma-1} \\ V_2 > V_C \implies T_C &> T_D \\ T_C &= T_2 \end{aligned}$$

$$\begin{aligned} P_B\,V_B &= k\,N\,T_B \\ P_2\,V_1 &= k\,N\,T_B \\ T_B &= \frac{P_2\,V_1}{k\,N} \end{aligned}$$

$$\begin{aligned} P_C\,V_C &= k\,N\,T_C \\ P_2\,V_C &= k\,N\,T_2 \\ V_C &= \frac{k\,N\,T_2}{P_2} \end{aligned}$$

$$\begin{aligned} P_C\,V_C^{\gamma} &= P_D\,V_D^{\gamma} \\ P_2\left(\frac{k\,N\,T_2}{P_2}\right)^{\gamma} &= P_D\,V_2^{\gamma} \\ P_D &= P_2\left(\frac{k\,N\,T_2}{P_2\,V_2}\right)^{\gamma} \end{aligned}$$

$$\begin{aligned} T_C\,V_C^{\gamma-1} &= T_D\,V_D^{\gamma-1} \\ T_2\left(\frac{k\,N\,T_2}{P_2}\right)^{\gamma-1} &= T_D\,V_2^{\gamma-1} \\ T_D &= T_2\left(\frac{k\,N\,T_2}{P_2\,V_2}\right)^{\gamma-1} \end{aligned}$$

$$(P_A, V_A, T_A) = (P_1, V_2, T_1) \qquad (P_C, V_C, T_C) = \left(P_2, \frac{k\,N\,T_2}{P_2}, T_2\right)$$

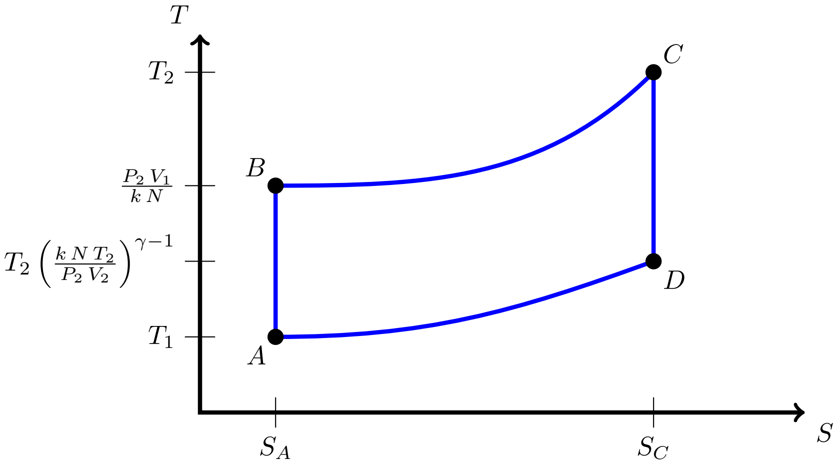
$$(P_B, V_B, T_B) = \left(P_2, V_1, \frac{P_2\,V_1}{k\,N}\right) \qquad (P_D, V_D, T_D) = \left(P_2\left(\frac{k\,N\,T_2}{P_2\,V_2}\right)^{\gamma}, V_2, T_2\left(\frac{k\,N\,T_2}{P_2\,V_2}\right)^{\gamma-1}\right)$$

2.

$$S = c\,k\,N\ln\left(\frac{E}{E_0}\right) + k\,N\ln\left(\frac{V}{V_0}\right) + f(N)$$

$$E = c\,k\,N\,T,\ N \text{ constant} \implies \Delta S_{i\to f} = S_f - S_i = c\,k\,N\ln\left(\frac{T_f}{T_i}\right) + k\,N\ln\left(\frac{V_f}{V_i}\right)$$

$$\begin{aligned} A\to B: T_B > T_A,\ \text{adiabatic} &\implies \Delta S_{A\to B} = 0 \\ B\to C: T_C > T_B,\ V_C > V_B &\implies \Delta S_{B\to C} = c\,k\,N\ln\left(\frac{T_C}{T_B}\right) + k\,N\ln\left(\frac{V_C}{V_B}\right) > 0 \\ C\to D: T_D < T_C,\ \text{adiabatic} &\implies \Delta S_{C\to D} = 0 \\ D\to A: T_A < T_D,\ V_A = V_D &\implies \Delta S_{D\to A} = c\,k\,N\ln\left(\frac{T_A}{T_D}\right) < 0 \end{aligned}$$



3.

$$\eta = \frac{W}{Q_{\text{abs}}} = \frac{Q_{\text{abs}} - Q_{\text{exp}}}{Q_{\text{abs}}} = 1 - \frac{Q_{\text{exp}}}{Q_{\text{abs}}}$$

We only need to calculate the heat transfer during $B \to C$ and $D \to A$, since $A \to B$ and $C \to D$ are adiabatic and thus have no heat transfer.

$$\begin{aligned} Q_{\text{abs}} &= đQ_{B\to C} \\ &= \Delta E_{B\to C} + đW_{B\to C} \\ &= c\,k\,N\,(T_C - T_B) - \int_{V_B}^{V_C} P\,dV \\ &= c\,k\,N\left(T_2 - \frac{P_2\,V_1}{k\,N}\right) - P_2\left(\frac{k\,N\,T_2}{P_2} - V_1\right) \\ &= (c-1)\,(k\,N\,T_2 - P_2\,V_1) \end{aligned}$$

$$\begin{aligned} -Q_{\text{exp}} &= đQ_{D\to A} \\ &= \Delta E_{D\to A} + đW_{D\to A} \\ &= c\,k\,N\,(T_A - T_D) - \int_{V_D}^{V_A} P\,dV \\ &= c\,k\,N\left(T_1 - T_2\left(\frac{k\,N\,T_2}{P_2\,V_2}\right)^{\gamma-1}\right) - 0 \\ &= c\,k\,N\left(T_1 - T_2\left(\frac{k\,N\,T_2}{P_2\,V_2}\right)^{\gamma-1}\right) \end{aligned}$$

$$\implies \eta = 1 + \frac{c\,k\,N}{(c-1)\,(k\,N\,T_2 - P_2\,V_1)}\left(T_1 - T_2\left(\frac{k\,N\,T_2}{P_2\,V_2}\right)^{\gamma-1}\right)$$

Exercise 3

$$
\begin{aligned}
\left.\frac{dP}{dT}\right|_{\text{boundary}} &= \frac{L}{T\,\Delta v} \\
&= \frac{L}{T\left(\frac{V_v}{N_v} - \frac{V_l}{N_l}\right)} \\
&= \frac{L}{T\,\frac{V_v}{N_v}}
\end{aligned}
$$

(neglecting the volume of the liquid compared to that of the vapor, i.e. $\frac{V_v}{N_v} \gg \frac{V_l}{N_l}$)

$$
\begin{aligned}
&= \frac{P\,L}{k\,T^2} \qquad \left(P = \frac{k\,N\,T}{V} \implies \frac{1}{\frac{V_v}{N_v}} = \frac{P}{k\,T}\right) \\
\frac{dP}{P} &= \frac{L}{k}\,\frac{dT}{T^2} \\
\int_{P_0}^{P} \frac{dP}{P} &= \frac{L}{k} \int_{T_0}^{T} \frac{dT}{T^2} \\
\ln\left(\frac{P}{P_0}\right) &= \frac{L}{k}\left(\frac{1}{T_0} - \frac{1}{T}\right) \\
P &= P_0 \exp\left(\frac{L}{k}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right)
\end{aligned}
$$

Exercise 4

1.

$$
P = \frac{k\,T}{\frac{V}{N} - b} - \frac{a\,N^2}{V^2}
$$

$$
\begin{aligned}
0 &= \left.\frac{\partial P}{\partial V}\right|_{\substack{\text{critical}\\ \text{point}}} \\
&= -\frac{k\,T_c}{N\left(\frac{V_c}{N} - b\right)^2} + \frac{2a\,N^2}{V_c^3} \\
\frac{6aN^2}{V_c^4} &= \frac{3k\,T_c}{N\,V_c\left(\frac{V_c}{N} - b\right)^2} \qquad (1)
\end{aligned}
$$

$$
\begin{aligned}
0 &= \left.\frac{\partial^2 P}{\partial V^2}\right|_{\substack{\text{critical}\\ \text{point}}} \\
&= \frac{2k\,T_c}{N^2\left(\frac{V_c}{N} - b\right)^3} - \frac{6aN^2}{V_c^4} \\
(1) \implies \frac{3k\,T_c}{N\,V_c\left(\frac{V_c}{N} - b\right)^2} &= \frac{2k\,T_c}{N^2\left(\frac{V_c}{N} - b\right)^3} \\
3N\left(\frac{V_c}{N} - b\right) &= 2V_c \\
V_c &= 3b\,N
\end{aligned}
$$

$$(1) \implies \frac{2a\,N^2}{27b^3\,N^3} = \frac{k\,T_c}{N\,(3b-b)^2}$$

$$T_c = \frac{4b^2\,N}{k}\,\frac{2a}{27b^3\,N}$$

$$= \frac{8a}{27k\,b}$$

$$P_c = \frac{k\,T_c}{\frac{V_c}{N} - b} - \frac{a\,N^2}{V_c^2}$$

$$= \frac{\frac{8a}{27b}}{3b-b} - \frac{a\,N^2}{9b^2\,N^2}$$

$$= \frac{4a}{27b^2} - \frac{a}{9b^2}$$

$$= \frac{a}{27b^2}$$

$$T_c = \frac{8a}{27\,k\,b} \qquad P_c = \frac{a}{27b^2} \qquad V_c = 3b\,N$$

2.

$$G = E + P\,V - T\,S$$

$$dG = T\,dS - P\,dV + \mu\,dN + V\,dP + P\,dV - S\,dT - T\,dS$$

$$= -S\,dT + V\,dP + \mu\,dN$$

$$dP = \left(\frac{\partial P}{\partial T}\right)_{V,N} dT + \left(\frac{\partial P}{\partial V}\right)_{T,N} dV + \left(\frac{\partial P}{\partial N}\right)_{T,V} dN$$

$$\implies dG = \left(V\left(\frac{\partial P}{\partial T}\right)_{V,N} - S\right) dT + V\left(\frac{\partial P}{\partial V}\right)_{T,N} dV + \left(\mu + \left(\frac{\partial P}{\partial N}\right)_{T,V}\right) dN$$

$$\left.\frac{\partial G}{\partial V}\right|_{\substack{\text{critical}\\ \text{point}}} = V\left(\frac{\partial P}{\partial V}\right)_{T,N}\Bigg|_{\substack{\text{critical}\\ \text{point}}}$$

$$= V_c \cdot 0$$

$$\left.\frac{\partial G}{\partial V}\right|_{\substack{\text{critical}\\ \text{point}}} = 0$$

$$\left.\frac{\partial^2 G}{\partial V^2}\right|_{\substack{\text{critical}\\ \text{point}}} = \frac{\partial}{\partial V}\left(V\left(\frac{\partial P}{\partial V}\right)_{T,N}\right)\Bigg|_{\substack{\text{critical}\\ \text{point}}}$$

$$= \left(\frac{\partial P}{\partial V}\right)_{T,N}\Bigg|_{\substack{\text{critical}\\ \text{point}}} + V\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,N}\Bigg|_{\substack{\text{critical}\\ \text{point}}}$$

$$\left.\frac{\partial^2 G}{\partial V^2}\right|_{\substack{\text{critical}\\ \text{point}}} = 0$$

Both first and second derivatives of the Gibbs free energy with respect to volume are zero at the critical point, implying that the critical point is a saddle point when considering G as a function of V at constant temperature. This is as expected, as the derivative on the boundary does not jump between values based on which phase the system is in due to it being at its critical point, i.e. a point at which phases are indistinguishable.