Statistical Mechanics 1. HW1. Minga Kim (kim4082@purdue.edu)

① maximum amount of work can be obtained ~~by~~ from two identical bodies

at $T = T_1, T_2$ ($T_1 > T_2$)

C_V is indep. of T.

$\left(T_1\right), \left(T_2\right) \longrightarrow \left(T_f\right), \left(T_f\right)$ say, two bodies thermalize to T_f temp.

initial energy

$$U_i = C_V(T_1 + T_2)$$

final energy

$$U_f = C_V(2T_f)$$

$$\Delta U = U_f - U_i$$

$$= C_V\left(2T_f - (T_1 + T_2)\right)$$

Entropies while thermalization

$$\boxed{\begin{aligned} * \quad & dQ = TdS = C_V dT. \\ & dS = \frac{1}{T} C_V dT \\ & \Delta S = C_V \int_{T_i}^{T_f} \frac{1}{T} dT = C_V \ln \frac{T_f}{T_i} \end{aligned}}$$

$$\Delta S = C_V \ln \frac{T_f}{T_1} + C_V \ln \frac{T_f}{T_2}$$

$$= C_V \ln \frac{T_f^2}{T_1 T_2} = 2C_V \ln \frac{T_f}{T_1 T_2}.$$

minimum entropy $\Rightarrow$ minimum work loss. $\because \Delta U = \Delta Q - \Delta W$.

$\Delta S = 0 \rightsquigarrow T_f = \sqrt{T_1 T_2} \Rightarrow$ Maximum work : $\left| -C_V\left(2\sqrt{T_1 T_2} - (T_1 + T_2)\right)\right.$

② ρ vs p ~~as~~ near critical point.

ρ vs T

vanderwaals equation of state

$$\left(p+\frac{a}{v^2}\right)(v-b)=k_BT \qquad \left(v=\frac{V}{N}\right)$$

v: volume

$\rho = 1/v$: ptcl density

* critical point

$$\begin{cases} \dfrac{dp}{dv} = -\dfrac{k_BT}{(v-b)^2}+\dfrac{2a}{v^3}\Big|_{v_c,T_c,p_c} = 0 \\[2ex] \dfrac{d^2p}{dv^2} = \dfrac{2k_BT}{(v-b)^3}-\dfrac{6a}{v^4}\Big|_{v_c,T_c,p_c} = 0. \end{cases}$$

$$k_BT_c = \frac{2a}{v_c^3}(v_c-b)^2 = \frac{3a}{v_c^4}(v_c-b)^3$$

$$\therefore\ 2 = \frac{3}{v_c}(v_c-b)$$

$$\begin{cases} v_c = 3b, \\ k_BT_c = \dfrac{2a}{27b^3}4b^2 = \dfrac{8a}{27b} \\ p_c = \dfrac{a}{27b^2} \end{cases}$$

$$\begin{cases} \bar p = \dfrac{p}{p_c} \\ \bar v = \dfrac{v}{v_c} \\ \bar T = \dfrac{T}{T_c} \end{cases}$$

$$\left(\frac{p}{p_c}+\frac{a}{(v/v_c)^2}\frac{1}{v_c^2p_c}\right)\left(\frac{v}{v_c}-\frac{b}{v_c}\right)=\frac{k_BT}{p_cv_c}$$

$$=\left(\bar p+\frac{a}{\bar v^2}\cdot\frac{3}{a}\right)\left(\bar v-\frac{1}{3}\right)=\frac{k_BT}{k_BT_c}\cdot\frac{k_BT_c}{p_cv_c}$$

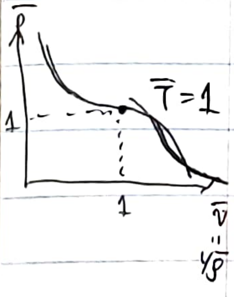
$$=\frac{T}{T_c}\,\frac{8a}{27b}\,\frac{27b^2}{3b\,a}=\frac{8}{3}\bar T$$

Law of corresponding states

$$\left(\bar p+\frac{3}{\bar v^2}\right)\left(\bar v-\frac{1}{3}\right)=\frac{8}{3}\bar T$$

or

$$\left(\bar p+3\bar\rho^2\right)\left(\frac{1}{\bar\rho}-\frac{1}{3}\right)=\frac{8}{3}\bar T$$



• ρ vs p near critical point. fix $\bar T = 1$

say, $\bar p = 1+\varepsilon_p = \dfrac{p}{p_c}$

$\bar\rho = 1+\varepsilon_\rho = \dfrac{\rho}{\rho_c}$

$$\begin{cases} \varepsilon_p = \dfrac{p-p_c}{p_c} \\ \varepsilon_\rho = \dfrac{\rho-\rho_c}{\rho_c} \end{cases}$$

Van der waals eqn.

$$\left((1+\varepsilon_\rho)+3((1+\varepsilon_\rho)^2\right)\left(\frac{1}{1+\varepsilon_\rho}-\frac{1}{3}\right)=\frac{8}{3}$$

$$\frac{1+\varepsilon_\rho}{1+\varepsilon_\rho}+\cancel{3}+\cancel{3\varepsilon_\rho}-\frac{1}{3}(\cancel{1}+\varepsilon_\rho)-1-\cancel{2\varepsilon_\rho}\,\varepsilon_\rho-\varepsilon_\rho^2=\cancel{\frac{8}{3}}$$

$$\cancel{(1+\varepsilon_\rho)=\left(1+\frac{\varepsilon_\rho}{3}+\varepsilon_\rho+\varepsilon_\rho^2\right)(1+\varepsilon_\rho)}$$

$$\varepsilon_p=\frac{3}{2}\frac{\varepsilon_\rho^3}{(1-\varepsilon_\rho/2)} \leftarrow \quad \cancel{\frac{2}{3}\varepsilon_p=2\varepsilon_\rho+\mathcal{O}(\varepsilon^2)}$$

$\therefore\ \varepsilon_p \sim \frac{\varepsilon_\rho^3}{1-\varepsilon_\rho/2}$ near critical point

$\therefore\ \boxed{\frac{p-p_c}{p_c}\sim\frac{3}{2}\left(\frac{\rho-\rho_c}{\rho_c}\right)^3}$ relation b/w p & ρ around critical point.

∘ ρ vs T near critical point.

$$(1+3\bar\rho^2)\left(\frac{1}{\bar\rho}-\frac{1}{3}\right)=\frac{8}{3}\bar T$$

$$\bar T=1+\varepsilon_T=\frac{T}{T_c}\qquad \left(\varepsilon_T=\frac{T-T_c}{T_c}\right.$$

$$\bar\rho=1+\varepsilon_\rho\qquad \left.\varepsilon_\rho=\frac{\rho-\rho_c}{\rho_c}\right)$$

$$\left(1+3(1+\varepsilon_\rho)^2\right)\left(\frac{1}{1+\varepsilon_\rho}-\frac{1}{3}\right)=\frac{8}{3}(1+\varepsilon_T)$$

$$\left(1+3(1+\varepsilon_\rho)^2\right)\left(1-\frac{1}{3}(1+\varepsilon_\rho)\right)=\frac{8}{3}(1+\varepsilon_T)(1+\varepsilon_\rho)$$

$$=1-\frac{1}{3}(1+\varepsilon_\rho)+3(1+\varepsilon_\rho)^2-(1+\varepsilon_\rho)^3=\frac{8}{3}(1+\varepsilon_T+\varepsilon_\rho+\varepsilon_T\varepsilon_\rho)$$

$$\Rightarrow -\frac{1}{3}\varepsilon_\rho+6\varepsilon_\rho-3\varepsilon_\rho=\frac{8}{3}(\varepsilon_T+\varepsilon_\rho)+\mathcal{O}(\varepsilon^2)$$

$$\hookrightarrow \varepsilon_\rho^3=\frac{8}{3}\varepsilon_T(1+\varepsilon_\rho)\qquad \varepsilon_T\sim\frac{3}{8}\frac{\varepsilon_\rho^3}{1+\varepsilon_\rho}\sim\frac{3}{8}\varepsilon_\rho^3$$

$$\boxed{\therefore\ \frac{T-T_c}{T_c}\sim\frac{3}{8}\left(\frac{\rho-\rho_c}{\rho_c}\right)^3}$$

critical exponent.

$$\left(\bar{P} + \frac{3}{\bar{v}^2}\right)\left(\bar{v} - \frac{1}{3}\right) = \frac{8}{3}\bar{T}$$

$$\bar{P} = \frac{8\bar{T}}{3\bar{v}_{liq} - 1} - \frac{3}{\bar{v}_{liq}^2} = \frac{8\bar{T}}{3\bar{v}_{gas} - 1} - \frac{3}{\bar{v}_{gas}^2}$$

$$\bar{T}\left(\frac{8}{3\bar{v}_{liq} - 1} - \frac{8}{3\bar{v}_{gas} - 1}\right) = \frac{3}{\bar{v}_{liq}^2} - \frac{3}{\bar{v}_{gas}^2}$$

$$8\bar{T}\frac{\cancel{3}\cancel{(\bar{v}_{gas} - \bar{v}_{liq})}}{(3\bar{v}_{liq} - 1)(3\bar{v}_{gas} - 1)} = \frac{\cancel{3}(\bar{v}_{liq} + \bar{v}_{gas})\cancel{(\bar{v}_{gas} - \bar{v}_{liq})}}{\bar{v}_{liq}^2\bar{v}_{gas}^2}$$

$$\boxed{\bar{T} = \frac{(3\bar{v}_{liq} - 1)(3\bar{v}_{gas} - 1)(\bar{v}_{liq} + \bar{v}_{gas})}{8\bar{v}_{liq}^2\bar{v}_{gas}^2}}$$

close to critical point,

$\bar{v}_{liq} = 1 - \epsilon/2$ where $\epsilon = \bar{v}_{gas} - \bar{v}_{liquid}$

$\bar{v}_{gas} = 1 + \epsilon/2$

$$\bar{T} \sim 1 - \frac{\epsilon^2}{16} - \frac{3\epsilon^4}{32} + \cdots$$

$$\therefore \underset{T/T_c}{\bar{T}} \sim 1 - \frac{1}{16}(\bar{v}_{gas} - \bar{v}_{liq})^2$$

$$\cancel{\bar{v}_{gas} - \bar{v}_{liq} \sim (T_c - T_0)^{1/2}}$$

$$\frac{1}{16}(\bar{v}_{gas} - \bar{v}_{liq})^2 = \frac{T_c - T}{T_c}$$

$$\boxed{\bar{v}_{gas} - \bar{v}_{liq} \sim 4(T_c - T)^{1/2}}$$

$\beta = 1/2$

from $\left.\frac{\partial P}{\partial v}\right|_{v_c P_c} = 0 = \left.\frac{\partial^2 P}{\partial v^2}\right|_{v_c P_c}$,

$$\boxed{P \sim (v - v_c)^3.}$$

$\delta = 3$

compressibility $\chi = -\left(v \frac{\partial p}{\partial v}\right)_T^{-1} \Big|_{v_c}$

$$= -\left(v_c \frac{\partial p}{\partial v}\Big|_{v_c}\right)_T^{-1}$$

$$\frac{\partial p}{\partial v} \sim (v-v_c)^2 \sim (T-T_c)$$

$$\therefore \boxed{\chi \sim (T-T_c)^{-1}} \qquad \gamma = 1$$

specific heat

mean critical point,

$$\Delta S = \int_{T_c-\varepsilon}^{T_c+\varepsilon} \underbrace{\frac{c_v}{T}}_{\text{say, } f'} dT.$$

$$= f(T_c+\varepsilon) - f(T_c-\varepsilon)$$

$$= f(T_c) + \varepsilon f'(T_c)$$
$$- f(T_c) + \varepsilon f'(T_c) + O(\varepsilon^2)$$

$$= 2\varepsilon \left(\frac{c_v}{T}\right)_{T_c}$$

$$= 2(T-T_c) \frac{c_v(T_c)}{T_c}$$

$$\therefore\ C_v(T_c) = \Delta S \frac{T_c}{2(T-T_c)}$$

from Maxwell relation

$$\frac{\partial S}{\partial v}\Big)_T = \frac{\partial p}{\partial T}\Big)_V$$

$$p \sim (v-v_c)^3 \sim (T_c-T)^{3/2} \qquad \frac{\partial p}{\partial T} \sim (T_c-T)^{1/2}$$

$$\Delta S \sim (T_c-T)^{1/2} \cdot (T_c-T)^{1/2} \sim T_c - T.$$

$$\therefore \boxed{C_v(T_c) \sim \frac{1}{2} T_c \sim (T_c-T)^0.} \qquad \alpha = 0.$$

③. Boiling point at a height of 3000 m & 6000 m.

At 3000 m $\quad P_{air} = 0.68$ atm

6000 m $\quad P_{air} = 0.47$ atm.

$\frac{dp}{dT} = \frac{L}{T(v_{gas} - v_{liq})}$

L: Latent heat

$\sim \frac{L}{T v_{gas}}$

$P v_{gas} = k_B T$

From Clausius-Clapeyron eqn,

$$\frac{dp}{dT} \sim \frac{LP}{k_B T^2}$$

$$\frac{1}{P} dP = \frac{L}{k_B} \frac{1}{T^2} dT$$

$$\ln \frac{P}{P_0} = \frac{L}{k_B} \left(+ \frac{1}{T_0} - \frac{1}{T} \right)$$

$$\frac{1}{T_0} - \left(\frac{k_B}{L} \ln \frac{P}{P_0} \right) = \frac{1}{T}$$

or

N_A: Avogadro's #.

N_A: 1/mol

$$\frac{1}{T_0} - \left(\frac{N_A k_B}{\underbrace{N_A L}} \ln \frac{P}{P_0} \right) = \frac{1}{T}$$

↳ Heat of vaporization ref. 40.66 kJ/mol for water

$$\therefore \frac{1}{T} = \frac{1}{373\text{K}} - \frac{8.314 \text{ J/mol·K}}{40.66 \text{kJ/mol}} \ln \left(\frac{P}{P_{atm}} \right)$$

• at 3000m, $P = 0.68$ atm

$$\frac{1}{T} = \frac{1}{373} - \frac{8.314}{40.66e^3} \ln 0.68 \quad \therefore \cancel{T = 383.844\text{K}}$$

$$\underline{T = 362.734\text{K}}$$

• at 6000m $\quad P = 0.47$ atm

$$\frac{1}{T} = \frac{1}{373} - \frac{8.314}{40.66e^3} \ln 0.47 \qquad \underline{T = 352.68\text{K}.}$$