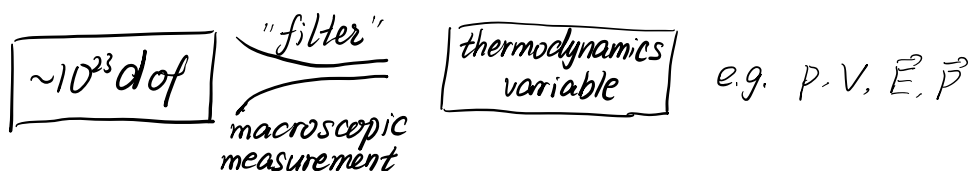


Equilibrium: properties remain unchanged over observation time.
 ↳ measurements coarse and slow (average over space & time)



0th Law $A \leftrightarrow C, B \leftrightarrow C$, then $A \leftrightarrow B$. \leftrightarrow is equilibrium

$\begin{matrix} A \\ \boxed{p_1, V_1} \end{matrix}$	$\begin{matrix} B \\ \boxed{p_2, V_2} \end{matrix}$	$\begin{matrix} C \\ \boxed{p_3, V_3} \end{matrix}$	$F_{AC}(p_1, V_1; p_3, V_3) = 0$ $F_{BC}(p_2, V_2; p_3, V_3) = 0$
---	---	---	--

$$\Rightarrow f_{AC}(p_1, V_1; p_3) = f_{BC}(p_2, V_2; p_3)$$

0th Law says: $F_{AB}(p_1, V_1; p_2, V_2) = 0$
 which is

There's a state function, not depend on C and equal between

A and B:

$$\theta_A(p_1, V_1) = \theta_B(p_2, V_2) \Rightarrow \text{Temperature} \quad v = \frac{V}{N}$$

$\theta = \theta(p, V)$ is equation of state, e.g. $pV = Nk_B T$, $(p + \frac{a}{V^2})(V - b) = k_B T$

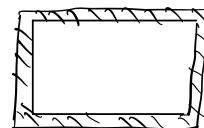
Virial Expansion $\frac{pV}{Nk_B T} = 1 + nB_1 + n^2 B_2 + \dots$

Ideal gas temperature scale $\frac{p_1}{p_2} = \frac{T_1}{T_2}$, $T = \frac{p}{p_0} T^\ominus$, $T^\ominus = T_{\text{triple}} = 273.16 K$

1st Law

* adiabatic wall / diathermic wall
 no heat exchange / heat exchange

* isolated system
 no heat exchange or work performed



state 1 $\xrightarrow{\text{adiabatic process}}$ state 2 $\oint dW = 0$

"POTENTIAL": internal energy (U) $W = U_2 - U_1$

* diathemic $Q = (U_2 - U_1) - W$ change of U that cannot be accounted for the work done
depend on path

$$\Delta U = Q + W \quad dU = dQ + dW \text{ (infinitesimal)}$$

* Quasi-static process $dW = -pdV$ generalized force (intensive)

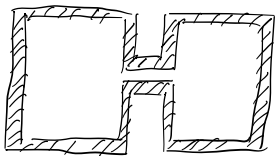
More generally: $dW = \sum_i F_i dx_i$ generalized displacement (extensive)

* Heat capacity $C = \left. \frac{dQ}{dT} \right|_{\text{path}}$

$$C_v = \left. \frac{dQ}{dT} \right|_v = \left(\frac{\partial U}{\partial T} \right)_v \text{ isovolumic}$$

$$C_p = \left. \frac{dQ}{dT} \right|_p = \left(\frac{\partial U}{\partial T} \right)_p + p \left(\frac{\partial V}{\partial T} \right)_p = \left(\frac{\partial H}{\partial T} \right)_p \text{ isobaric, } H \equiv U + pV \text{ (enthalpy)}$$

e.g. Ideal Gas Joule's Expansion



U depends only on T

$$C_p - C_v = p \left(\frac{\partial V}{\partial T} \right)_p = Nk_B$$

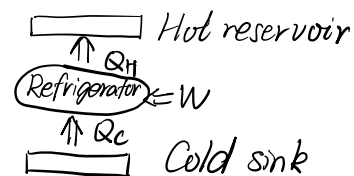
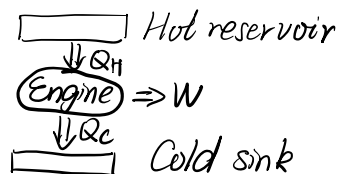
2nd Law

* Heat Engine

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \leq 1$$

Refrigerator

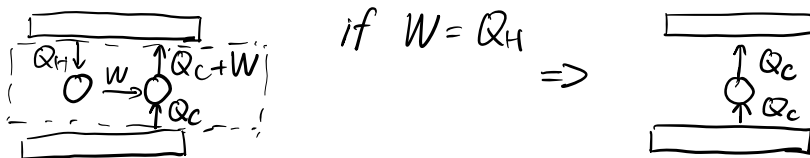
$$\tilde{\eta} = \frac{Q_C}{W} = \frac{Q_C}{Q_H - Q_C}$$



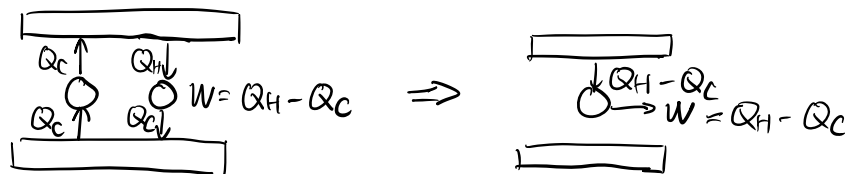
Kelvin: No process is possible whose sole effect is complete conversion of heat to work (No Perfect Heat Engine)

Clausius: transfer heat from colder to hotter body (No Ideal Fridge)

① $C \rightarrow K$ ($\bar{K} \rightarrow \bar{C}$)



② $K \rightarrow C$ ($\bar{C} \rightarrow \bar{K}$)

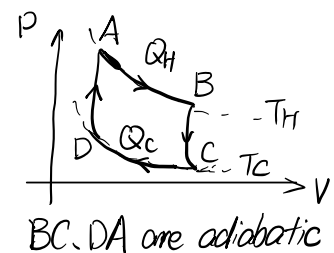
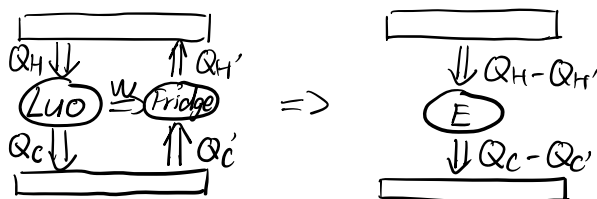


* Carnot Engine

where all heat exchanges happen

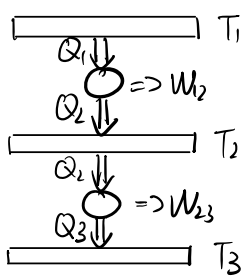
Cycle, Reversible, operates between two heat baths at temp T_H & T_C

Carnot Thm: Carnot is the best!



Clausius $Q_H - Q_{H'} \geq 0$, $\eta_{Luo} = \frac{W}{Q_H} \leq \frac{W}{Q_{H'}} = \eta_{Carnot}$

η depends only on $T_H, T_C \Rightarrow$ Thermodynamic Temperature Scale



$$\begin{aligned}
 & \left\{ \begin{aligned} Q_2 &= Q_1 - W_{12} = Q_1 [1 - \eta(T_1, T_2)] \\ Q_3 &= Q_2 [1 - \eta(T_2, T_3)] = Q_1 [1 - \eta(T_1, T_2)] [1 - \eta(T_2, T_3)] \end{aligned} \right. \\
 & Q_3 = Q_1 [1 - \eta(T_1, T_3)] \\
 & \Rightarrow [1 - \eta(T_1, T_2)] [1 - \eta(T_2, T_3)] = 1 - \eta(T_1, T_3) \\
 & 1 - \eta(T_1, T_2) = \frac{f(T_2)}{f(T_1)} = \frac{T_2}{T_1}
 \end{aligned}$$

* Clausius Inequality

$$\eta = 1 - \frac{T_c}{T_H} = 1 - \frac{Q_c}{Q_H} \Rightarrow \frac{Q_H}{T_H} + \frac{(-Q_c)}{T_c} = 0 \quad \sum_i \frac{Q_i}{T_i} = 0$$

$$\Rightarrow \oint \frac{dQ}{T} \leq 0 \quad "=" \text{ for reversible}$$

"<" for IR, $T \Rightarrow$ temp of heat bath

For reversible process:

"POTENTIAL" entropy $S_B - S_A = \int_A^B \frac{dQ}{T}$

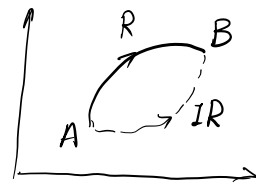
infinitesimal form $dQ = Tds$

$$dU = Tds - pdV$$

Irreversible: $\oint \frac{dQ}{T} < 0$

$$\int_{IR} \frac{dQ}{T} - \int_R \frac{dQ}{T} \xrightarrow{S_B - S_A} < 0$$

$$\Rightarrow S_B - S_A > \int_{IR} \frac{dQ}{T} \quad \text{or} \quad dQ < Tds$$

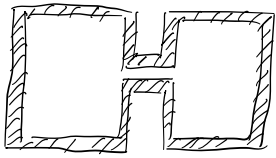


◦ Adiabatic process

$$dQ = 0, \quad \Delta S \geq 0 \quad \int = \text{reversible}$$

| > irreversible

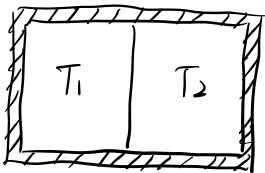
e.g. Joule experiment



$$\Delta Q = 0 \quad \Delta W = 0$$

$$T_i = T_f \quad \Delta S = S_f - S_i = \int \frac{dQ}{T} = \int_{V_i}^{V_f} \frac{pdV}{T} = Nk_B \int_{V_i}^{V_f} \frac{dV}{V} \\ V_i \rightarrow V_f \quad (dQ = -dW = pdV) = Nk_B \ln \frac{V_f}{V_i} > 0$$

e.g. 2 diathermic wall



$$T_1 > T_2$$

$$T_f = \frac{1}{2}(T_1 + T_2) \quad \text{isovolumic process}$$

$$\Delta S_1 = \int_{T_1}^{T_f} \frac{dQ}{T} = \int_{T_1}^{T_f} \frac{C_v dT}{T} = C_v \ln \frac{T_f}{T_1}$$

$$\Delta S_2 = \int_{T_2}^{T_f} \frac{dQ}{T} = \int_{T_2}^{T_f} \frac{C_v dT}{T} = C_v \ln \frac{T_f}{T_2}$$

$$\Delta S = \Delta S_1 + \Delta S_2 = C_v \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}$$

$$dU = TdS - pdV$$

$U(S, V)$ natural variable S, V

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

* one additional generalization: system w/ variable

particle # can happen: ① open system ② phase

transition; ③ chemical reaction

$$\boxed{dU = TdS - pdV + \mu dN} \quad \mu: \text{chemical potential}$$

$$U = U(S, V, N), \quad \mu = \left(\frac{\partial U}{\partial N}\right)_{S, V}$$

* U extensivity $U = U_1 + U_2$

① Thermodynamic limit

$$N \rightarrow \infty \quad V \rightarrow \infty, \quad n = \frac{N}{V} \text{ fixed}$$

② Short-range interaction

* Consequence of extensivity

$U(S, V, N)$ λ scale factor

$$U(\lambda S, \lambda V, \lambda N) = \lambda U(S, V, N) \quad \left. \frac{d}{d\lambda} \right|_{\lambda=1}$$

$$\underbrace{\left. \frac{\partial U}{\partial (\lambda S)} \right|_{\lambda=1}}_T S + \underbrace{\left. \frac{\partial U}{\partial (\lambda V)} \right|_{\lambda=1}}_{-p} V + \underbrace{\left. \frac{\partial U}{\partial (\lambda N)} \right|_{\lambda=1}}_{\mu} N = U$$

$$U = TS - pV + \mu N \quad \text{Extensivity}$$

$$\Rightarrow dU = (TdS - pdV + \mu dN) + (SdT - Vdp + Nd\mu)$$

$$\Rightarrow SdT - Vdp + Nd\mu = 0 \quad \text{Gibbs-Duhem Relationship}$$

$$d\mu = -s dT + v dp$$

* Thermodynamic potentials

$$U = U(S, V, N)$$

we are at liberty to choose other variable

$$H \equiv U + pV, \quad dH = TdS + Vdp + \mu dN, \quad H = H(S, p, N)$$

$F \equiv U - TS$ (Helmholtz free energy) $dF = -SdT - pdV + \mu dN$

$$F = F(T, V, N)$$

$G \equiv H - TS = F + pV$ (Gibbs free energy) $dG = -SdT + Vdp + \mu dN$

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

◦ Grand potential 巨熱力勢

$$\begin{aligned}\psi &\equiv F - \mu N \Rightarrow d\psi = -SdT - pdV - Nd\mu \quad \psi = \psi(T, V, \mu) \\ &= U - TS - \mu N = -pV\end{aligned}$$

Legendre transformation! $\left(\frac{\partial U}{\partial S}\right)_{V, N} = T$

Why bother?

* Towards Equilibrium ~~$\Delta F \leq 0$~~

① 2nd Law: U, V fixed $\Delta S \geq 0$ $\delta S = 0$ $\delta^2 S \leq 0$

② T, V fixed, $\Delta F = \Delta U - T\Delta S = Q + \overset{0}{W} - T\Delta S \leq 0$ $\delta F = 0$ $\delta^2 F \geq 0$

③ T, p fixed $\Delta G = \Delta U - T\Delta S + p\Delta V = Q + \cancel{W} - T\Delta S + p\Delta V \leq 0$

* Maxwell's relation (N fixed)

$$dU = TdS - pdV \Rightarrow \left(\frac{\partial U}{\partial S}\right)_V = T \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

exchange order of taking mixed partial derivatives

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V} \Rightarrow \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V = \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

* Relate quantities to experimentally measurable quantities

E.g. Heat capacities

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V \quad S = S(T, V)$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P \quad \begin{array}{l} S = S(T, P) = S(T, V(P, T)) \downarrow \\ \text{(Recall } dH = TdS + VdP) \end{array}$$

$$\begin{aligned} C_P - C_V &= T \left[\left(\frac{\partial S}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V \right] = T \left[\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_V \right] \\ &= T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \end{aligned}$$

Response function

$$\text{Expansivity} \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

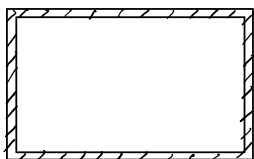
$$\text{Compressibility} \quad \kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{\kappa_T V} \cdot \alpha V = \frac{\alpha}{\kappa_T}$$

$$\boxed{C_P - C_V = \frac{TV\alpha^2}{\kappa_T}} \geq 0$$

Phase Equilibrium



Partition into uniform subsystems

$$S = S(U, V, N) = \sum_a S^a(u_a, v_a, N_a)$$

$$\text{Maximize} \quad S = \sum_a S^a$$

subject to constraint $\sum_a V_a = V, \sum_a U_a = U, \sum_a N_a = N$

Lagrangian multiplier

$$f(\{U_a\}, \{V_a\}, \{N_a\}) = \sum_a S^a(U_a, V_a, N_a) - \alpha (\sum_a U_a - U) - \beta (\sum_a V_a - V) - \gamma (\sum_a N_a - N)$$

$$\frac{\partial f}{\partial U_a} = 0 \Rightarrow \frac{\partial S^a}{\partial U_a} = \alpha \quad \frac{1}{T_a} = \alpha$$

$$\frac{\partial f}{\partial V_a} = 0 \Rightarrow \frac{\partial S^a}{\partial V_a} = \beta \quad \frac{p_a}{T_a} = \beta$$

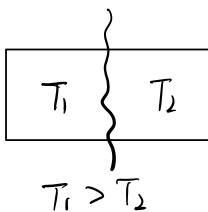
$$\frac{\partial f}{\partial N_a} = 0 \Rightarrow \frac{\partial S^a}{\partial N_a} = \gamma \quad -\frac{\mu_a}{T_a} = \gamma$$

$$dU = TdS - pdV + \mu dN$$

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu}{T}dN$$

At equilibrium

$$\begin{cases} T_1 = T_2 = \dots = T & \text{thermal} \\ p_1 = p_2 = \dots = P & \text{mechanical} \\ \mu_1 = \mu_2 = \dots = \mu & \text{chemical} \end{cases}$$



$$S = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2) \quad U = U_1 + U_2$$

$$\delta S = \frac{\partial S_1}{\partial U_1} \delta U_1 + \frac{\partial S_2}{\partial U_2} (-\delta U_1)$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta U_1 > 0 \Rightarrow \delta U_1 < 0 \quad \text{heat flows from } 1 \rightarrow 2$$

$$\mu_1 > \mu_2 \quad \delta S = \left(-\frac{\mu_1}{T} + \frac{\mu_2}{T} \right) \delta N_1 > 0 \Rightarrow \delta N_1 < 0$$

* Stability Condition

$$S \text{ is maximized} \quad S = \sum_a S^a(U_a, V_a, N_a)$$

$$V_a \quad \frac{\partial^2 S}{\partial x_i \partial x_j} \delta x_i \delta x_j \leq 0, \quad \{x_i\} \rightarrow \{U_a, V_a, N_a\}$$

Hessian matrix $\frac{\partial^2 S}{\partial x_i \partial x_j}$ negative semi-definite

$$\frac{\partial}{\partial x_j} \left(\underbrace{\frac{\partial S^a}{\partial x_i}}_{\text{Force } J_i} \right) \delta x_j \delta x_i \Rightarrow \delta J_i \cdot \delta x_i \leq 0$$

$$\delta S = \frac{1}{T} \delta U + \frac{P}{T} \delta V - \frac{\mu}{T} \delta N$$

$$\delta \left(\frac{1}{T} \right) \delta U + \delta \left(\frac{P}{T} \right) \delta V - \delta \left(\frac{\mu}{T} \right) \delta N \leq 0$$

$$- \frac{\delta T}{T^2} \delta U + \frac{T \delta P - P \delta T}{T^2} \delta V - \frac{T \delta \mu - \mu \delta T}{T^2} \delta N \leq 0$$

$$- \frac{\delta U + P \delta V - \mu \delta N}{T^2} \delta T + \frac{1}{T} (\delta P \delta V - \delta \mu \delta N) \leq 0$$

$$\frac{1}{T} (\delta P \delta V - \delta T \delta S - \delta \mu \delta N) \leq 0$$

$$\Rightarrow \delta T \delta S - \delta P \delta V + \delta \mu \delta N \geq 0$$

e.g. if $\delta N = 0$, choose T, V as independent variables

$$S = S(T, V), \quad p = p(T, V)$$

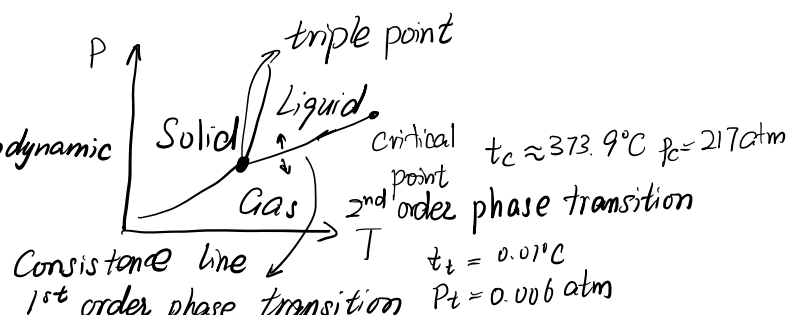
$$\delta T \left[\left(\frac{\partial S}{\partial T} \right)_V \delta T + \left(\frac{\partial S}{\partial V} \right)_T \delta V \right] - \delta V \left[\left(\frac{\partial p}{\partial T} \right)_V \delta T + \left(\frac{\partial p}{\partial V} \right)_T \delta V \right] \geq 0$$

$$C_V (\delta T)^2 - \left(\frac{\partial p}{\partial V} \right)_T (\delta V)^2 \geq 0$$

$$\Rightarrow C_V > 0, \quad - \left(\frac{\partial p}{\partial V} \right)_T > 0 \Rightarrow K_T > 0$$

Liquid-Gas Transition

→ Non-analyticity for thermodynamic function (in T.D. limit)



Equilibrium: $\mu_L(p, T) = \mu_G(p, T) \Rightarrow$ a line on p - T plane

$\mu_L(p, T) = \mu_G(p, T) = \mu_S(p, T) \Rightarrow$ a point on p - T plane

$$d\mu_L(p, T) = d\mu_G(p, T)$$

$$\begin{cases} d\mu_L = -S_L dT + v_L dp \\ d\mu_G = -S_G dT + v_G dp \end{cases} \Rightarrow \frac{dp}{dT} = \frac{S_L - S_G}{v_L - v_G}$$

Latent heat $L = T(S_G - S_L) \Rightarrow \frac{dp}{dT} = \frac{L}{T(v_G - v_L)}$ Clapeyron Equation

Simplification ① $v_L \ll v_G$ ② $\frac{\partial L}{\partial T} = 0$

$$\textcircled{3} pV = Nk_B T \Rightarrow p = Ae^{-\frac{L}{k_B T}}$$

$$dU = TdS - pdV + \mu dN$$

$$U = TS - pV + \sum_a \mu_a \cdot N_a$$

$$SdT - pdV + \sum_a \mu_a dN_a = 0$$

Van der Waals Equation

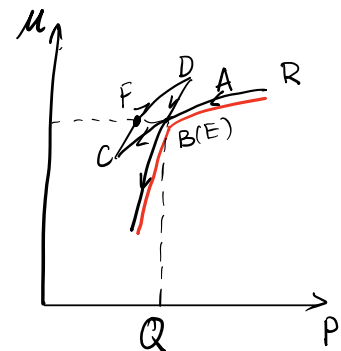
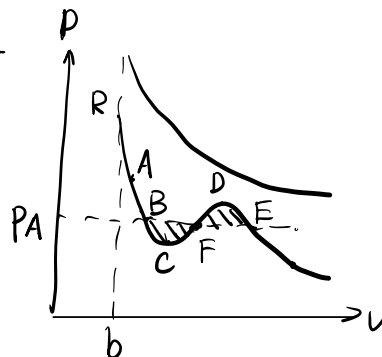
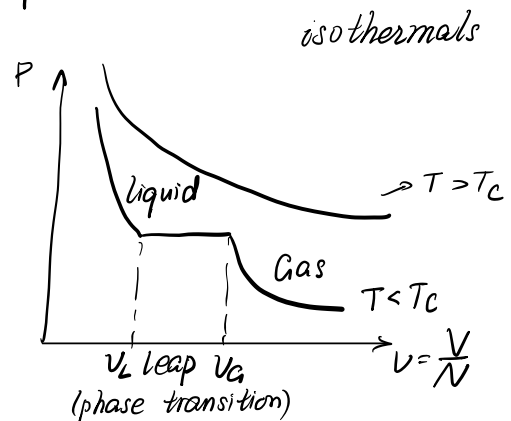
$$(p + \frac{a}{v^2})(v - b) = k_B T$$

$$d\mu = -s dT + v dp = v dp$$

minimized


$$\mu = \mu_A + \int v dp$$

$$\text{since } \mu_B = \mu_E, \int_{BCDEF} v dp = 0 \Leftrightarrow S_{BCF} = S_{DEF}$$



G
↑

G
↑

1st order phase transition  $v = \left(\frac{\partial \mu}{\partial p}\right)_T$ leaps "order parameter"

$$\begin{cases} \frac{\partial p}{\partial v} \big|_{T_c, v_c} = 0 \\ \frac{\partial^2 p}{\partial v^2} \big|_{T_c, v_c} = 0 \end{cases} \Rightarrow T_c = \frac{8a}{27k_B b} \quad p_c = \frac{a}{27b^2} \quad \frac{p_c v_c}{k_B T_c} = \frac{3}{8} \\ v_c = 3b$$

Define $p^* = \frac{p}{p_c}$, $v^* = \frac{v}{v_c}$, $T^* = \frac{T}{T_c}$, then:
dimension ratio $(p^* + \frac{3}{v^{*2}})(v^* - \frac{1}{3}) = \frac{8}{3}$

what if beyond 'Critical Point'? \nearrow response function
 $v = \left(\frac{\partial \mu}{\partial p}\right)_T$ continuous, but $\kappa_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T \sim \frac{\partial^2 \mu}{\partial p^2}$ divergent
"2nd order phase transition"

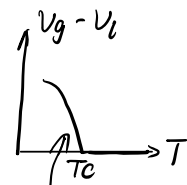
Critical Point: $\begin{cases} \frac{\partial p}{\partial v} = 0 \\ \frac{\partial^2 p}{\partial v^2} = 0 \end{cases}$ two extreme points merge

the stability condition requires: $\delta T \delta s - \delta p \delta v + \delta \mu \delta N \geq 0$
 $\Rightarrow \delta p \delta v \leq 0 \quad \Rightarrow \frac{\partial p}{\partial v} (\delta v)^2 + \frac{1}{2!} \frac{\partial^2 p}{\partial v^2} (\delta v)^2 + \frac{1}{3!} \frac{\partial^3 p}{\partial v^3} (\delta v)^3 \leq 0$
 $\Rightarrow \frac{\partial^3 p}{\partial v^3} \leq 0$

$\tilde{p} = f(\tilde{t}, \tilde{v})$ hope to find 'Law of corresponding law'
 \Rightarrow does not work

A First Look at Critical Exponent

① $v_g - v_l$ \tilde{t} in the neighborhood of 1 ($\tilde{t} \leq 1$)



$$\frac{\partial \tilde{p}}{\partial \tilde{v}} = 0 \Rightarrow -\frac{8}{3} \frac{\tilde{t}}{(\tilde{v} - \frac{1}{3})^2} + \frac{6}{\tilde{v}^3} = 0$$

let $\tilde{v} = 1 \pm \varepsilon$ expand in powers of ε

$$\Rightarrow \tilde{t} = 1 - \# \varepsilon', \quad \varepsilon \sim v_g - v_i \Rightarrow (v_g - v_i) \sim (T_c - T)^{\frac{1}{2}}$$

② shape of $p-v$ curve near (p_c, v_c) $p - p_c \sim v - v_c$?

$$p - p_c \sim (v - v_c)^3, \quad v - v_c \sim (p - p_c)^{\frac{1}{3}}$$

③ Response function

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \sim (T - T_c)?$$

$$\frac{\partial p}{\partial v} \Big|_{v_c, T} = \frac{\partial p}{\partial v} \Big|_{v_c, T_c} + \frac{\partial^2 p}{\partial v^2} \Big|_{v_c, T_c} (T - T_c), \quad \frac{\partial p}{\partial v} = -a(T - T_c) \quad a > 0$$

$$K_T \sim (T - T_c)^{-1}$$

* Examine how various quantities change as one approaches

the c.p. in different ways.

$$\text{Actually: } v_g - v_i \sim (T_c - T)^{0.32}$$

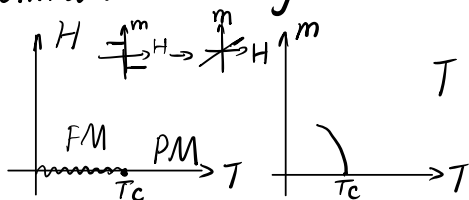
$$v - v_c \sim (p - p_c)^{\frac{1}{4.8}}$$

$$K_T \sim (T - T_c)^{-1.2}$$

mean field?

this hypothesis breaks down in the neighbourhood of critical point

Uniaxial magnet $T < T_c$ Ferromagnet ($\langle m \rangle \neq 0$ when $H=0$)



$T > T_c$ Paramagnet ($\langle m \rangle = 0$ when $H=0$)

$$m \sim (T_c - T)^{0.32}$$

$$m \sim H^{\frac{1}{4.8}} \quad \text{at } T_c$$

$$\begin{array}{lcl} v_g - v_l & \Leftrightarrow & m \\ p & \Leftrightarrow & H \\ k_T & \Leftrightarrow & \chi \end{array}$$

$$\chi = \left(\frac{\partial m}{\partial H} \right) \sim (T - T_c)^{-1.2}$$

Universal Class \Rightarrow dimension & symmetry

When turned to the critical point, different systems behave similarly, regardless of microscopics.

Conventional notations of critical exponents

① order parameter as $T \rightarrow T_c$ at zero external field
($m, v_g - v_l$)

$$m \sim (t_c - t)^\beta$$

② sitting at T_c , order parameter \sim external field

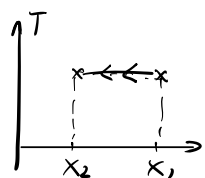
$$m \sim H^\delta$$

③ Response function as $T \rightarrow T_c$

$$\chi = \left. \frac{\partial m}{\partial H} \right|_{H \rightarrow 0} \sim (t - t_c)^{-\gamma}$$

($\beta, \delta, \gamma, \dots$) are critical exponents

3rd Law of thermodynamics



$$\text{Nernst} \quad \Delta S(T) = \int_{x_1}^{x_2} \frac{dQ}{T} \Big|_T = S(x_2, T) - S(x_1, T)$$

$$\lim_{T \rightarrow 0} \Delta S(T) = 0 \quad \text{the entropy when } T \rightarrow 0 \text{ depends only on } T$$

more ambitious version: $\lim_{T \rightarrow 0} S(x, T) = 0$, for all x

Consequence

$$\textcircled{1} \quad S(x, T) - S(x, 0) = \int \frac{dQ}{T} = \int_0^x C_x(T) \frac{dT}{T}$$

no divergence $C_x(T) \rightarrow 0$ as $T \rightarrow 0$

more precisely $C_x(T) \sim T^n \quad n \geq 1$

$$\textcircled{2} \quad \text{Expansibility} \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = - \frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T \xrightarrow{T \rightarrow 0} 0$$

$$C_p - C_v = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \xrightarrow{T \rightarrow 0} 0 \quad \lim_{T \rightarrow 0} C_p = \lim_{T \rightarrow 0} C_v$$