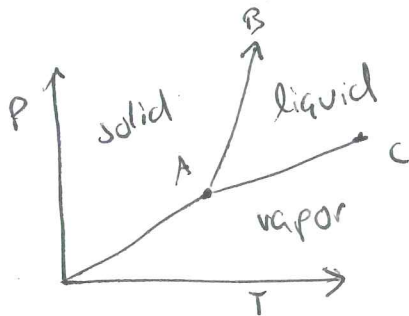


Pure PVT Systems

- composed of only one type of molecule
- repulsive core, short-range attractive region outside core
- $\Rightarrow$ gas phase / liquid phase / solid phase

Phase diagrams & Coexistence Curves

typical phase diagram (although there are exceptions like He)

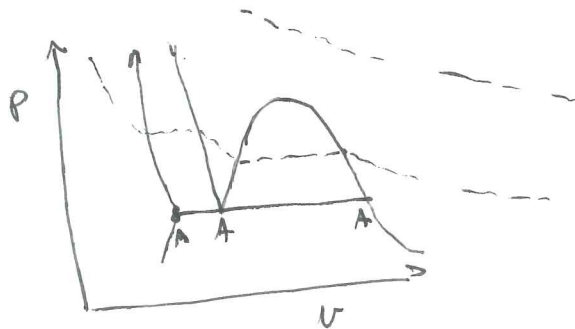


A - triple point

C - critical point

- first-order transitions accompanied by latent heat / change in volume

P-v isotherms (v - molar volume)



Coexistence Curves: Clausius - Clapeyron Equation

molar Gibbs free energies of two coexisting phases must be equal:

- if we change pressure and temperature at which the two phases coexist $\Rightarrow$ molar Gibbs free energies change by equal amounts

Gibbs free energy

$$U = TS + PV + \mu N$$
$$dU = TdS + PdV + \mu dN$$

$$G = U - TS + PV$$

(Legendre transformation
applicable to system at constant
 N, P, T)

$$dG = -SdT + VdP + \mu dN$$

or in molar quantities

$$dg = -sdT + v dP + \mu dN$$

$$s = S/N$$

$$v = V/N$$

$$g = G/N$$

$$dg^I = dg^II \Rightarrow -s^I dT + v^I dP = -s^{II} dT + v^{II} dP$$
$$(v^I - v^{II}) dP = (s^I - s^{II}) dT$$

Clausius-Clapeyron: $\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$

$$\Delta S = S^I - S^{II} = -\left(\frac{\partial G}{\partial T}\right)^I + \left(\frac{\partial G}{\partial T}\right)^{II}$$

$H = G + TS$
 $\downarrow$

$$\Delta H = H^I - H^{II} = T \Delta S \quad (\text{since } G^I = G^{II})$$

$\Rightarrow$ Clausius-Clapeyron: $\frac{dP}{dT} = \frac{\Delta H}{T \Delta V} = \frac{\Delta h}{T \Delta v}$ (molar quantities)

discuss Clausius - Clapeyron for three coexistence curves

vaporization curve

$$\frac{dP}{dT} = \frac{\Delta H_{lg}}{T \Delta V} = \frac{\Delta h_{lg}}{T \Delta v}$$

$$PV = NkT$$

$$Pv = RT$$

assumption: the change in volume is due mainly
to change in vapor pressure, and the
volume of liquid does not change appreciably

$$\Rightarrow \left(\frac{dP}{dT} \right)_{\text{coex}} = \frac{P \Delta h}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta h dT}{RT^2}$$

$$\ln P \Big|_{P_i}^{P_f} = - \frac{\Delta h_{\text{coex}}}{RT} \Big|_{T_i}^{T_f}$$

$$P_f = P_i \exp \left[- \frac{\Delta h_{\text{coex}}}{R} \left(\frac{1}{T_f} - \frac{1}{T_i} \right) \right]$$

- Fusion curve:

$$\left(\frac{dP}{dT} \right)_{\text{coex}} = \frac{\Delta h_{sl}}{T \Delta v_{sl}}$$

- here volume changes are comparable

$\Rightarrow$ can not use same reasoning as for vaporization

if $V_s < V_l \Rightarrow$ slope positive

$V_s > V_l \Rightarrow$ slope negative

water $\Rightarrow$ fusion curve has negative slope

$\Rightarrow$ makes ice-skating possible

- Sublimation curve

solid $\rightarrow$ gas

- again one can assume that volume change is due mostly to change in volume of gas

$$\left(\frac{dP}{dT} \right)_{\text{coex}} = \frac{\Delta h_{sg}}{T \Delta v_{sg}} = \frac{P \Delta h_{sg}}{RT^2}$$

$$P_f = P_i \Rightarrow -R \frac{d \ln P}{d(1/T)} = \Delta h_{sg}$$

at moderately low temperatures vapour pressure is low

$$\text{write } dh = T ds + v dP$$

$$= T \frac{\partial S}{\partial T} dT + T \frac{\partial S}{\partial P} dP + v dP$$

$$= C_p dT + v(1 - T\alpha_p) dP$$

C_p - specific heat at constant pressure

α_p - thermal expansivity

$$\rightarrow \alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Maxwell relation:

$$dG = -SdT - VdP + \mu N$$

$$S = -\frac{\partial G}{\partial T}$$

$$V = -\frac{\partial G}{\partial P}$$

$$\frac{\partial S}{\partial P} = -\frac{\partial^2 G}{\partial P \partial T}$$

$$\frac{\partial V}{\partial T} = -\frac{\partial^2 G}{\partial P \partial T}$$

$$\alpha_p = \frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_T$$

$$T \frac{\partial S}{\partial T} = -T \frac{\partial^2 G}{\partial T^2} = C_p$$

$$dh = C_p dT + v(1 - T\alpha_p) dP$$

pressure change negligible

$$dh_g - dh_s = d\Delta h_{gs} = (C_p^g - C_p^s) dT$$

$$\Delta h_{gs} = \Delta h_{gs}^{(0)} + \int_{T_0}^T (C_p^g - C_p^s) dT'$$

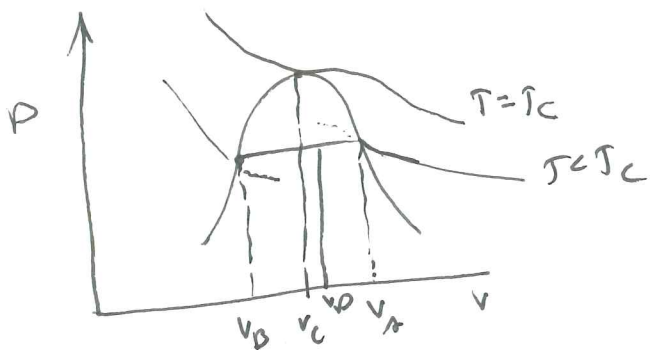
$$\Rightarrow -R \frac{d \ln P}{d(1/T)} = \Delta h_{gs}^{(0)} + \int_{T_0}^T (C_p^g - C_p^s) dT$$

$\Downarrow$

$$-R \ln(P_f/P_i) = \Delta h_{gs}^{(0)} \left(\frac{1}{T_f} - \frac{1}{T_i} \right)$$

$$+ \int_{T_0}^{T_f} \frac{dT'}{T'^2} \int_{T_0}^{T'} dT'' (C_p^g - C_p^s)$$

Liquid-Vapor Coexistence Region



Solid lines - stable thermodynamic states

lever rule: gives amounts of liquid and vapor

- consider system w/ $T_0 < T_c$, pressure P_0 , total molar volume v_D

$$v_D = x_l v_l + x_g v_g$$

x_l - mole fraction of liquid at pt. D
 x_g - mole fraction of gas at pt. D

$$\text{since } x_l + x_g = 1$$

$$v_D(x_l + x_g) = x_l v_l + x_g v_g$$

$$x_g(v_D - v_g) = x_l(v_l - v_D) \Rightarrow$$

$$\boxed{\frac{x_l}{x_g} = \frac{(v_D - v_g)}{(v_l - v_D)}}$$

- as long as $\left(\frac{\partial v}{\partial P}\right)_T < 0 \Rightarrow$ phase mechanically stable

- dotted lines in figure - metastable states

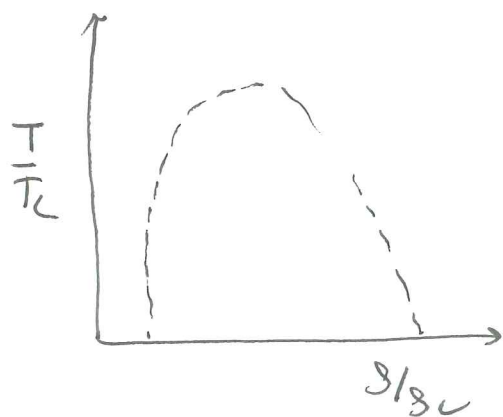
$\Rightarrow$ supercooled vapor / superheated liquid

- as critical temperature approached

$\Rightarrow$ region of metastable states decreases

$\Rightarrow$ no metastability at T_c

coexistence curve in T-S (ρ - mass density)



$\text{Ne} / \text{Ar} / \text{Kr} / \text{Xe} / \text{N}_2 / \text{O}_2 / \text{CO} / \text{CH}_4$

all fall on same curve

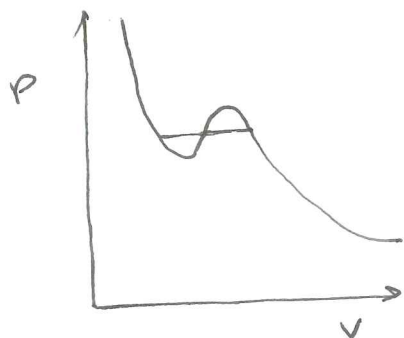
↓

law of corresponding states

⇒ phase diagram does not seem to depend on microscopic detail

van der Waals equation

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0 \Rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \left(\frac{vdN}{EdS}\right)$$



⇒ three roots

~~as $T \rightarrow T_c$~~

as $T \rightarrow \infty \Rightarrow v = \frac{RT}{P}$

∃ T_c where three roots coalesce

$$\frac{\partial P}{\partial v} = 0 \quad \frac{\partial^2 P}{\partial v^2} = 0$$

⇒ gives T_c, P_c, v_c

$$\frac{\partial P}{\partial v} = -\frac{RT}{(v-b)^2} + \frac{2a}{v^3} = 0 \Rightarrow \frac{2a}{v^3} = \frac{RT}{(v-b)^2}$$

$$\frac{\partial^2 P}{\partial v^2} = \frac{2RT}{(v-b)^3} - \frac{6a}{v^4} = 0 \Rightarrow \frac{2RT}{(v-b)^3} - \frac{3RT}{(v-b)^2 v} = 0$$

$$\frac{2}{v-b} - \frac{3}{v} = 0 \Rightarrow v_c = 3b$$

$$\frac{2a}{27b^3} = \frac{RT}{4b^2}$$

$$T_c = \frac{8a}{27Rb}$$

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

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

independent of $a, b \Rightarrow$ law of corresponding states

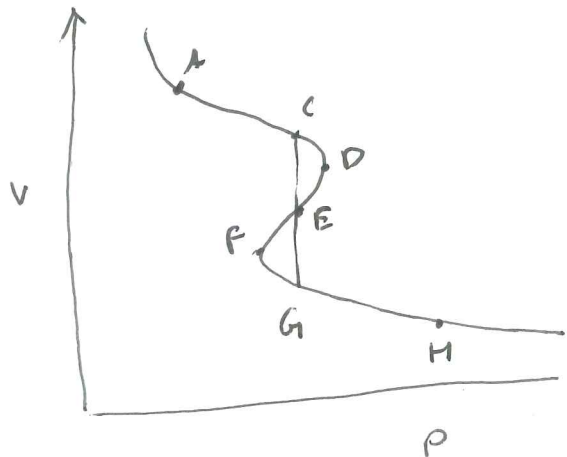
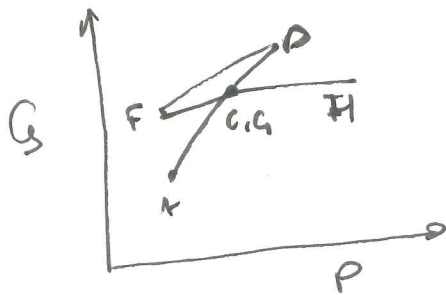
-unphysical aspect of vdW EOS.

$\Rightarrow \frac{\partial P}{\partial V}$ has positive slope in coexistence region
(at least in some places) $\Rightarrow$ mechanically unstable states

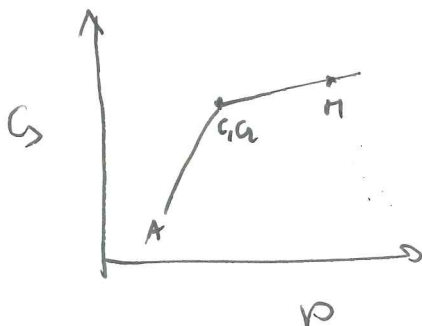
$$dg = -sdT + vdp$$

for isotherms: $dg = vdp$

$$g_2 - g_1 = \int_{p_1}^{p_2} v(p) dp$$



only states along curve ACI correspond to thermodynamic equilibrium
states F, C, D - metastable

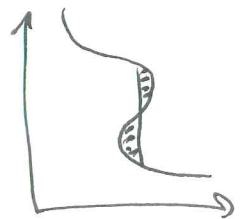


$\Rightarrow v, P$ curve $C \rightarrow G$ must be a straight line (otherwise Gibbs free energy would not be constant)

- how to determine where C and G lie?

$$\int_{p_C}^{p_G} v(p) dp = 0 \Rightarrow \int_{p_C}^{p_D} v(p) dp + \int_{p_D}^{p_E} v(p) dp + \int_{p_E}^{p_F} v(p) dp + \int_{p_F}^{p_G} v(p) dp = 0$$

equal area construction (Maxwell):



$$\int_{P_c}^{P_0} v(P) dP - \int_{P_c}^{P_p} v(P) dP = \int_{P_c}^{P_E} v(P) dP - \int_{P_c}^{P_g} v(P) dP$$

Continuous phase transitions

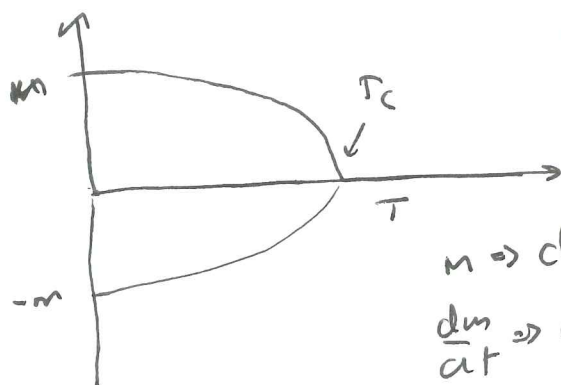
Curie transition: paramagnetic to ferromagnetic @ T_c

examples: iron/copper/zinc

above $T_c \Rightarrow$ apply magnetic field $\vec{B}$
magnetization: $\vec{m} = \mu \vec{B}$

below $T_c \Rightarrow$ ferromagnetic state

- $\vec{m}$ finite even in the absence of $\vec{B}$ -field



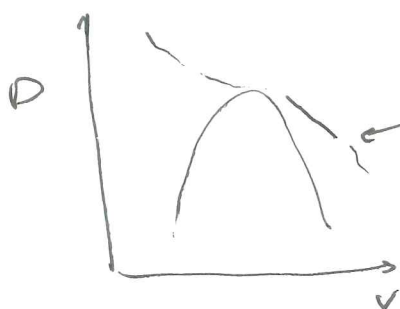
(symmetric)

$m \Rightarrow$ changes continuously at T_c

$\frac{dm}{dT} \Rightarrow$ changes discontinuously at T_c

(for 1st order transitions volume/energy change abruptly)

for first-order phase transitions $\Rightarrow$ latent heat vanishes at critical point



phase transition along isotherm $T=T_c$ is continuous

Divergences and Critical Exponents

- specific heat often diverges, even if there is no latent heat

$$C \sim |T - T_c|^{-\alpha} \quad \alpha > 0$$

α - critical exponent

- describes singular behaviour of quantities around/at continuous phase transition

latent heat:
$$L = \int_{T_c^-}^{T_c^+} C(T) dT$$

L must vanish as we pass through transition for a second order phase transition

- C - can diverge logarithmically

~~log~~ $\log(T_c/|T - T_c|)$

$$\log\left(\frac{1}{x}\right) = \frac{1}{\alpha} (x^{-\alpha} - 1)$$

- C - can have a finite peak as $T \rightarrow T_c$

$$C(T) \propto \frac{1}{|\alpha|} (1 - x^{|\alpha|}) \quad x = \frac{|T - T_c|}{T_c}$$

- C - can have power law divergence

$$|T - T_c|^{-\alpha} \Rightarrow \alpha > 0$$

$\alpha < 1$
otherwise there would be latent heat

$\Downarrow$
we write
$$C(T) \approx \frac{1}{\alpha} \left(\left| \frac{T - T_c}{T_c} \right|^{-\alpha} - 1 \right)$$

Curie: c_p of iron has a finite peak at T_c

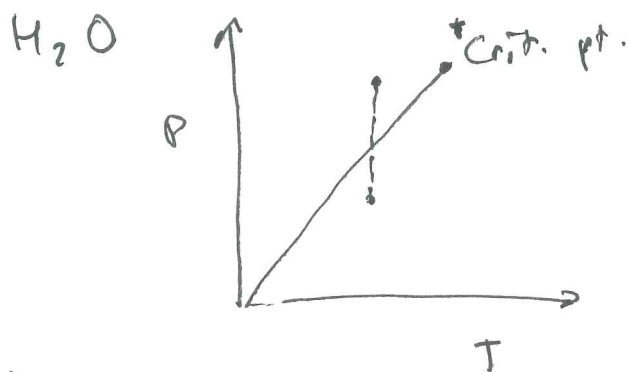
$$\alpha \approx -0.03$$

for H_2O : $T \rightarrow T_c$ c_v diverges $\Rightarrow \alpha > 0$

for $T \rightarrow T_c$ from above $c \sim |T - T_c|^{-\alpha}$
 $T \rightarrow T_c$ from below $c \sim |T - T_c|^{-\alpha'}$

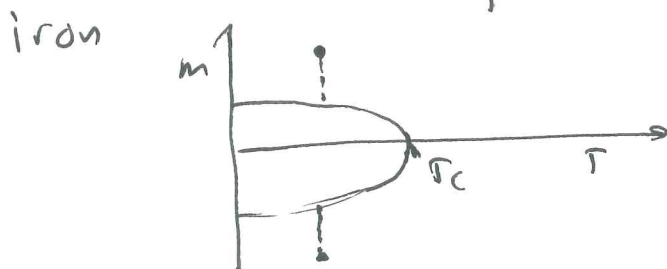
in most cases $\alpha = \alpha'$

for 1st order phase transitions one cannot approach T_c from below (since specific heat diverges)



specific heat diverges below T_c
according to a δ -law.

no integrable singularity



- as line is crossed
magnetization changes abruptly
but between two symmetric
states ($-m \rightarrow m$ or vice versa)

$\Rightarrow$ no latent heat

$\Rightarrow$ below T_c specific heat is in no way
singular

$\Rightarrow$ we can ask about divergence when
 $T \rightarrow T_c$ from below

Other diverging quantity

in H_2O : χ_T (isothermal compressibility)

$$\chi_T \sim (T - T_c)^{-\gamma} \quad \gamma = 1.2$$

notice: c_p diverges as $T \rightarrow T_c$ from above
below T_c latent heat (non zero difference
between enthalpies)

χ_T diverges as $T \rightarrow T_c$ from above
below T_c there is a finite difference
between densities $\rho_g - \rho_c = \Delta \rho$

for iron: magnetic susceptibility χ_T diverges at T_c
when $T \rightarrow T_c$

$$\chi_T = \left(\frac{\partial m}{\partial B} \right)_T \sim (T - T_c)^{-\gamma} \quad \gamma \approx 1.3$$

in magnetic system: m_0 (magnetization below T_c)

$$m_0 \sim (T_c - T)^\beta \quad \beta \approx 0.35 \text{ (iron)}$$

correspondingly: densities of liquid and gas
approach each other as $T \rightarrow T_c$ from
below

$$\Delta \rho = \rho_g - \rho_c \sim (T_c - T)^\beta \quad \beta \approx 0.35$$

at T_c magnetization ~~becomes~~ becomes proportional

$$\text{to } B \quad m \sim B^{1/\delta} \quad \delta \approx 4.3 \text{ for iron}$$

for gas liquid $\Rightarrow$ on critical isotherm

$$\rho \sim (p - p_c)^{1/\delta} \quad \delta \approx 4 \text{ for } H_2O$$

divergence in $\chi_T, c_v \Rightarrow$ indication of large
fluctuations

Order parameter

- quantity whose thermal average vanishes on one side (usually high-temperature side) of phase diagram and is finite on other side
- in general it could fluctuate in space and time $\phi(\vec{r}, t)$
 - glass transition
 - but for our purposes, fluctuations in space only
- $\phi(\vec{r})$
- critical exponents $\alpha, \beta, \gamma, \delta \Rightarrow$ refer to fluctuations thermally of the mean

Liquid-gas transition

$$\phi(\vec{r}) = \rho(\vec{r}) - \rho_{\text{gas}}(\vec{r})$$

Binary fluids

example: mixture of polar and apolar fluids

methanol + hexane

mixing these substances leads to phase

separation $\Rightarrow$ two-component phase

above some critical temperature (42.4°C)

these substances mix $\Rightarrow$ one-component phase

$\Rightarrow$ at critical mixing ratios $\Rightarrow$ there is only a one-component phase $\Rightarrow$ continuous transition to two-component phase
for $T > T_c$

order parameter: below T_c

$$\phi(\vec{r}) = \chi'(\vec{r}) - \bar{\chi}'$$

χ' = density of one of the constituents