Phase stability and phase transitions

chemical potential μ: $\mu = G_m$ — for a one-component system it is the molar Gibbs energy

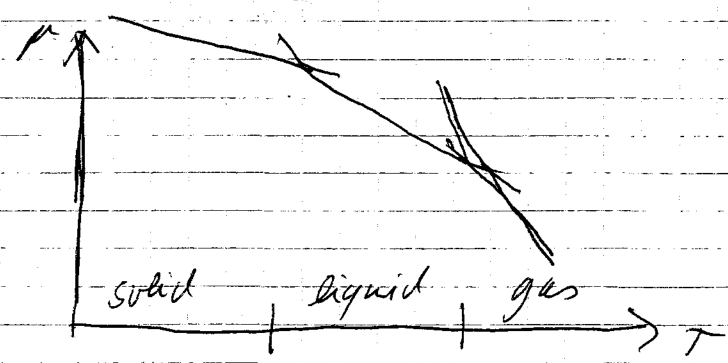
At equilibrium, the chemical potential of a substance is the same throughout a sample, regardless of how many phases are present

proof $\quad \mu_1 > \mu_2 \quad$ amount dn transferred from $1 \to 2$

$\Rightarrow \; dG = (\mu_2 - \mu_1)\,dn < 0 \;\Rightarrow$ spontaneous reaction

$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m \quad \Rightarrow$ temperature raised $\Leftrightarrow$ chemical potential of pure substance decreases since $S_m > 0$

$S_m(g) > S_m(l) > S_m(s)$



$$\left.\frac{\partial \mu}{\partial p}\right|_T = V_m \qquad V_m(l) > V_m(s)$$

$\Rightarrow$ pressure increases μ in a liquid more than in a solid

$\Rightarrow$ most substances melt at a higher temperature when subject to pressure

Location of phase boundaries between a phase α and β which are in equilibrium:

$$\mu_\alpha(p,T) = \mu_\beta(p,T)$$

$\Rightarrow$ resulting slopes of phase boundaries

$$d\mu = -S_m\,dT + V_m\,dp \qquad d\mu_\alpha = d\mu_\beta$$

$$-S_{\alpha,m}\,dT + V_{\alpha,m}\,dp = -S_{\beta,m}\,dT + V_{\beta,m}\,dp$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}} \qquad \text{Clapeyron equat}$$

solid - liquid: $\dfrac{dp}{dT} = \dfrac{\overbrace{\Delta_{fus} H}^{>0}}{T \underbrace{\Delta_{fus} V}_{\approx 0,\, >0}} > 0$, steep

$\Rightarrow$ phase boundary:

$$\int_{p^*}^{p} dp = \underbrace{\frac{\Delta_{fus} H}{\Delta_{fus} V}}_{\text{approximated } T\text{-independent}} \int_{T^*}^{T} \frac{dT}{T}$$

$$\Rightarrow p \simeq \underbrace{p^*}_{\text{melting pressure at } T^*} + \frac{\Delta_{fus} H}{\Delta_{fus} V} \ln \frac{T}{T^*}$$

$$T \simeq T^* \qquad \ln\frac{T}{T^*} \simeq \frac{T-T^*}{T^*} \Rightarrow \boxed{p \simeq p^* + \frac{\Delta_{fus} H}{\Delta_{fus} V}(T-T^*)}$$

liquid – vapour:

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T\Delta_{vap}V} > 0,\ \text{small}$$

$\Delta_{vap}H$: ~~> 0, large~~

$\Delta_{vap}V$: > 0, large

$\Delta_{vap}V \approx V_m(g)$ perfect: $V_m(g) = RT/p$

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T(RT/p)} \Rightarrow \frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}$$ Clausius–Clapeyron

$$\left(\frac{dx}{x} = d\ln x\right)$$

$\Delta_{vap}H$ temperature independent

$$p = p^* e^{-\chi} \qquad \chi = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$$

p^*: vapor pressure at T^*

Phase Transition, Ehrenfest classification

first-order phase transition $\Leftrightarrow$ first derivative of the chemical potential with respect to temperature is discontinuous

heating required!

second-order phase transition $\Leftrightarrow$ first derivative of μ with respect to T is continuous but its second ~~deriv~~ derivative is discontinuous

no jump in volume or entropy

λ-transition $\Leftrightarrow$ not first-order but heat capacity becomes infinite at transition temperature

Phase transitions, the Ehrenfest classification:

transition from a phase α to a phase β

$$\frac{\partial \mu_\beta}{\partial p}\Big|_T - \frac{\partial \mu_\alpha}{\partial p}\Big|_T = V_{\beta m} - V_{\alpha m} = \Delta_{trs} V$$

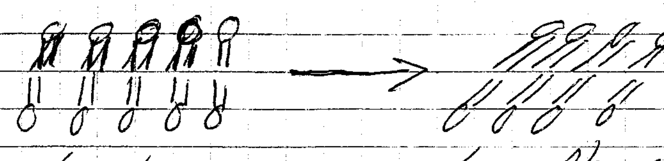
$$\frac{\partial \mu_\beta}{\partial T}\Big|_p - \frac{\partial \mu_\alpha}{\partial T}\Big|_p = -S_{\beta,m} + S_{\alpha,m} = \Delta_{trs} S = -\frac{\Delta_{trs} H}{T_{trs}}$$

nonzero for melting and vaporization

first-order phase transition:

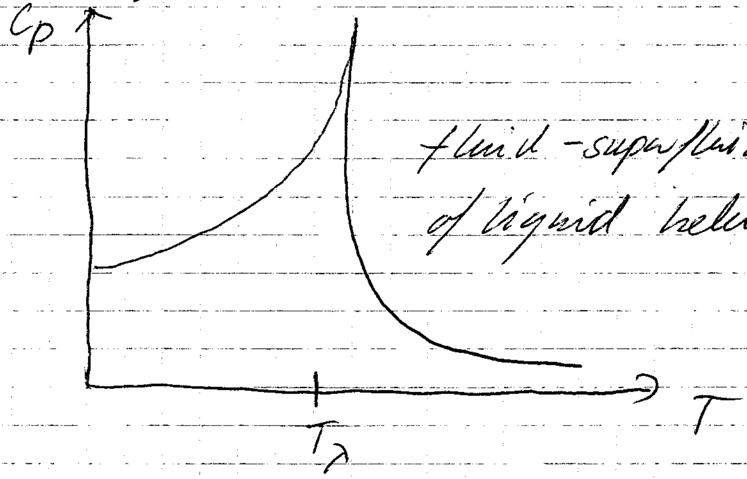
- first derivative of the chemical potential with respect to temperature is discontinuous
- C_p becomes infinite

second-order phase transition:

- first derivative of μ with respect to temperature is continous, but its second derivative is discontinous
- volume and entropy (and hence the enthalpy) do jump at the transition
- C_p is discontinuous but not infinite
- 

L_α-phase $\qquad\qquad$ L_β-phase λ-transition:

- not first order, but heat capacity becomes infinite
- c_p begins to increase well before the transition



- e.g.: order-disorder transition in β-brass (Cu Zn)

  - orderly array of alternating Cu and Zn-atoms at low T
  - higher T ⇒ islands of disorder form
    transition becomes cooperative since these islands support further disorder
  - at high T random array of atoms

The liquid surface:

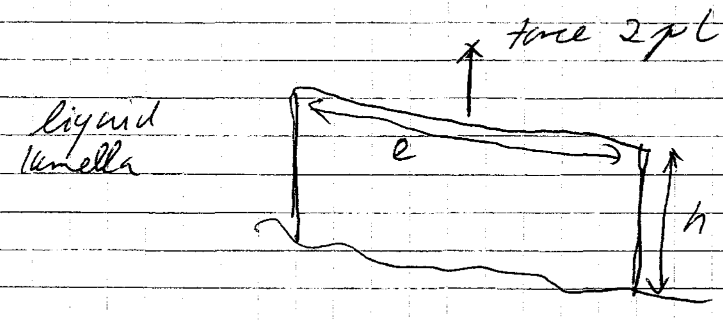
surface tension γ

- liquids tend to minimize their surface
- work needed to change the surface area σ

$$dw = \gamma\, d\sigma \underset{\substack{V=\text{const}\\ T=\text{const}}}{=} dA \;\Rightarrow\; dA < 0 \text{ for } d\sigma < 0$$

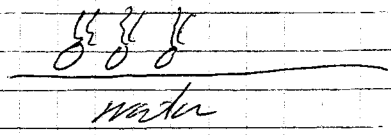
i.e. surfaces have a natural tendency to contract

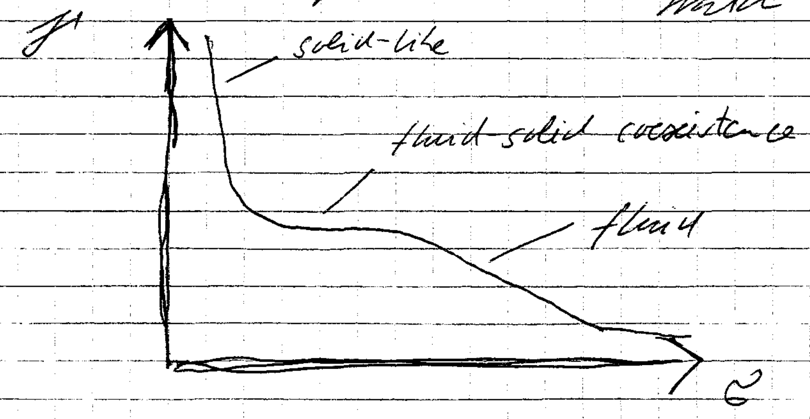
- $[\gamma] = \frac{J}{m^2} = \frac{N}{m}$
- Filmbalance



total area $2hl$

$\Rightarrow$ lipid monolayers:





<u>bubble</u>: vapor or gas trapped by thin film

<u>cavity</u>: vapour or gas - filled hole in liquid

<u>droplet</u>: small volume of liquid in contact with vapour or gas

Laplace equation: $\boxed{p_{in} = p_{out} + \frac{2\gamma}{r}}$

proof: outward force acting on droplet:

$$4\pi r^2 p_{in}$$

inward force (from pressure): $4\pi r^2 p_{out}$

$$d\sigma = 4\pi (r + dr)^2 - 4\pi r^2 = 8\pi r\, dr$$

$dr^2 \approx 0$

$\Rightarrow dw = 8\pi \gamma r\, dr$

force opposing stretching: $F = 8\pi \gamma r$

$\Rightarrow$ total inward force: $4\pi r^2 p_{out} + 8\pi \gamma r$

equilibrium: $4\pi r^2 p_{in} = 4\pi r^2 p_{out} + 8\pi \gamma r$

Rain clouds: "Nucleation"

difference in pressure decreases for small droplets

⇒ Kelvin equation

$$p = p_{vap}\, e^{2\gamma V_m / rRT}$$

vapour pressure of a droplet of radius r

⇒ microscopic water droplets which could form clouds are instable due to increased vapour pressure, seeding of ~~ctr~~ clouds, bubble chamber

⇒ supersaturated vapour

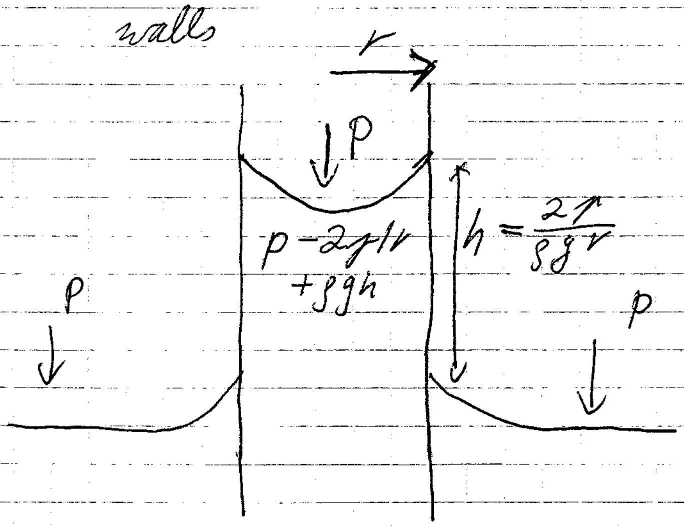
nucleation centres are required!

also superheated and supercooled liquids

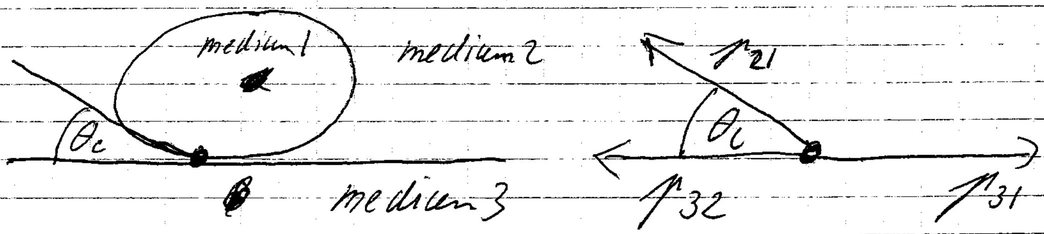
unstirred beaker

Capillary action:

liquid that has a tendency to adhere to walls



The contact angle



$$\gamma_{31} = \gamma_{32} + \gamma_{21} \cos\theta_c \iff \cos\theta_c = \frac{\gamma_{31} - \gamma_{32}}{\gamma_{21}}$$

work of adhesion of medium 1 to medium 3

$$w_{ad} = \gamma_{31} + \gamma_{21} - \gamma_{32}$$

$$\Rightarrow \boxed{\cos\theta_c = \frac{w_{ad}}{\gamma_{21}} - 1}$$

wetting: $0^\circ < \theta_c < 90^\circ \iff 1 < \frac{w_{ad}}{\gamma_{21}} < 2$

non-wetting: $90^\circ < \theta_c < 180^\circ \iff 0 < \frac{w_{ad}}{\gamma_{21}} < 1$

potential exercises:

6.15, 6.14, 6.9, 6.10

potential problems:

6.4, 6.7,