

Entropy of phase transitions:

at the transition temperature (reversible) : $\Delta_{trs} S = \frac{\Delta_{trs} H}{T_{trs}}$

freezing, condensing \Rightarrow exothermic $\Rightarrow \Delta_{trs} H < 0$

$\Rightarrow \Delta_{trs} S < 0$

\Rightarrow system becomes more ordered

melting, vaporizing \Rightarrow endothermic $\Rightarrow \Delta_{trs} H > 0$

$\Rightarrow \Delta S > 0$

\Rightarrow system becomes more disordered

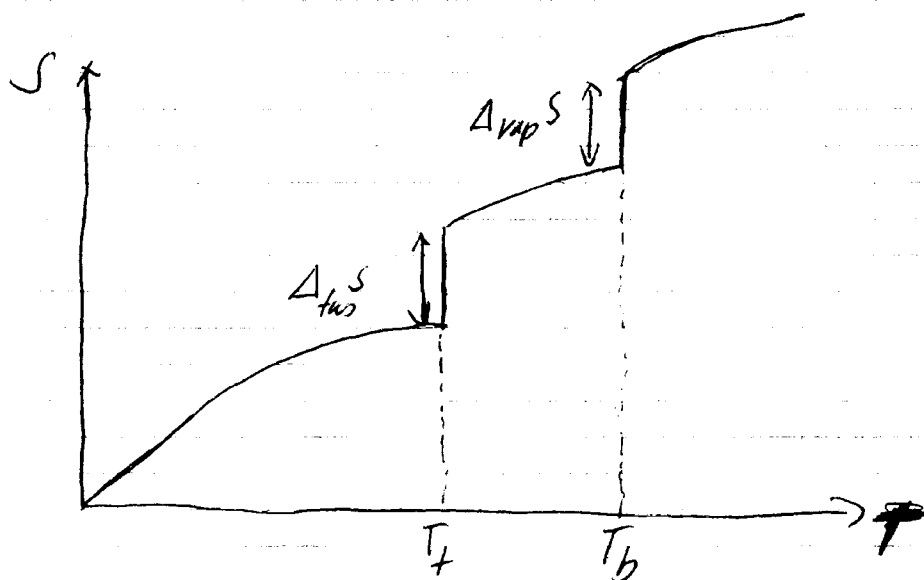
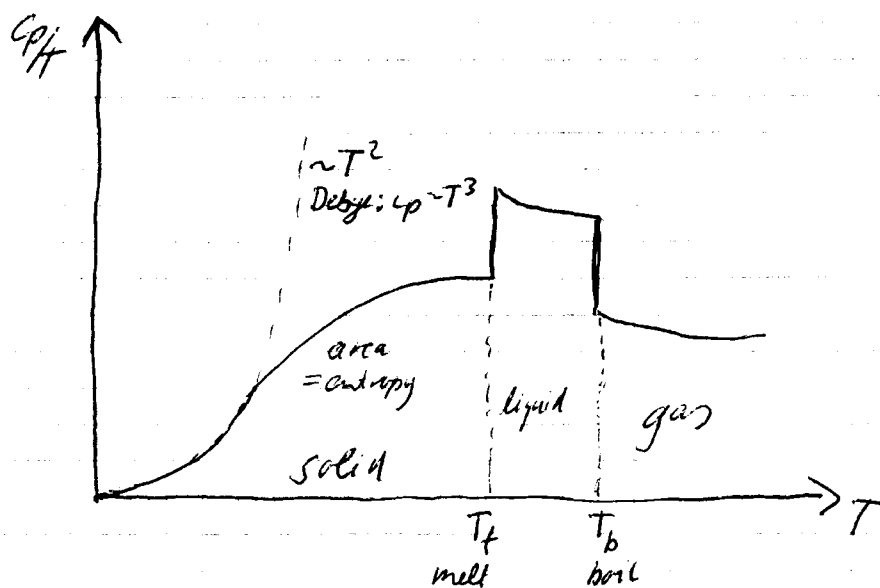
\Rightarrow Trautz's rule:

A wide range of liquids give approximately the same standard entropy of vaporization $\approx 85 \frac{J}{Kmol}$

\Rightarrow comparable amount of disorder is generated when any liquid evaporates and becomes a gas

(water has a larger entropy of vaporization arising from hydrogen bonding)

Calorimetry and the measurement of entropy:



$$S(T) = S_0 + \int_0^{T_f} \frac{C_p(\text{solid})}{T} dT + \frac{\Delta S_{fus} + H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(\text{liquid})}{T} dT + \frac{\Delta S_{vap} + H}{T_b} + \int_{T_b}^T \frac{C_p(\text{gas})}{T} dT$$

1.6. Cohesive forces:

$$V + dV: U' = U + \left. \frac{\partial U}{\partial V} \right|_T dV$$

$$T + dT: U' = U + \left. \frac{\partial U}{\partial T} \right|_V dT$$

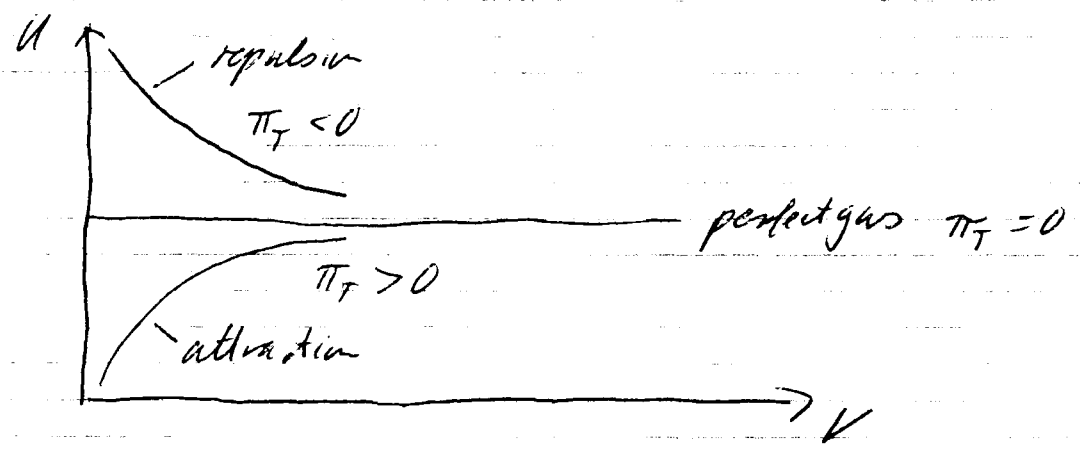
$$U' = U + \left. \frac{\partial U}{\partial V} \right|_T dV + \left. \frac{\partial U}{\partial T} \right|_V dT$$

$$dU = \left. \frac{\partial U}{\partial V} \right|_T dV + \left. \frac{\partial U}{\partial T} \right|_V dT$$

$$= \left. \frac{\partial U}{\partial V} \right|_T dV + c_V dT$$

\searrow = π_T internal pressure

$$dU = \pi_T dV + c_V dT$$



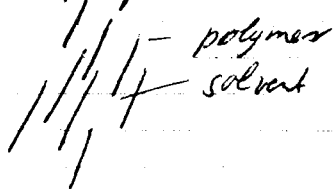
2. Physical Transformations of pure substances

2.1. Phase Diagrams

A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state (various solid phases, liquid, gas)

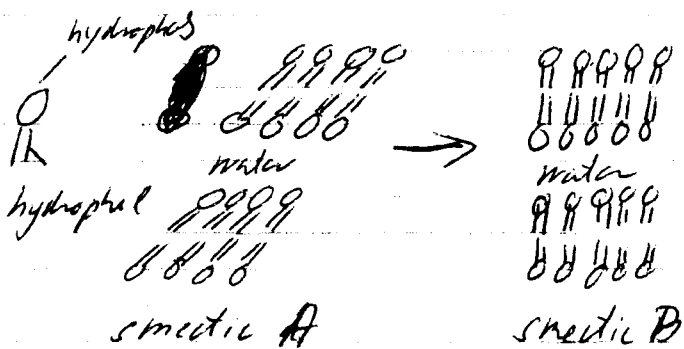
BUT: Liquid Crystals

- rigid polymer (e.g. microtubule)



⇒ nematic phase

- Lipids ⇒ cell membranes



- chiral polymer (e.g. DNA)



cholesteric phase

⇒ Landau's definition of a phase:

phases can be distinguished by their degree of order

⇒ introduces concept of order parameter!

(Note: gas and liquid the same phase?)

phase transitions: spontaneous change of one phase into another phase

transitions can be infinitely slow

⇒ metastable states ⇒ glasses

• sand:

perfect: hexagonal order

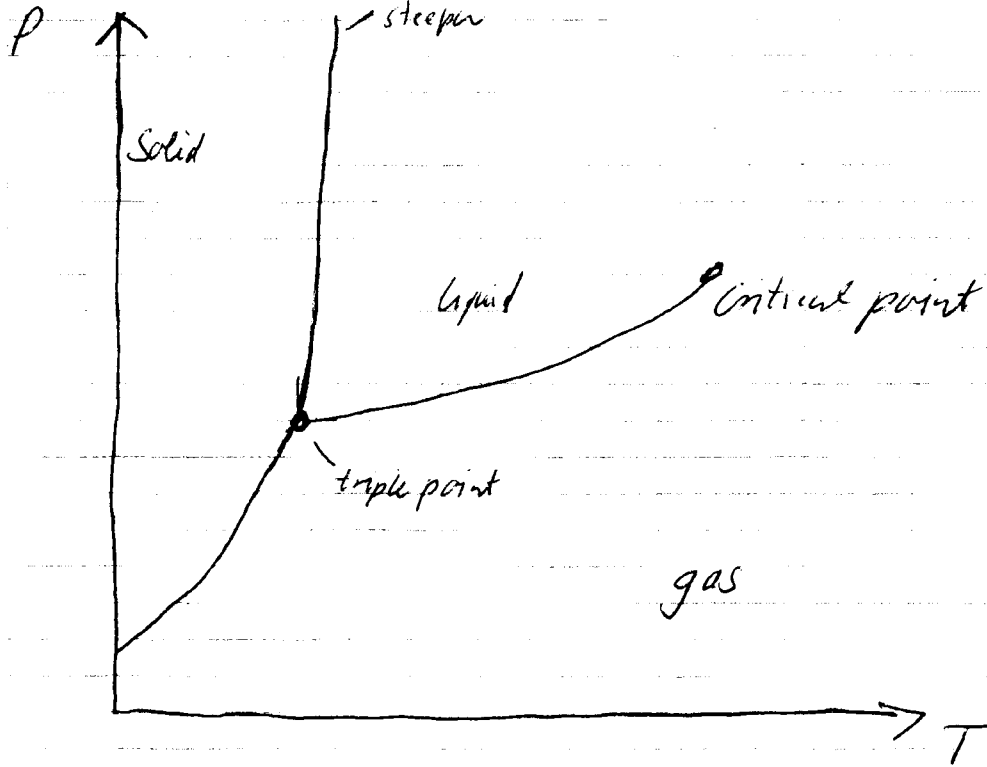
real: jamming prevents perfect orders
⇒ much less neighbors

• diamonds are metastable ⇒ ground state ~~graphite~~
graphite!

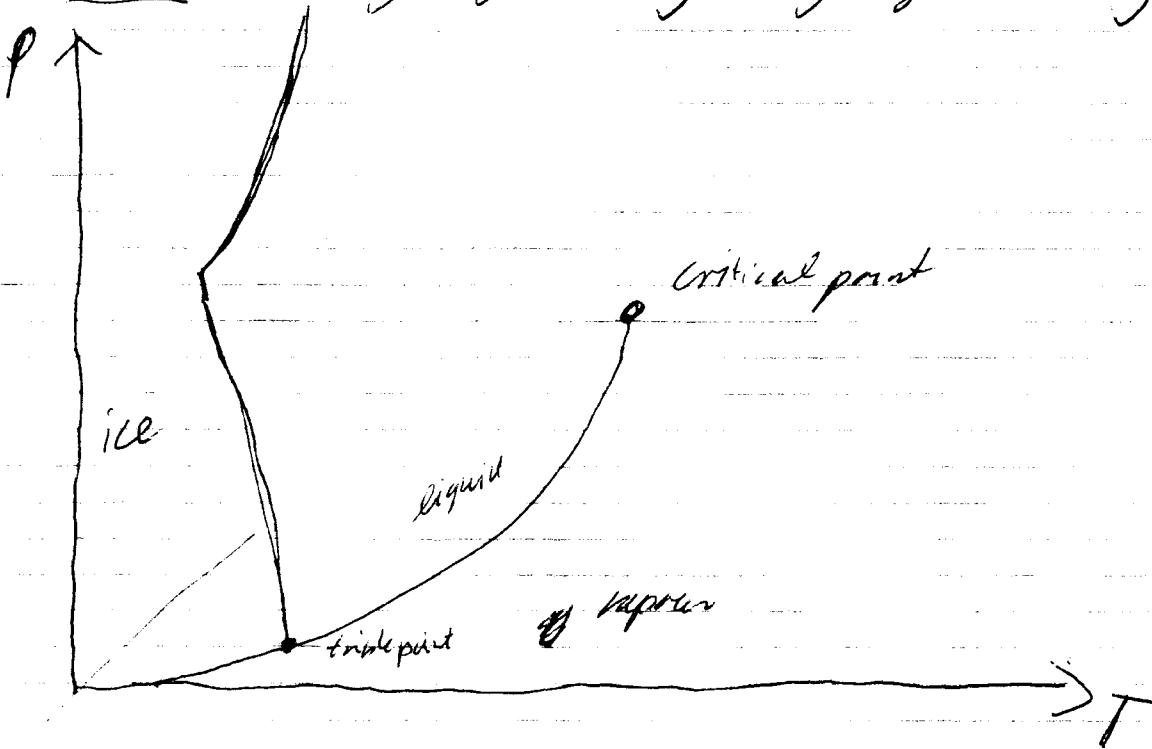
typical phase diagrams

36

1. CO_2 characteristic of most substances



2. water ~~high boiling point~~ hydrogen bonding!



Ice has larger volume than water

2.2. Phase stability and phase transitions

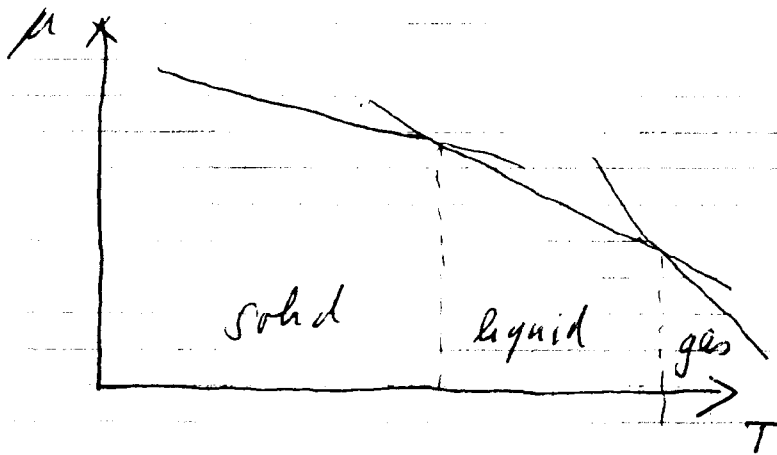
37

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

Proof: $\mu_1 > \mu_2$ amount dn transferred from 1 \rightarrow 2
 $\Rightarrow dG = (\mu_2 - \mu_1) dn < 0$
spontaneous reaction

- $S(\text{gas}) > S(\text{fluid}) > S(\text{solid})$

$$\left. \frac{\partial \mu}{\partial T} \right|_P = -S$$



- $\left. \frac{\partial \mu}{\partial P} \right|_T = V$ $V(\text{liquid}) > V(\text{solid})$

- pressure increases μ more in a liquid than in a solid
- most substances melt at a higher temperature when subjected to pressure

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

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

$$\Rightarrow d\mu_{\alpha} = d\mu_{\beta} \quad \wedge \quad d\mu = -S_m dT + V_m dp$$

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

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{S_{\beta,m} - S_{\alpha,m}}{V_{\beta,m} - V_{\alpha,m}} = \frac{\Delta_{tr} S}{\Delta_{tr} V}} \quad \text{Clapeyron equation}$$

solid-liquid:

$$\frac{dp}{dT} = \frac{\Delta_{tr} H}{T \Delta_{tr} V} \Rightarrow \begin{matrix} / > 0 \\ \approx 0, > 0 \end{matrix} \Rightarrow > 0, \text{ steep!}$$

\Rightarrow phase boundary: p, p^*, T, T^* melting pressures and temperatures
* known values

$$\int_{p^*}^p dp = \frac{\Delta_{tr} H}{\Delta_{tr} V} \int_{T^*}^T \frac{dT}{T}$$

$\Delta_{tr} H, \Delta_{tr} V \approx T\text{-independent}$

$$\Rightarrow \boxed{p = p^* + \frac{\Delta_{tr} H}{\Delta_{tr} V} \ln \frac{T}{T^*}}$$

for $T \approx T^*$: $\Rightarrow \ln \frac{T}{T^*} \approx \frac{T - T^*}{T^*}$

$$\Rightarrow p \approx p^* + \frac{\Delta_{tr} H}{\Delta_{tr} V} (T - T^*)$$

Liquid-vapour:

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

\searrow
 $\Rightarrow 0$

$$\Delta_{\text{trs}} V \approx V_{\text{m}}(\text{gas})$$

$$\text{ideal gas: } V_{\text{m}}(\text{gas}) = \frac{RT}{p}$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta_{\text{trs}} H}{T \left(\frac{RT}{p}\right)} \Rightarrow \boxed{\frac{d \ln p}{dT} = \frac{\Delta_{\text{trs}} H}{RT^2}}$$

Clausius -
Clapeyron
equation

$\frac{dx}{x} = d \ln x$

$\Delta_{\text{trs}} H \approx$ temperature independent, integrate equation

$$p = p^* e^{-x}$$

with $x = \frac{\Delta_{\text{trs}} H}{R} \left(\frac{1}{T} - \frac{1}{T^*} \right)$

2.4 Phase transitions, the Ehrenfest classification:

transition from a phase α to a phase β

$$\left. \frac{\partial \mu_\alpha}{\partial p} \right|_T - \left. \frac{\partial \mu_\alpha}{\partial p} \right|_T = V_{\beta,m} - V_{\alpha,m} = \Delta_{\text{tr}} V \quad \text{Volume change!}$$

$$\left. \frac{\partial \mu_\beta}{\partial T} \right|_p - \left. \frac{\partial \mu_\alpha}{\partial T} \right|_p = -S_{\beta,m} + S_{\alpha,m} = -\Delta_{\text{tr}} S = -\frac{\Delta_{\text{tr}} H}{T_{\text{tr}}} \quad \text{heat uptake!}$$

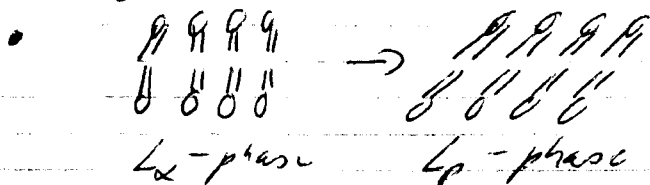
first-order phase transition

- first derivative of the chemical potential with respect to temperature T is discontinuous
- latent heat!
- c_p becomes infinite! • e.g. melting transitions

second-order phase transition:

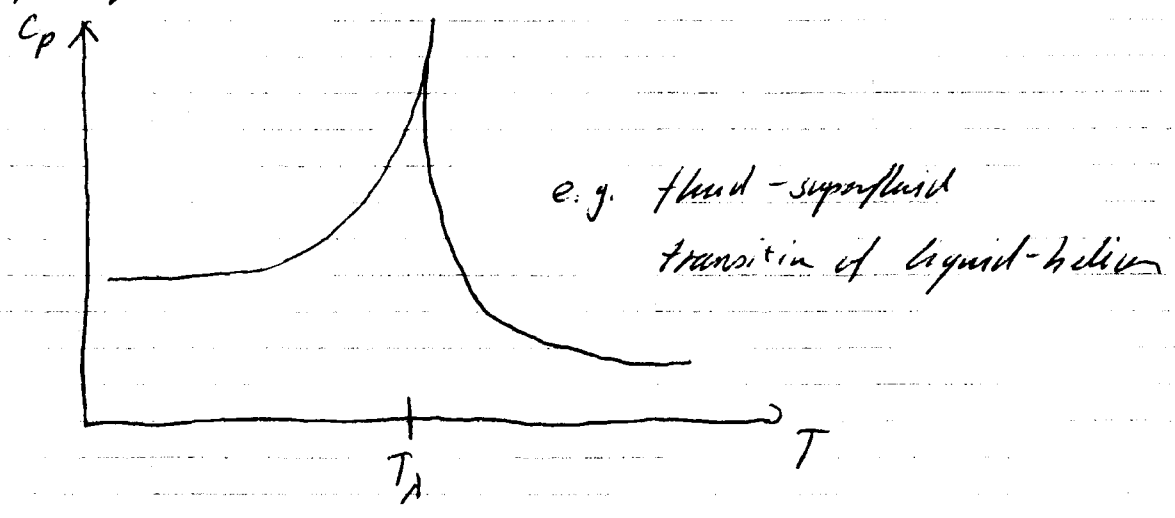
- first derivative of μ with respect to temperature T is continuous, but its second derivative is discontinuous
- volume and entropy (and hence the enthalpy) do jump at the transition
- c_p is discontinuous, but not infinite

~~...~~



λ -transitions:

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

Note: Landau defines phase transitions by discontinuous derivatives of the order parameter!

2.5 The liquid surface:

• surface tension γ :

- liquids such as water to minimize their air-liquid surface (e.g. for water molecules no hydrogen bonding with air makes surface unfavorable) \Rightarrow leads to droplets

• work needed to change the surface area Δ

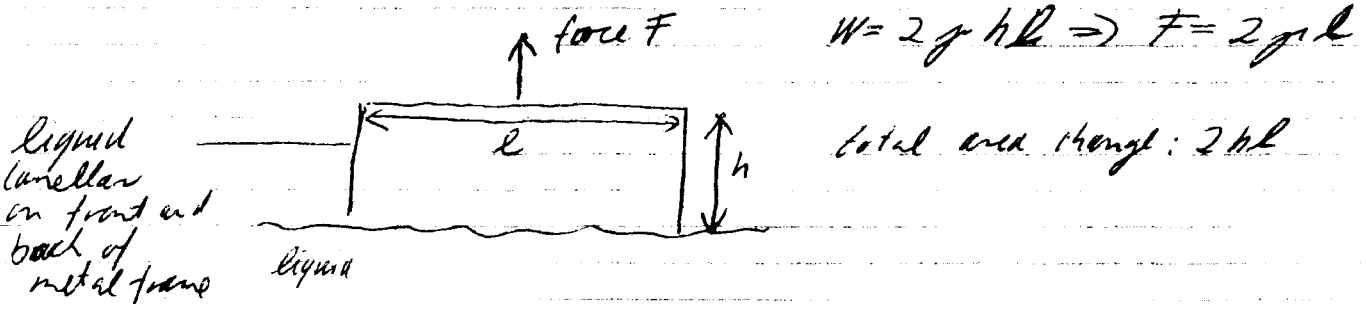
$$dW = \gamma d\Delta = dH$$

\uparrow
 $V = \text{const}$
 $T = \text{const}$

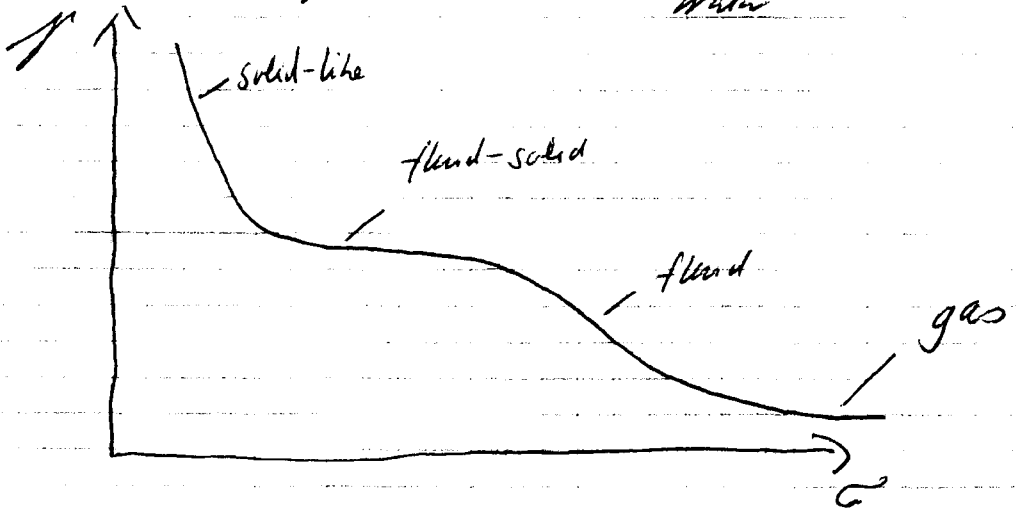
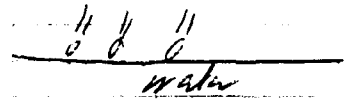
Helmholtz energy

• $[\gamma] = \frac{J}{m^2} = \frac{N}{m}$ "2-dimensional pressure"

• film balance

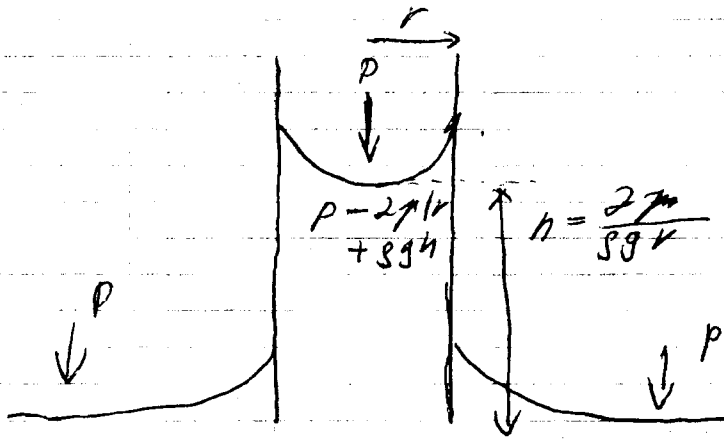


\Rightarrow lipid monolayers:

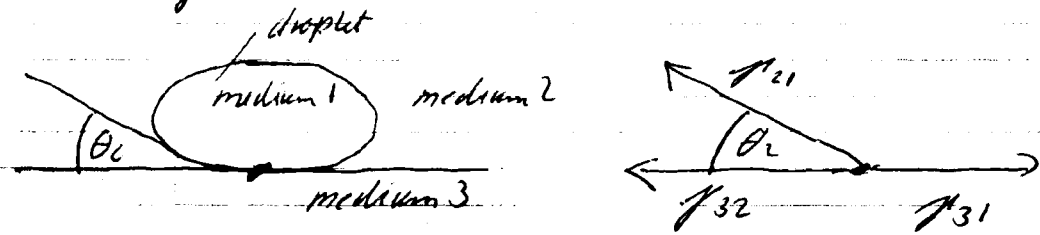


• Capillary action

liquid that has a tendency to adhere to walls



• contact angle θ_c



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

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

adhesion work of medium 1 to ~~medium~~ medium 3:

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

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

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

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