

Molecular Physics

Mid term  
exam

18. 12

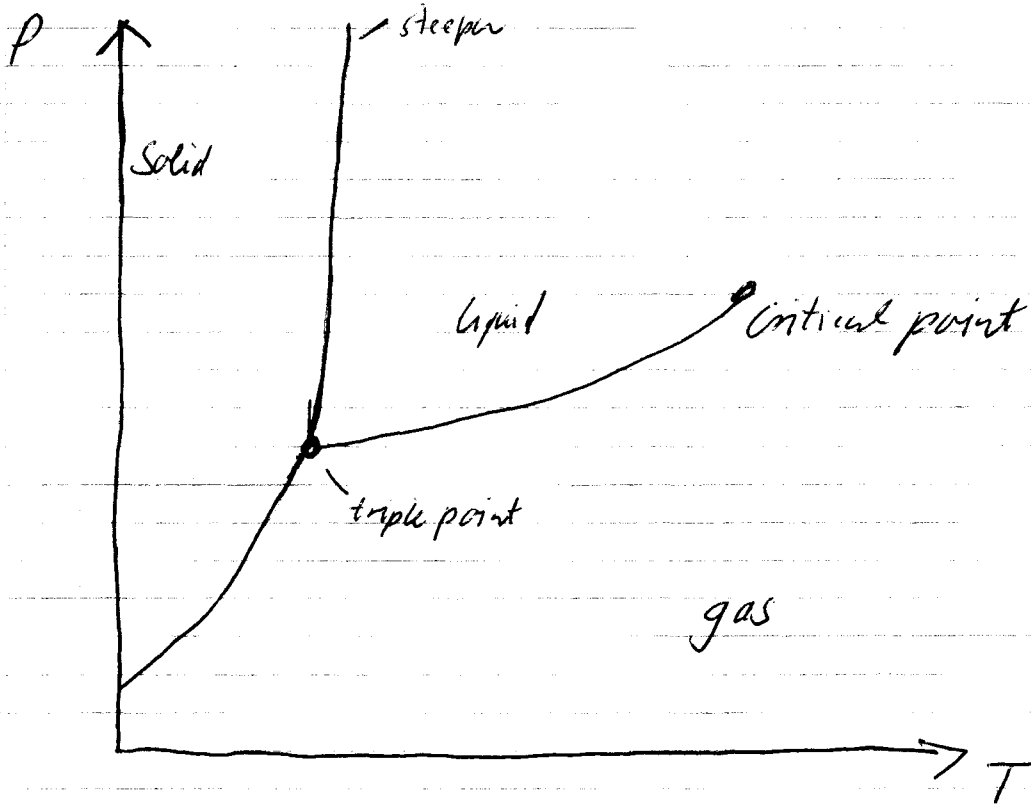
Mo 9.15 - 10.45

SR 224

# typical phase diagrams

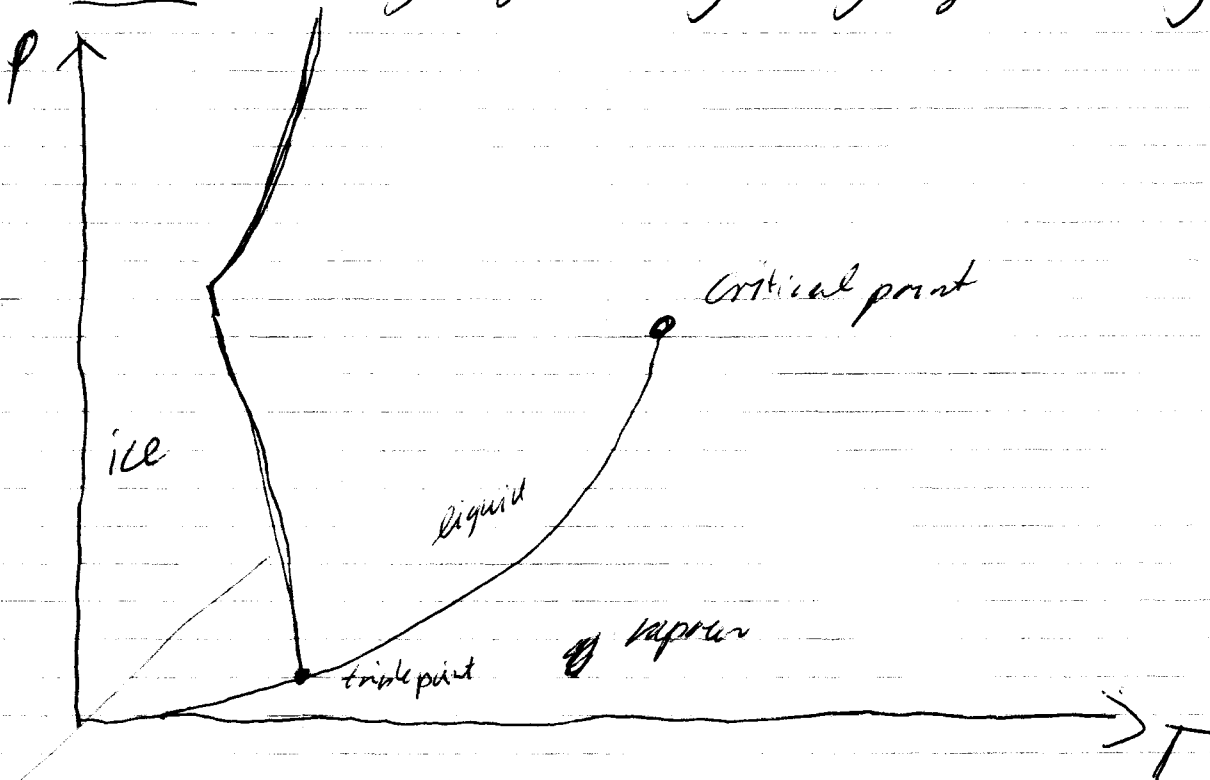
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1.  $\text{CO}_2$  characteristic of most substances



2. water

~~hydrogen bonding~~ hydrogen bonding!



Ice has larger volume than water

## 2.2. Phase stability and phase transitions

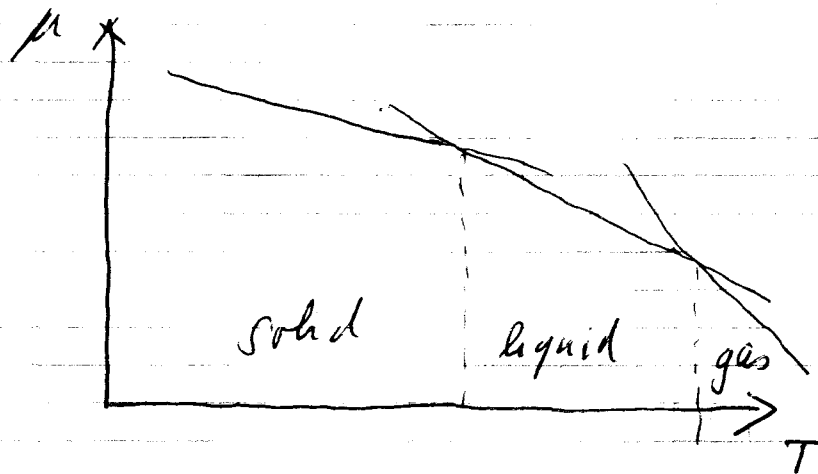
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- At equilibrium the chemical potential of a substance is the same throughout a sample regardless of how many phases are present

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  $\mu$  more in a liquid than in a solid
- most substances melt at a higher temperature when subject to pressure

2.3 Location of phase boundaries between a phase  $\alpha$  and  $\beta$  which are in equilibrium:

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

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

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

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

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:

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

↘

→ 0

$$\Delta_{tr} V \approx V_m(\text{gas}) \quad \text{ideal gas: } V_m(\text{gas}) = \frac{RT}{p}$$

$$\Rightarrow \frac{dp}{dT} = \frac{\Delta_{tr} H}{T \left(\frac{RT}{p}\right)} \Rightarrow \boxed{\frac{d \ln p}{dT} = \frac{\Delta_{tr} H}{RT^2}} \quad \begin{array}{l} \text{Clausius-} \\ \text{Clapeyron} \\ \text{equation} \end{array}$$

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

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

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

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

2.4 Phase transitions, the Ehrenfest classification:

transition from a phase  $\alpha$  to a phase  $\beta$

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

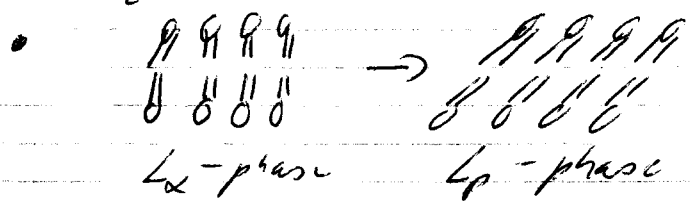
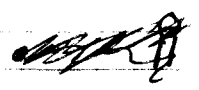
$$\left. \frac{\partial \mu_\beta}{\partial T} \right|_p - \left. \frac{\partial \mu_\alpha}{\partial T} \right|_p = -S_{\beta,m} + S_{\alpha,m} = -\Delta_{tr} S = - \frac{\Delta_{tr} H}{T_{tr}} \quad \text{heat uptake!}$$

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

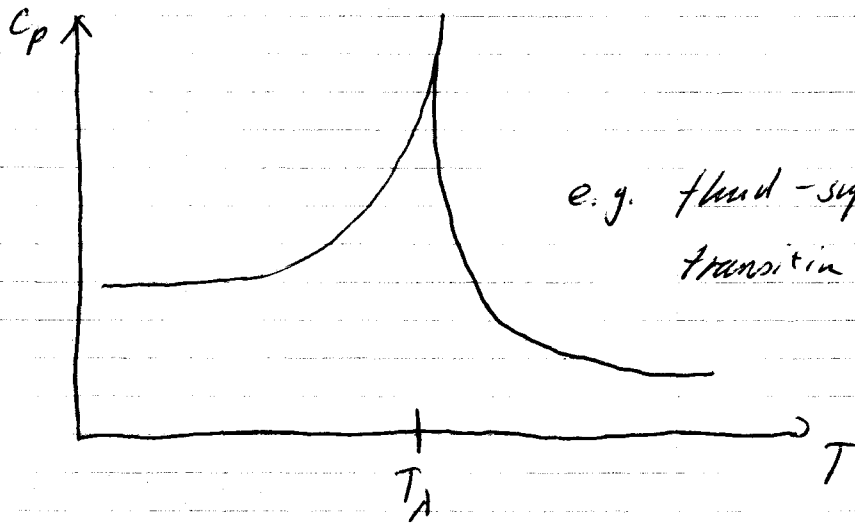
second-order phase transition:

- first derivative of  $\mu$  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



$\lambda$ -transitions:

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



e.g. fluid-superfluid transition of liquid-helium

- e.g. order-disorder transition in  $\beta$ -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  $\gamma$ :

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

- work needed to change the surface area  $\Delta$

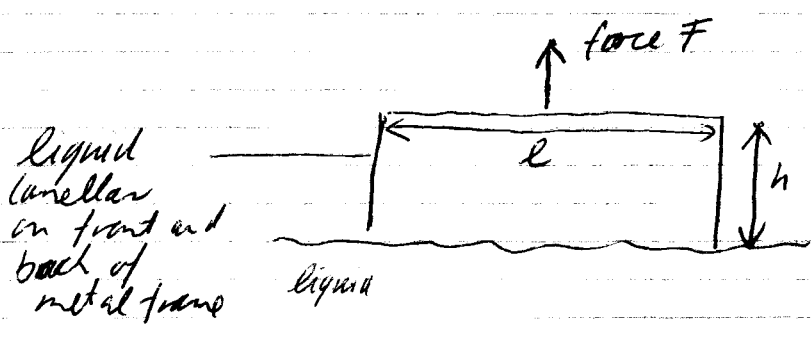
$$dW = \gamma dA = dH$$

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

Helmholtz energy

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

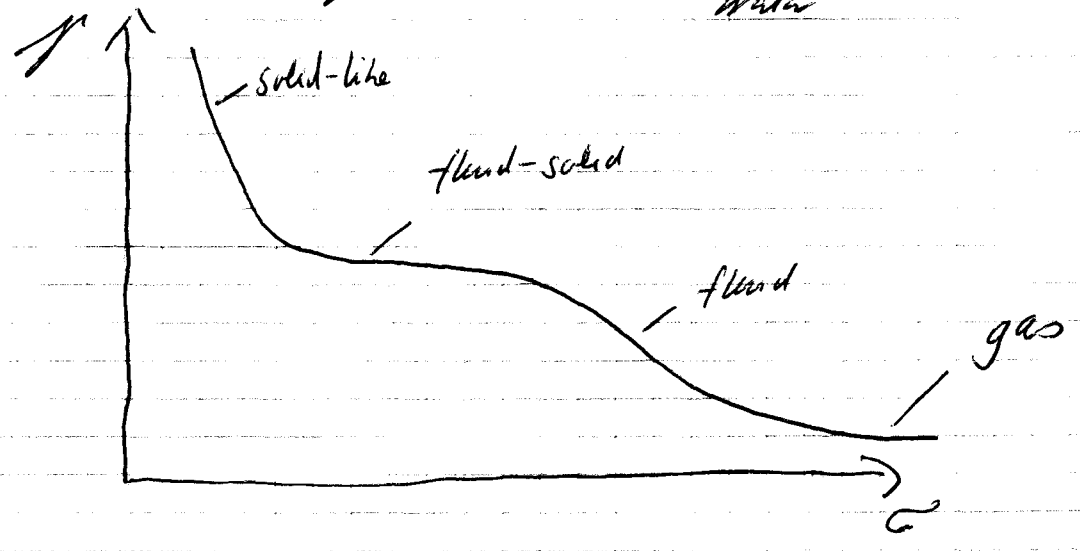
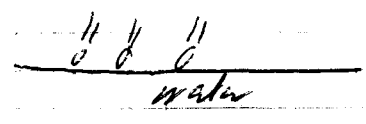
• film balance:



$$W = 2\gamma h l \Rightarrow F = 2\gamma l$$

total area change:  $2hl$

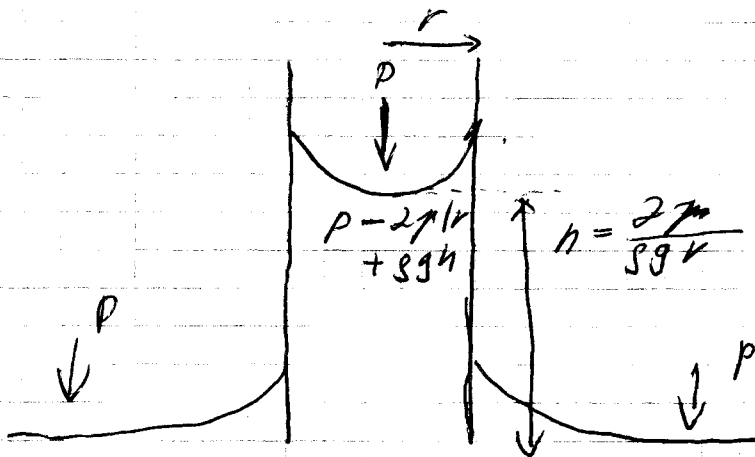
$\Rightarrow$  lipid monolayers:



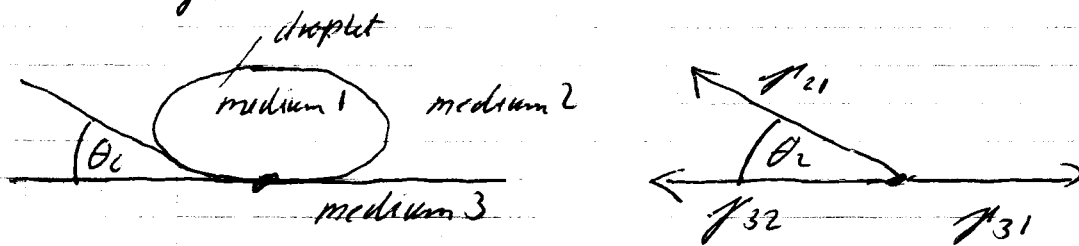


• Capillary action

liquid that has a tendency to adhere to walls



• contact angle  $\theta_c$



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

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

adhesion work of medium 1 to ~~the~~ 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:  $90^\circ < \theta_c < 180^\circ \Leftrightarrow 0 < \frac{W_{ad}}{\gamma_{21}} < 1$