

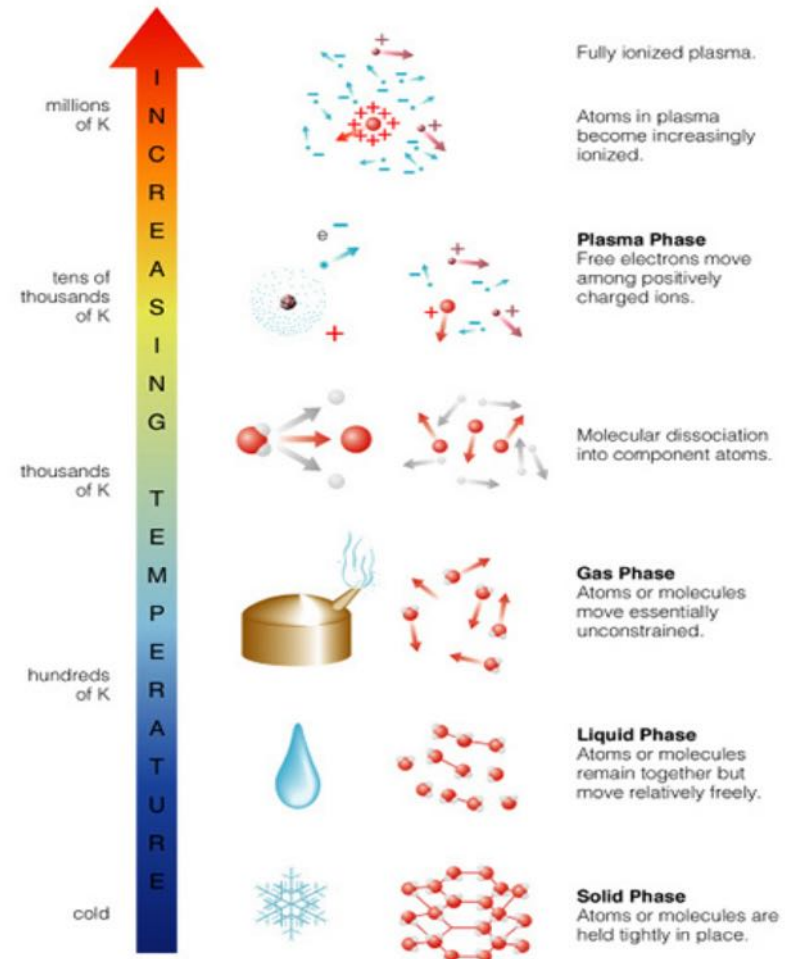
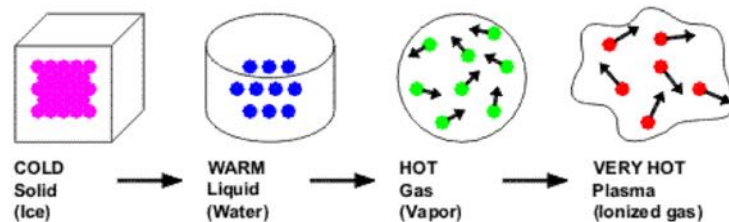
# Lecture 12

01.10.2018

Phase transformations

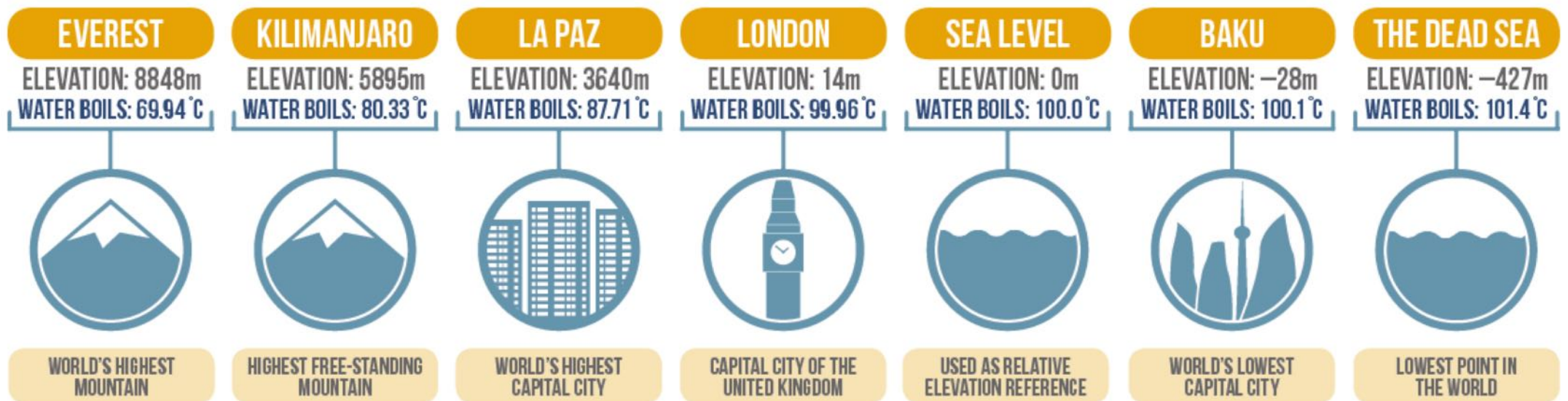
# A phase transformation

- **Discontinuous change** in the properties of substance when the environment is changed infinitesimally.
- Change between **phases** – different forms of the substance
- Example: water vs. temperature...



# A phase transformation

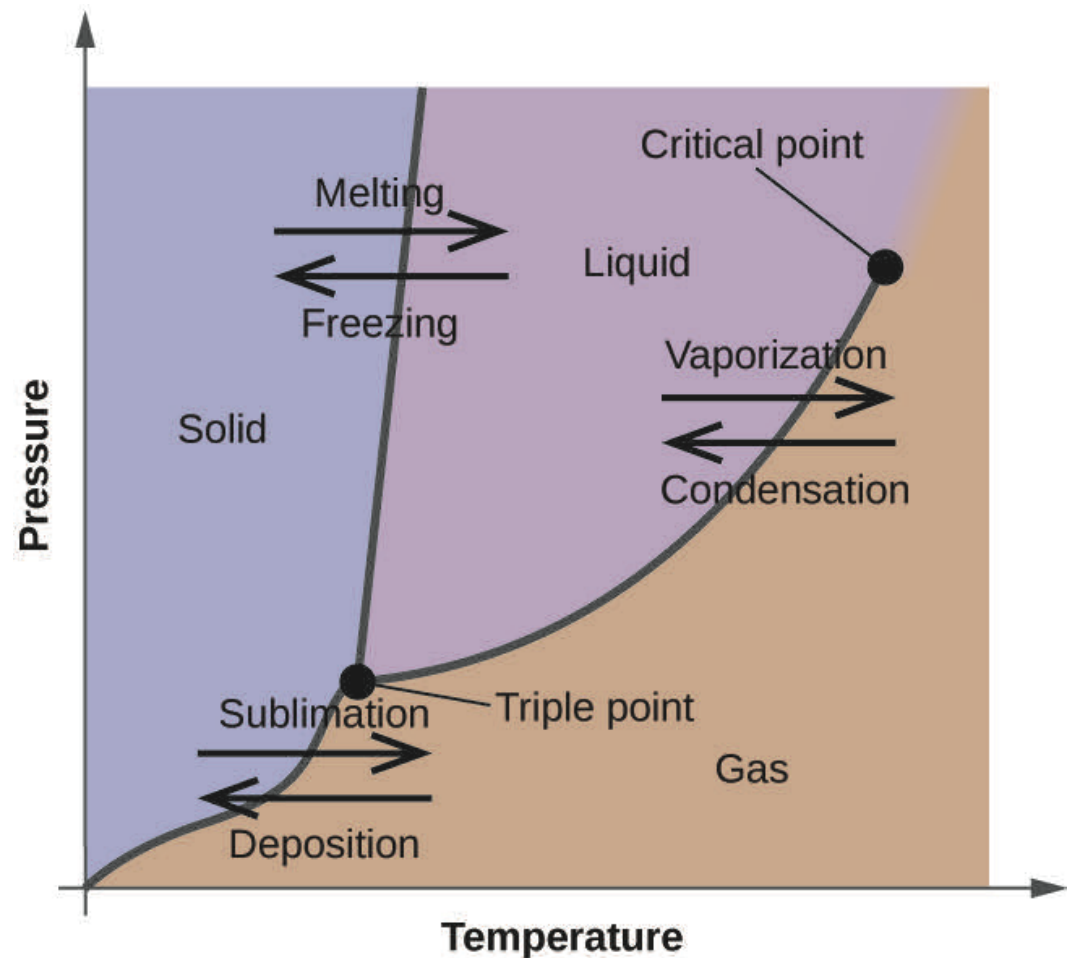
- Often more than one variable that affects the phase of substance (eg, temperature & pressure)



After: [www.compoundchem.com](http://www.compoundchem.com)

# Phase diagram

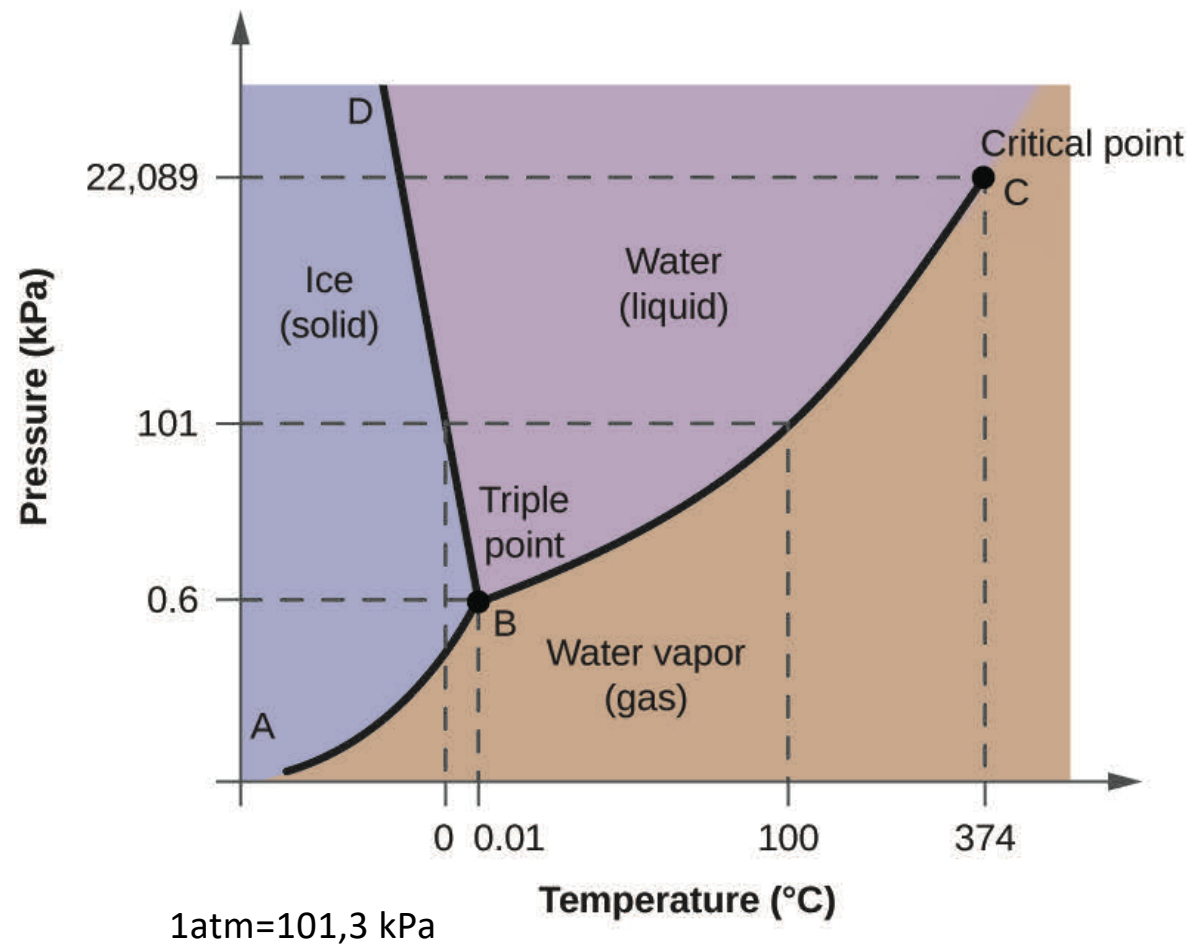
- A graph showing the equilibrium phases as a function of pressure and temperature.
- Critical point – gas too dense -> fluid...



After: *Chemistry, OpenStax*

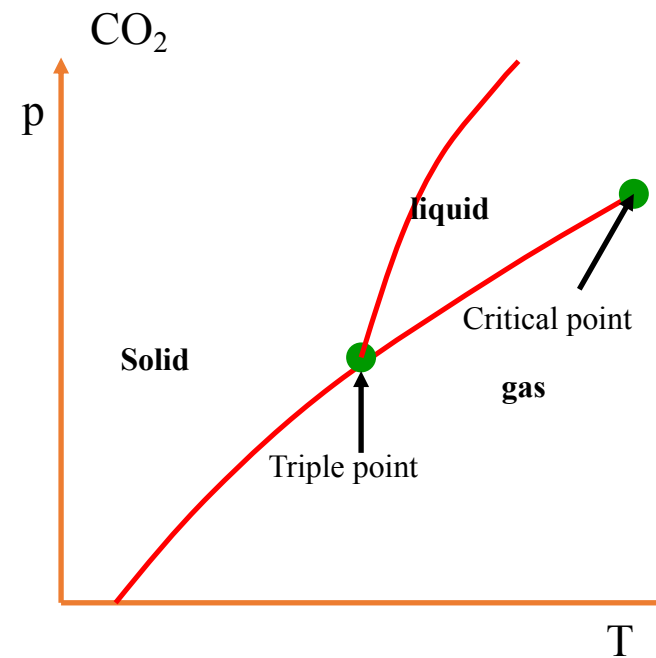
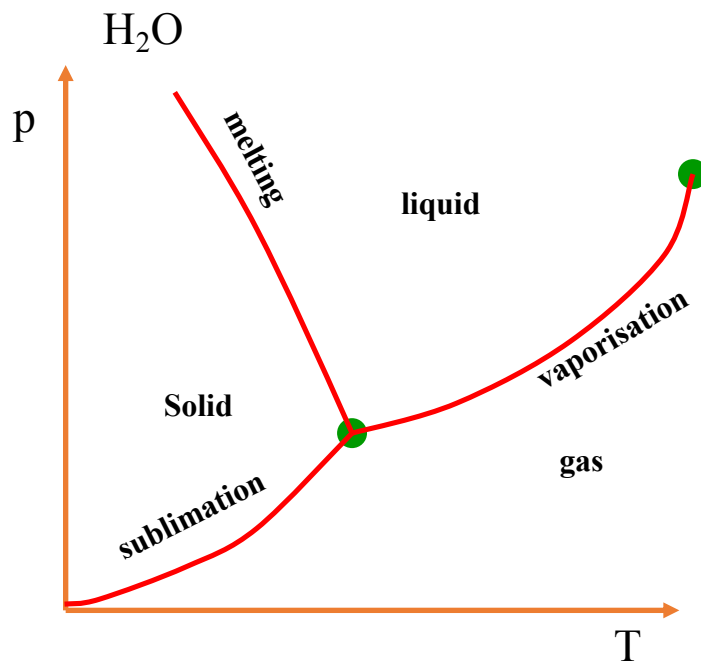
# Phase diagram, H<sub>2</sub>O

- Let us consider water, H<sub>2</sub>O
- Vapour pressure: coexisting gas and solid/liquid phase.
- Triple and critical points.
- Low pressures: no liquid phase
- We can still have metastable phases (superheated, supercooled)

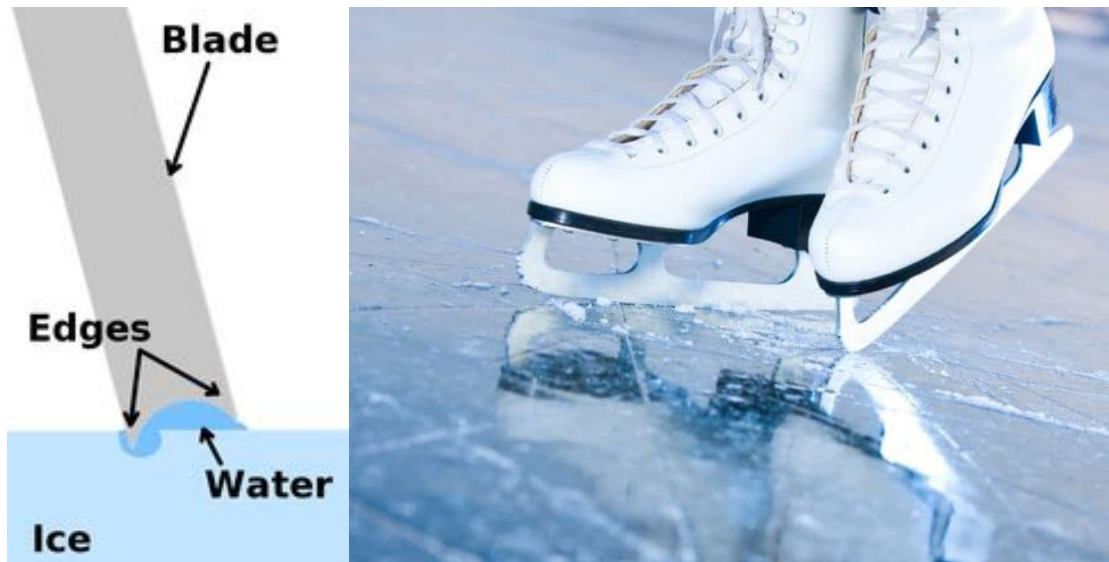


# Phase diagram, H<sub>2</sub>O

- H<sub>2</sub>O vs. other most other substances – different slope of liquid/solid.



# Peculiarity of Ice



Ice less dense than water...

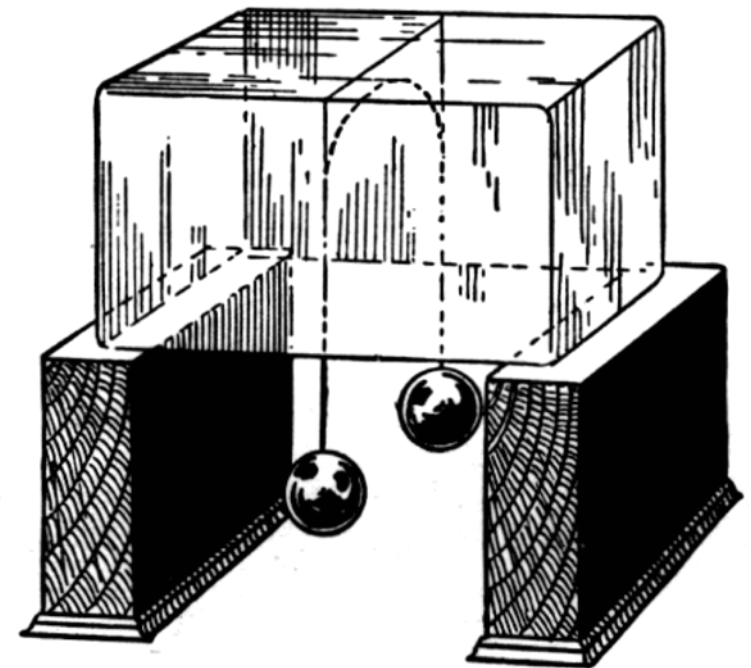


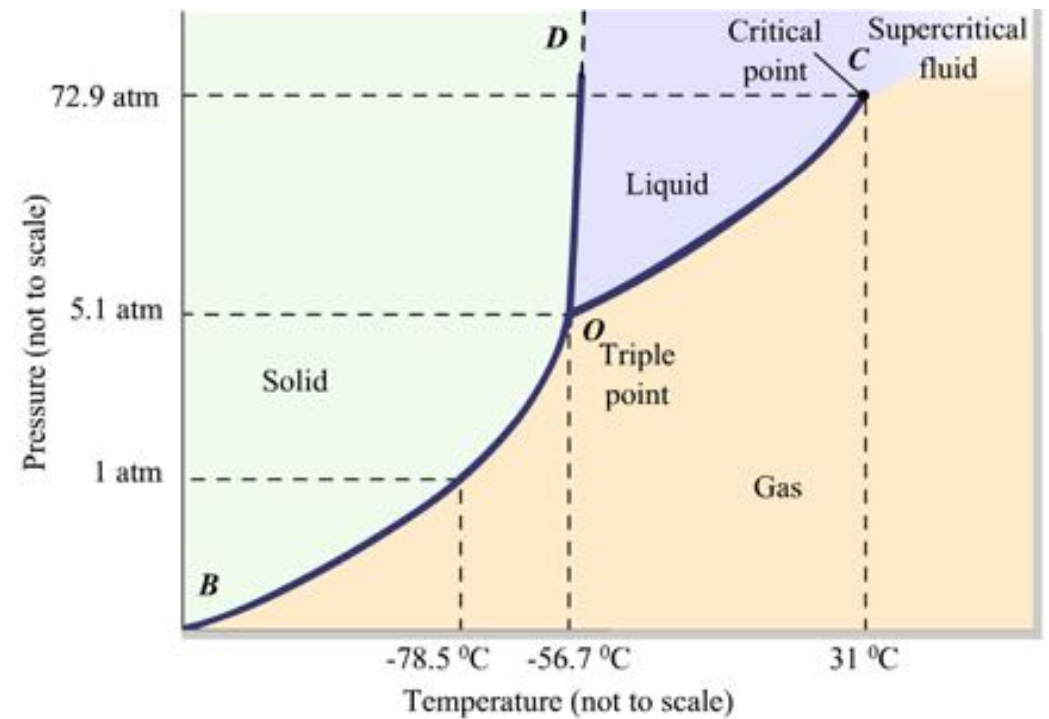
FIG. 47.—Wire cutting through ice (from Tyndall).

*Bragg, Concerning the Nature of Things, 1925*



# Phase diagram, CO<sub>2</sub>

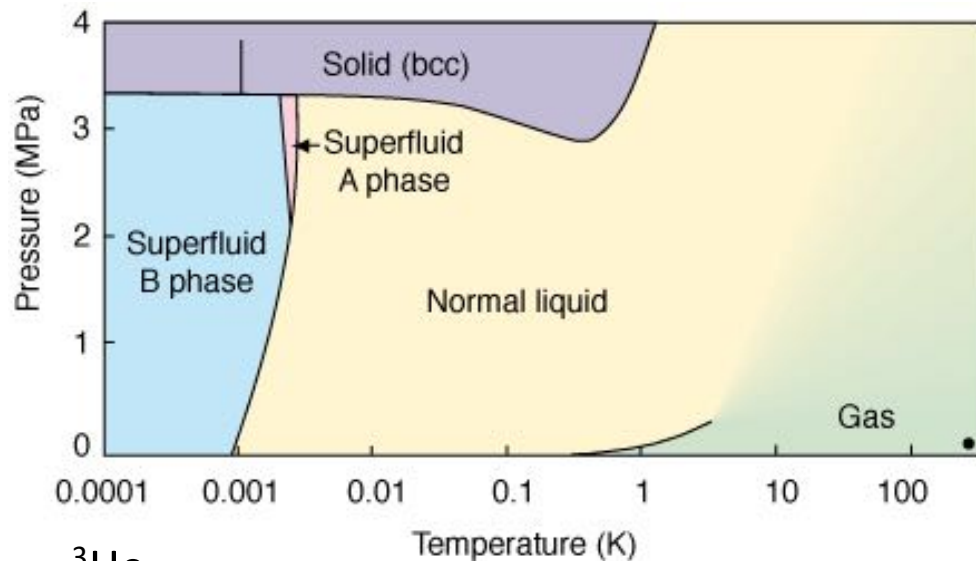
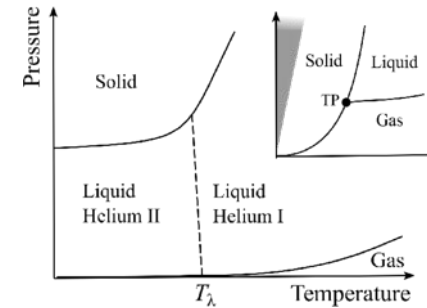
- Higher pressure raises melting temperature.
- Dry ice sublimation is easily observed for CO<sub>2</sub>





# Phase diagram, Helium

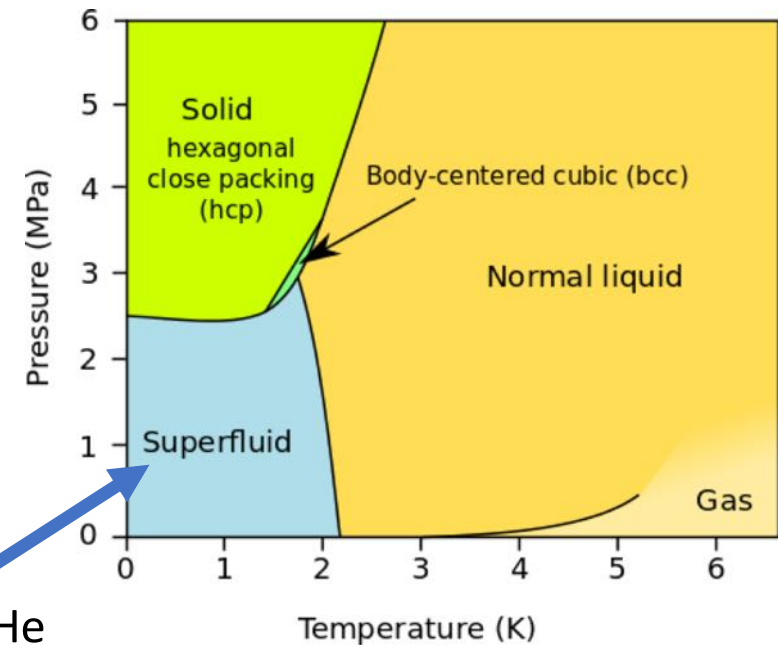
- The most «exotic» phase behavior
- Liquid at zero T.



$^3\text{He}$

Zero viscosity, very high thermal conductivity

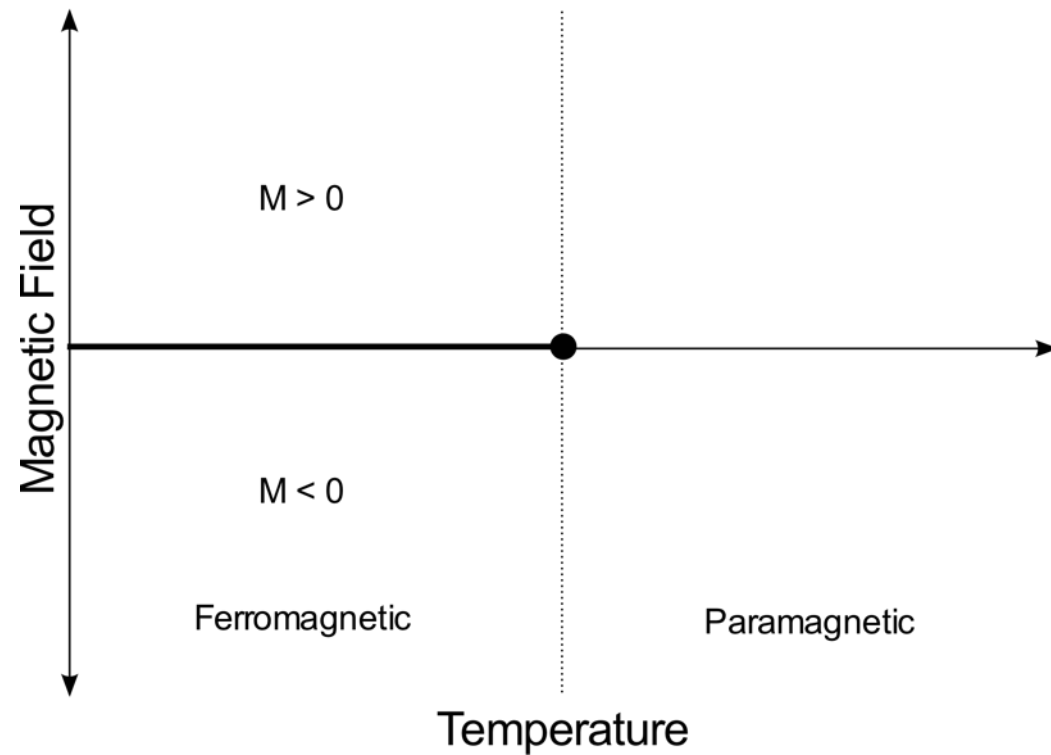
Fys2160, 2018



$^4\text{He}$

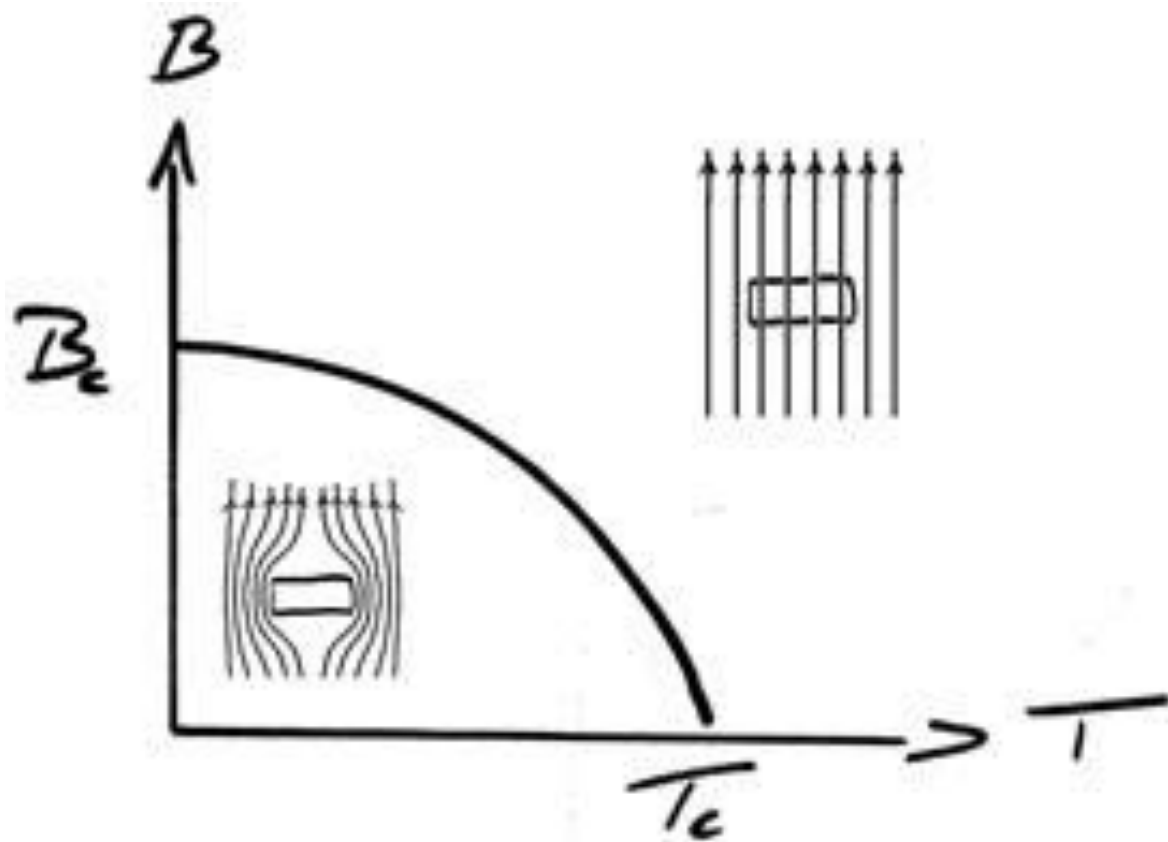
# Ferromagnet

- Curie temperature (iron 1043 K) magnetization disappears – no more phase boundary above critical point



# Superconductor

- Type I – tin, mercury, lead
- Low B-field and T gives zero electrical resistivity.

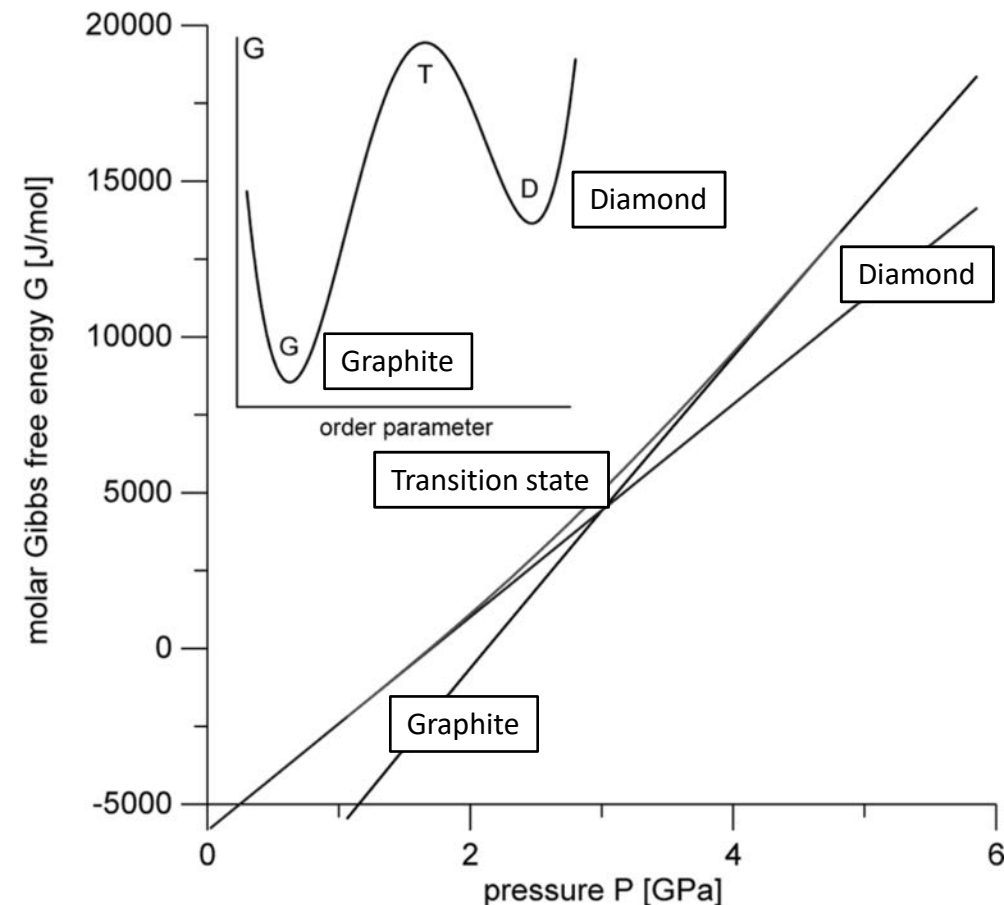


Ice less dense than water...

# Graphite vs. Diamonds

- Graphite more stable than diamond
- Gibbs free energy (G) is larger by 2900 J from graphite per mole at 1atm and room temperature.
- G – thermodynamic potential with thermal bath and fixed pressure.

$$G = U - TS + PV$$



# Graphite vs. Diamonds

- Pressure dependence of Gibbs free energy depends on volume

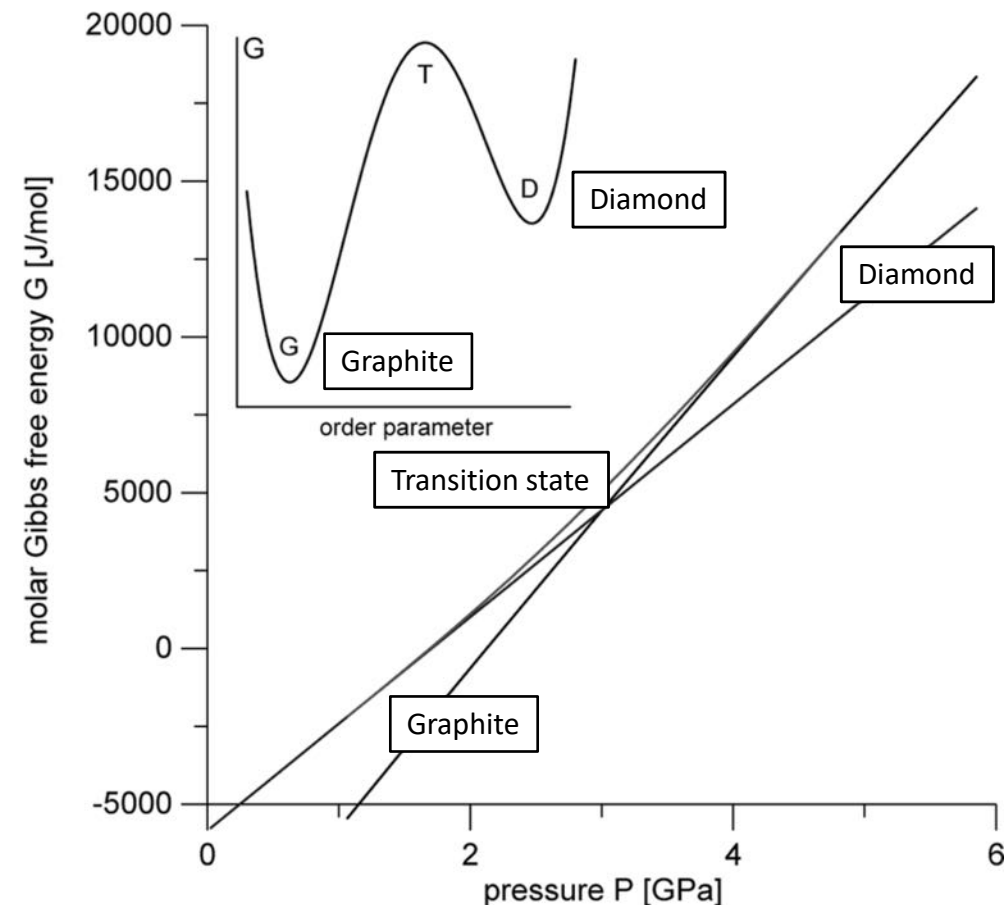
$$\left(\frac{\partial G}{\partial P}\right)_{T,N} = V$$

- This gives us slope:

$$V = 5.31 \times 10^{-6} \text{ m}^3 \text{ (graphite)}$$

$$V = 3.42 \times 10^{-6} \text{ m}^3 \text{ (diamond)}$$

15 GPa => 50 km into the Earth.

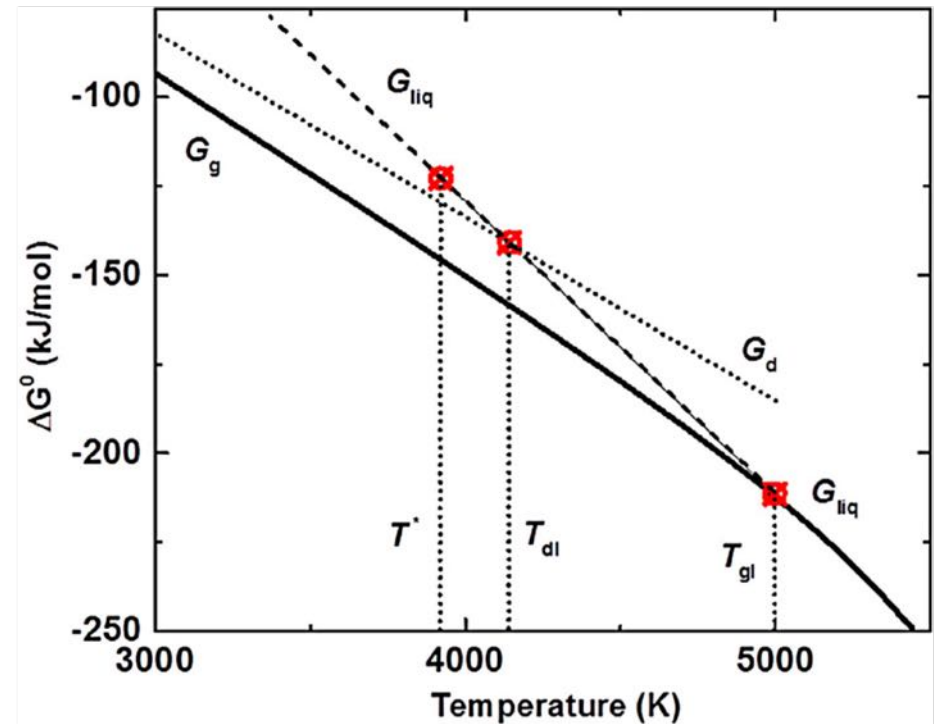


# Graphite vs. Diamonds

- Temperature dependence of Gibbs free energy depends on entropy

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$$

- Larger temperature => Lower G.
- Decrease in G is larger for graphite which has more entropy.
- High T => more pressure needed to keep diamonds stable



**Figure 1.** Gibbs free energy vs. temperature for graphite (G<sub>g</sub>), liquid carbon (G<sub>liq</sub>), and diamond (G<sub>d</sub>).

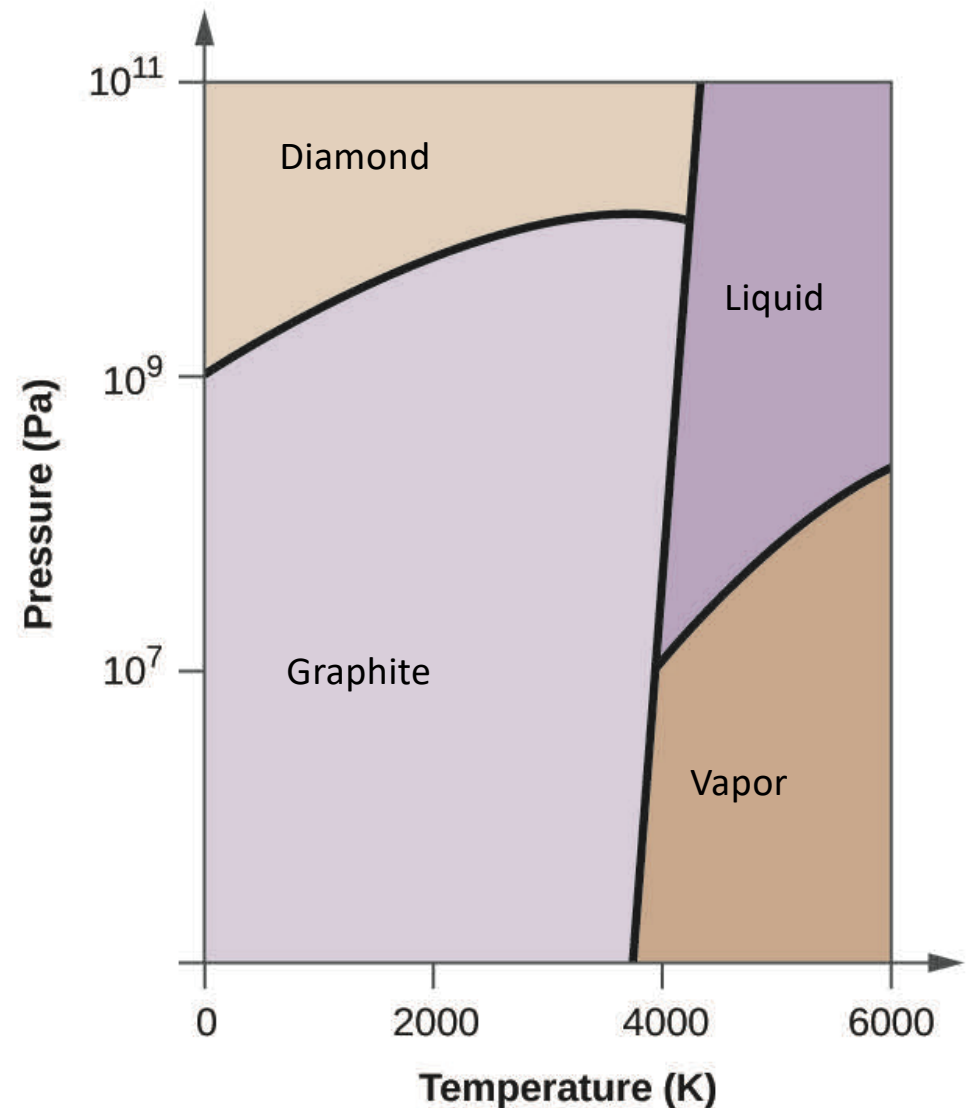
From : *Mat. Res. Lett.* 7, 353, 2018

# Graphite vs. Diamonds

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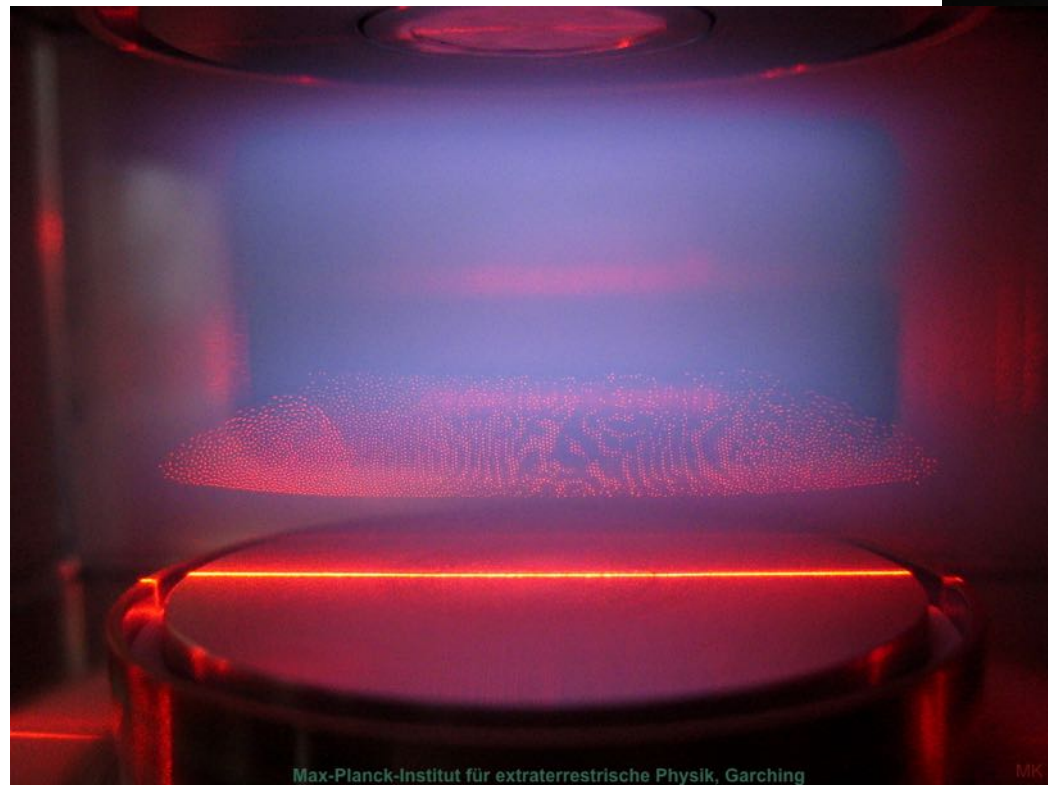


# Complex plasmas

Plasmas = ionised gas,  
electrically conductive

99% of visible matter in the  
universe

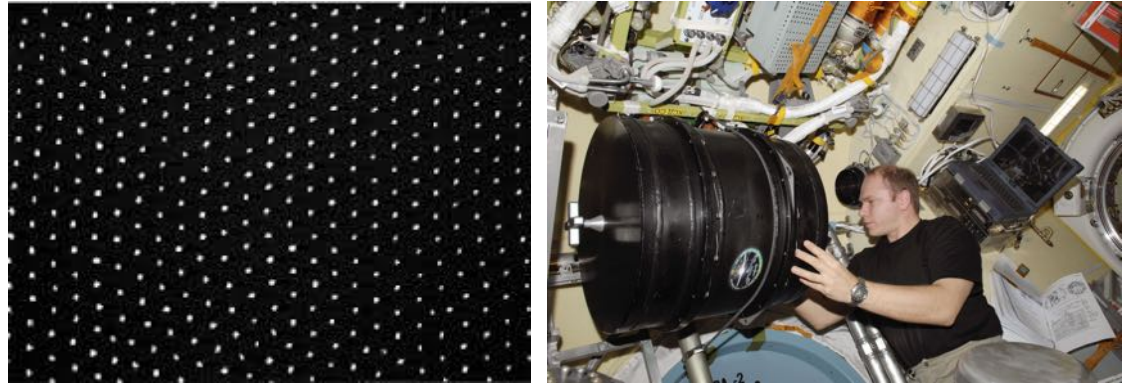
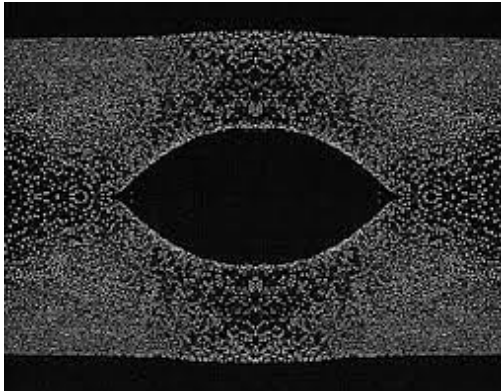
Complex plasma – small  
particles injected into plasma -  
get charged and interact with  
each other.



# Plasma crystal

To counteract the gravity we carry out experiments on parabolic flights or in on ISS

First experiment in physics on ISS!



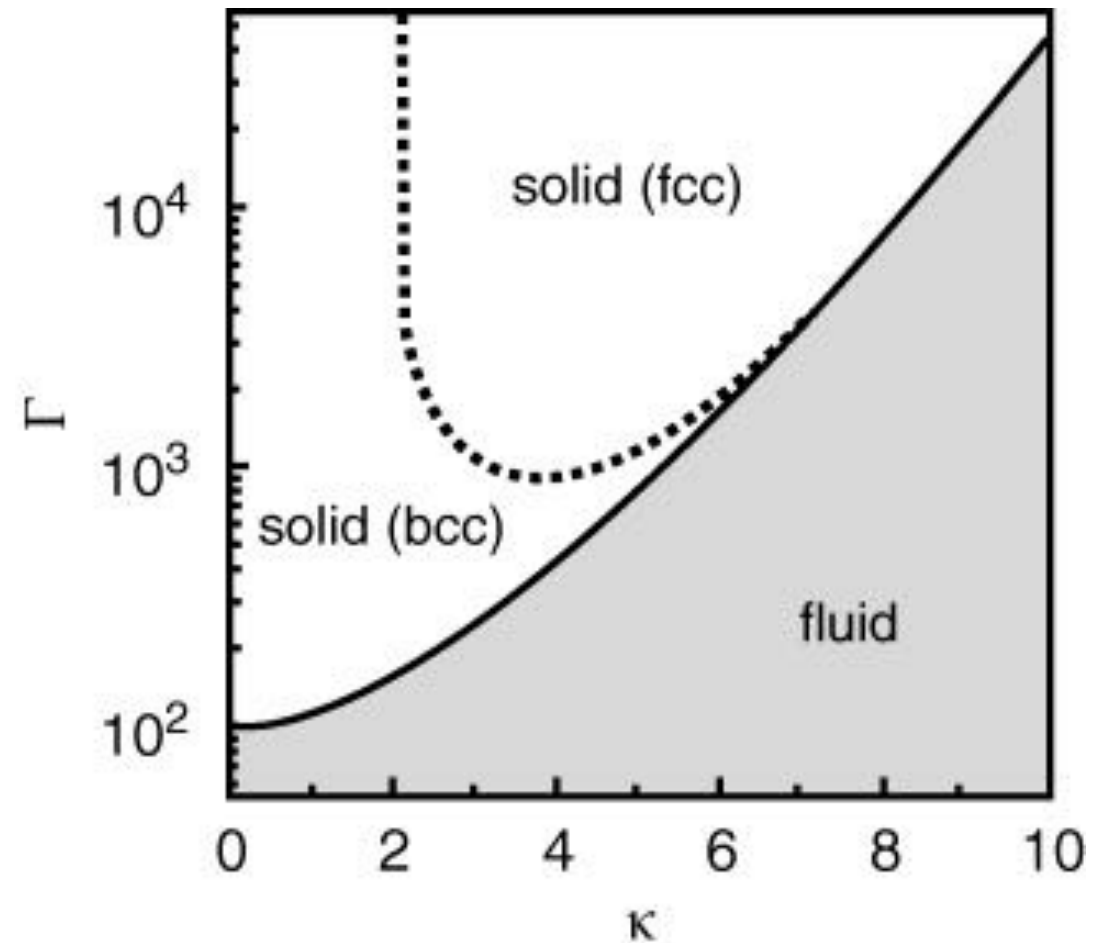
# Complex plasmas

- Potential energy vs. Kinetic energy (coupling parameter)

$$\Gamma = \frac{Z_d^2 e^2}{4\pi\epsilon_0 \Delta k_B T_d}$$

- Interparticle distance vs. screening length

$$\kappa = \frac{\Delta}{\lambda_D}$$



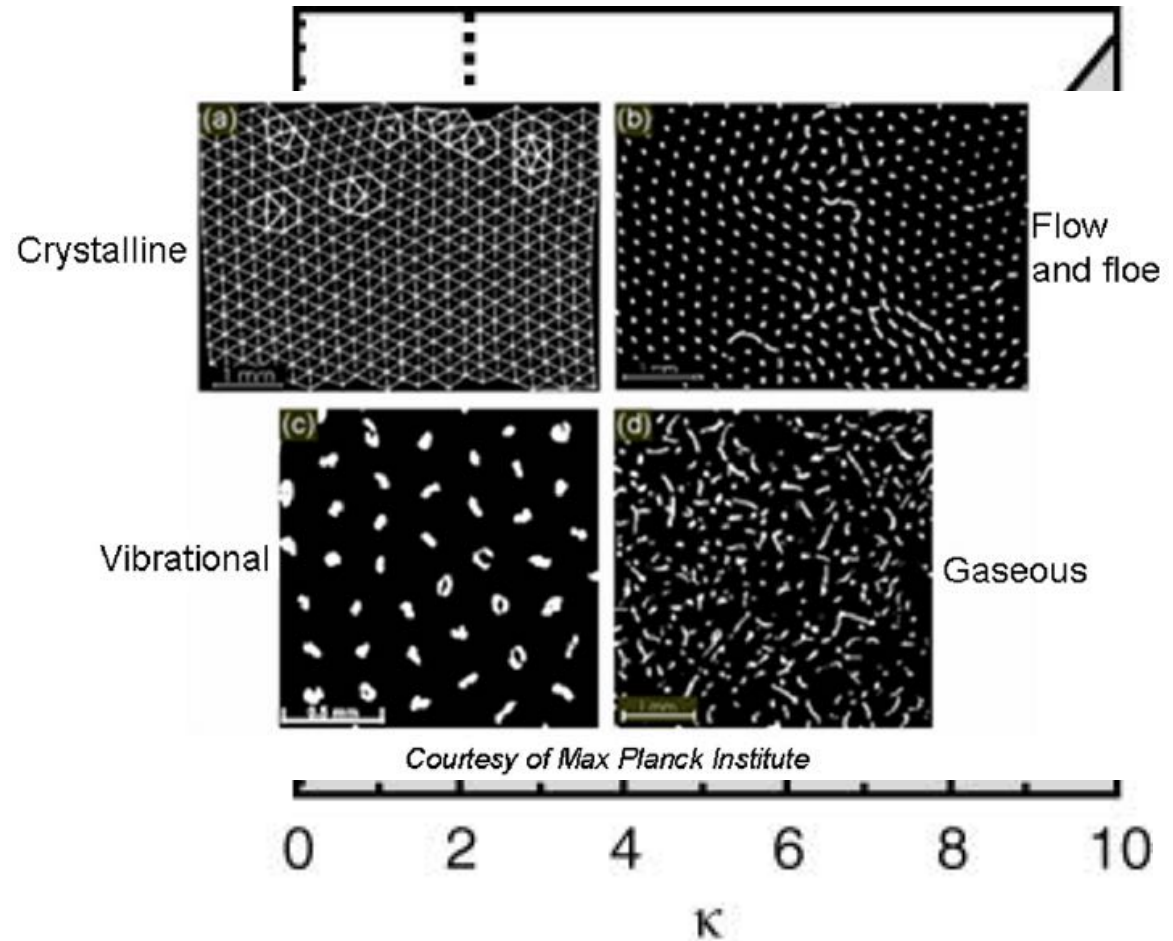
# Complex plasmas

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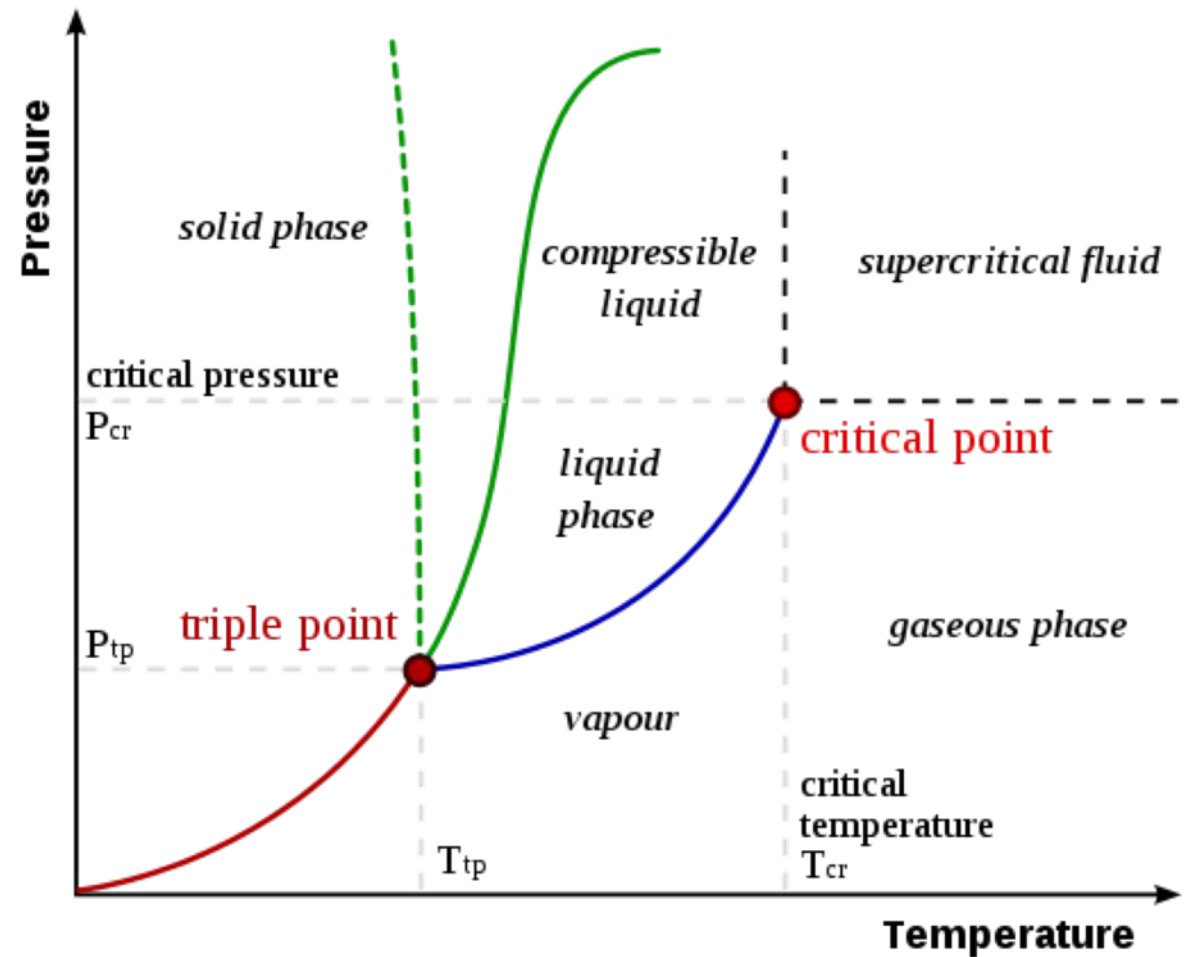
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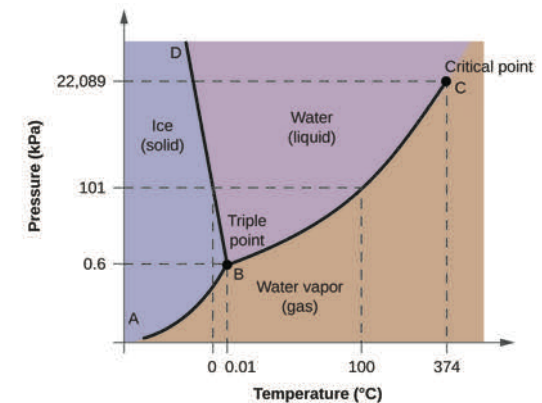
# Phase diagram

- A summary



# Clausius-Clapeyron Relation

- Entropy determines the temperature dependence of the Gibbs free energy
- Volume determines the pressure dependence of the Gibbs free energy.
- The line on the phase transition diagram can be related to the entropies and volumes of the two phases!





# Clausius-Clapeyron Relation

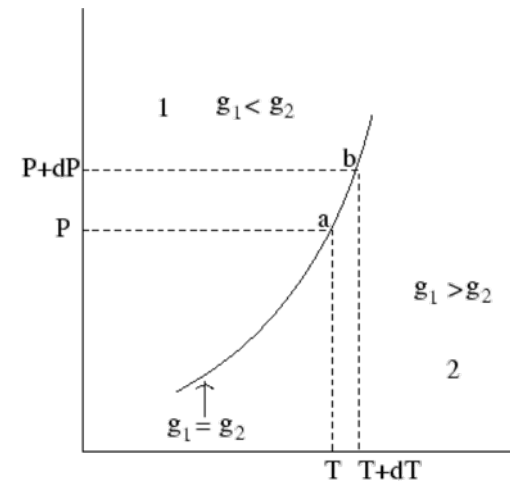
- Let us consider a mole of material, and for example liquid to gas transition.
- At the phase boundary the Gibbs free energy must be the same:

$$G_l = G_g$$

(the same is valid for their chemical potentials i.e., G/molecule)

- Now let us change T and P by dT and dP in such a way that we stay on the line.

$$dG_l = dG_g$$





# Clausius-Clapeyron Relation

If we now take that

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

we can obtain (we do not change  $N$  in the system)

$$-S_l dT + V_l dP = -S_g dT + V_g dP$$

and we get the slope of the line:

$$\frac{dP}{dT} = \frac{S_g - S_l}{V_g - V_l}$$

# Clausius-Clapeyron Relation

Often it is more convenient to use difference in entropies:

$$S_g - S_l = L/T$$

where  $L$  is latent heat needed for converting the materials phase.

An we get the **Clausius-Clapeyron Relation**:

$$\frac{dP}{dT} = \frac{L}{T\Delta V}$$

# The van der Waals Model

Ideal gas law modified for liquid-gas system to account for interactions:

$$\left( P + \frac{aN^2}{V^2} \right) (V - Nb) = NkT$$

Volume modified by  $Nb$  – we can not compress a fluid to  $V=0$ !

$b$  – minimum volume occupied by a molecule  $\times N$

Pressure modified by  $aN^2/V^2$  reflects short range interactions between molecules.

# The van der Waals Model

Pressure modified by  $aN^2/V^2$  reflects short range interactions between molecules.

Potential interactions of single molecule with all its neighbors is proportional to the density:  $\sim N/V$

Total potential energy ( $N$  molecules):  $E = -\frac{aN^2}{V}$

From thermodynamic identity and fixed entropy («frozen» particles):

$$dU = -PdV \rightarrow P = -(\partial U / \partial V)_S$$

Thus the pressure due to interactions between molecules:

$$P_e = -\frac{d}{dV} \left( -\frac{aN^2}{V} \right) = -\frac{aN^2}{V^2}$$

van der Waals equation 
$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

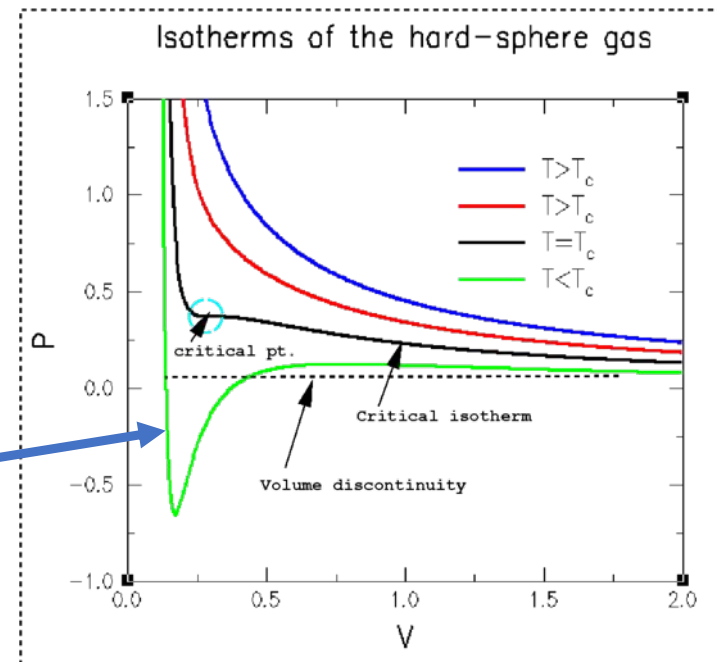
- Is qualitative exact for describing fluids.
- Does not account for that gas gets denser with P and clusterisation can occur.

- $a$  and  $b$  depend on substances.

Eg. water:  $b \sim (4 \text{ \AA})^3$ ,  $a \sim 10 \text{ eV \AA}^3$

Eg. nitrogen:  $b \sim (4 \text{ \AA})^3$ ,  $a \sim 2.5 \text{ eV \AA}^3$

Problem: Pressure decreases when we compress a fluid???



van der Waals equation 
$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

Equilibrium state at given T and P is determined by the Gibbs energy

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

we find, for a fixed amount N:

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = V \left(\frac{\partial P}{\partial V}\right)_{N,T}$$

we can now use the van der Waals equation and get:

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = \frac{NkTV}{(V - Nb)^2} + \frac{aN^2}{V^2}$$

van der Waals equation  $P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = \frac{NkTV}{(V - Nb)^2} + \frac{aN^2}{V^2}$$

After taking  $V=(V-Nb)+Nb$  and integrating the last equation we get:

$$G = -NkT \ln(V - Nb) + \frac{(NkT)(Nb)}{(V - Nb)} - \frac{2aN^2}{V} + c(T)$$

which allows us to plot G for any given T.



# van der Waals equation

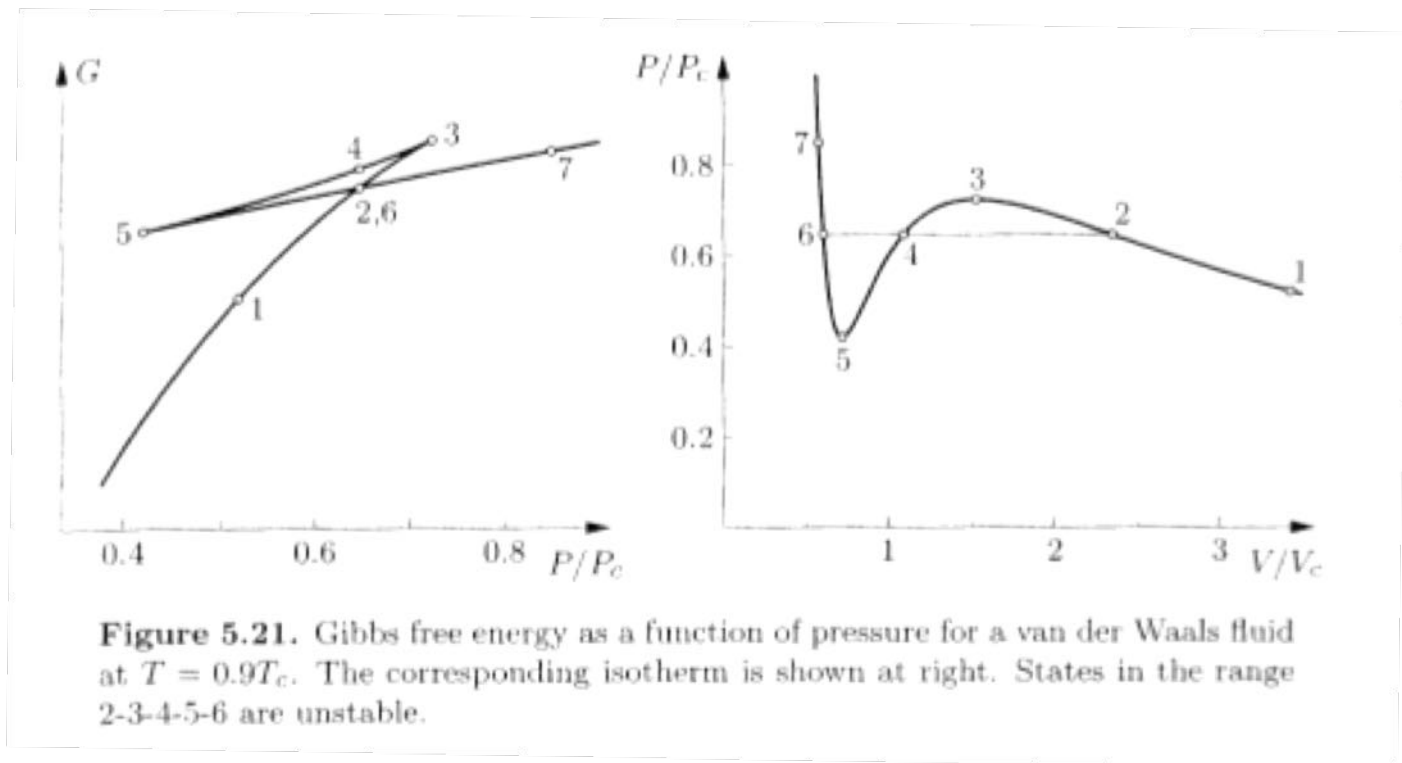
Thermodynamically stable  
are only the lowest Gibbs  
energies

We should go straight from  
point 2 to 6

What is the pressure at the  
phase transformation?

We can find it from the  
figure, but also calculate it  
from PV diagram...

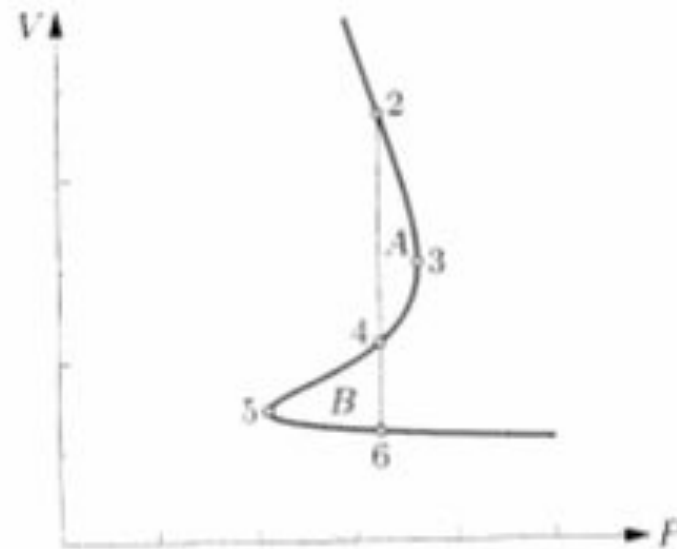
Let us integrate around the  
closed loop... 2-3-4-5-6



# van der Waals equation

$$0 = \int_{\text{loop}} dG = \int_{\text{loop}} \left( \frac{\partial G}{\partial P} \right)_T dP = \int_{\text{loop}} V dP$$

This corresponds to the area below A – area below B. If A=B we found the pressure!



# Phase diagrams...

- Vapor pressure at phase transition
- We have critical temperature  $T_c$  and critical volume and pressure:  $V$  and  $P$  at  $T_c$
- They all together define the critical point

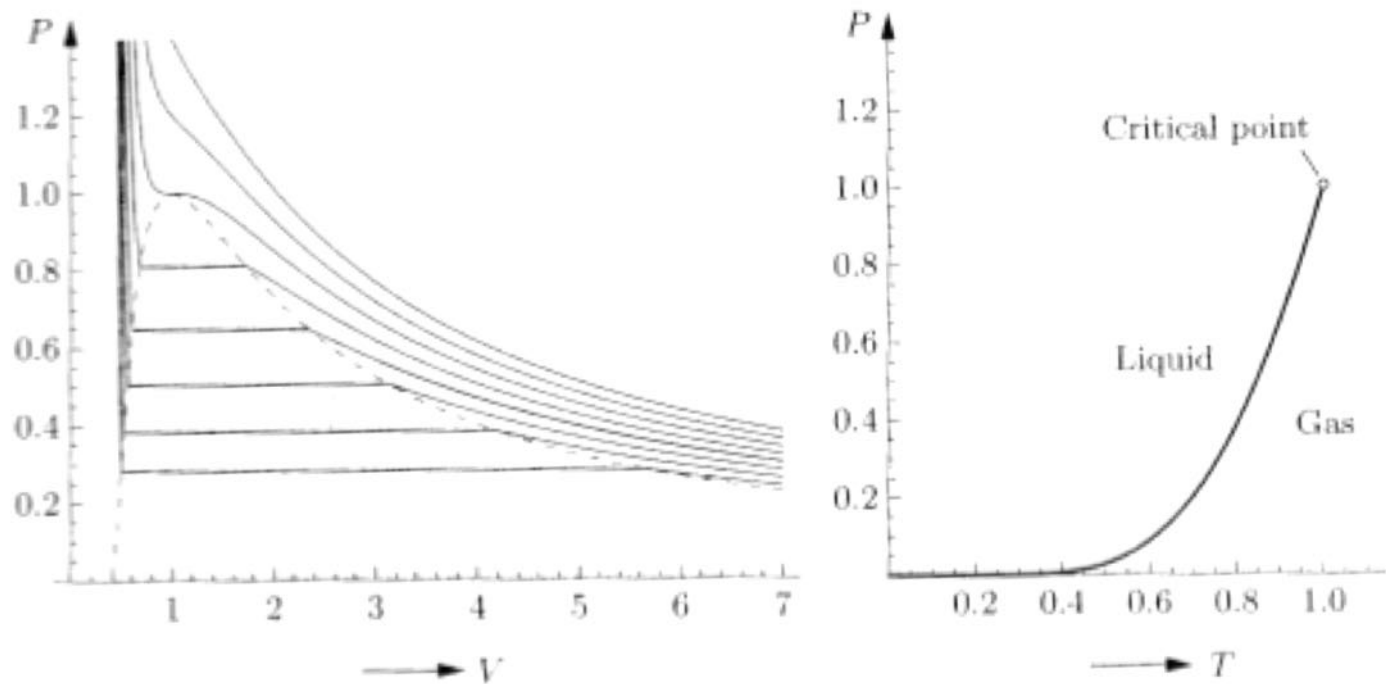


Figure 5.23. Complete phase diagrams predicted by the van der Waals model.