

# Complex Liquids and Soft Condensed Matter

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LESSON 02

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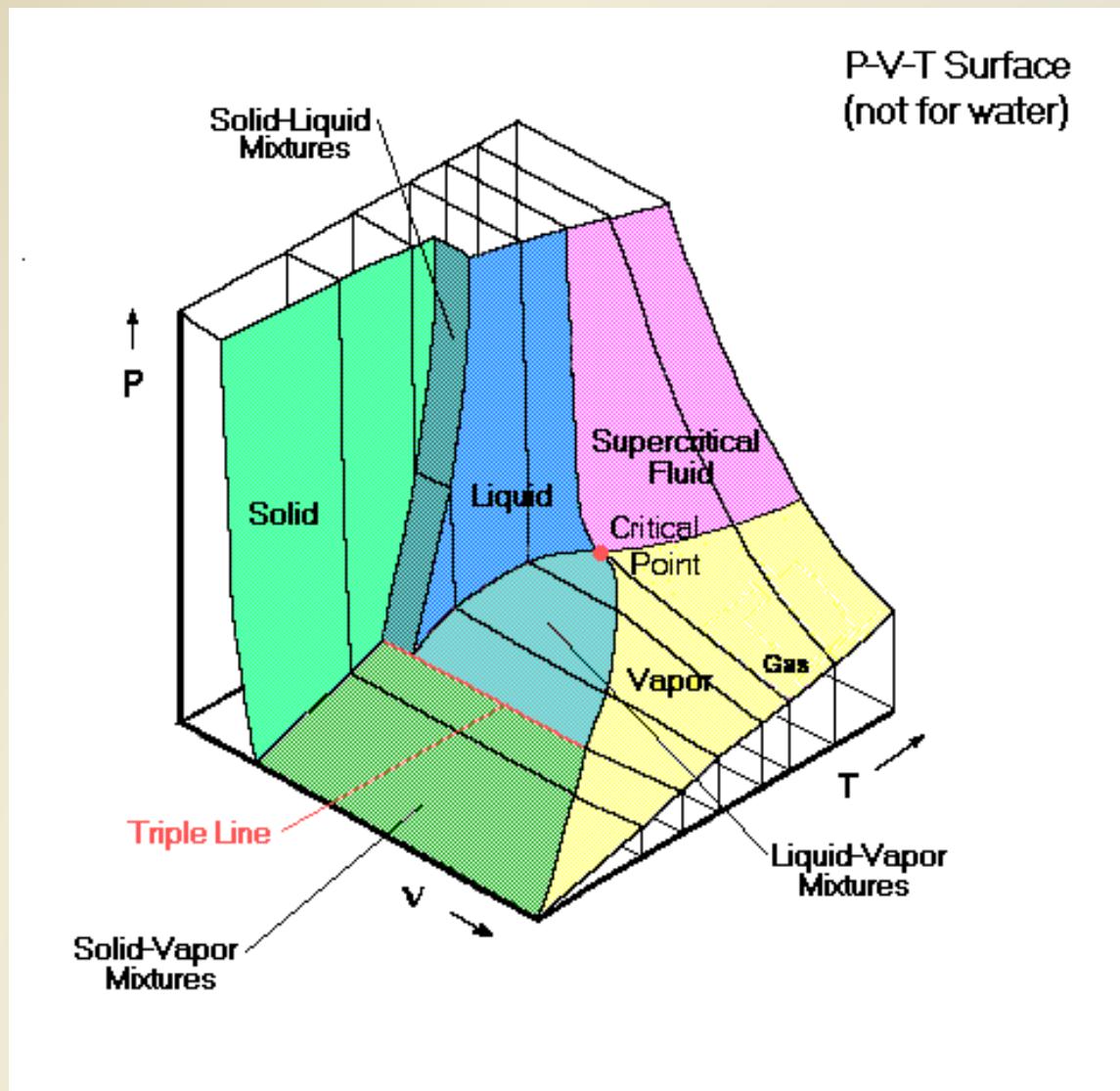
Tel 055-4572495

LENS stanza 62

<https://sites.google.com/a/lens.unifi.it/torre/>

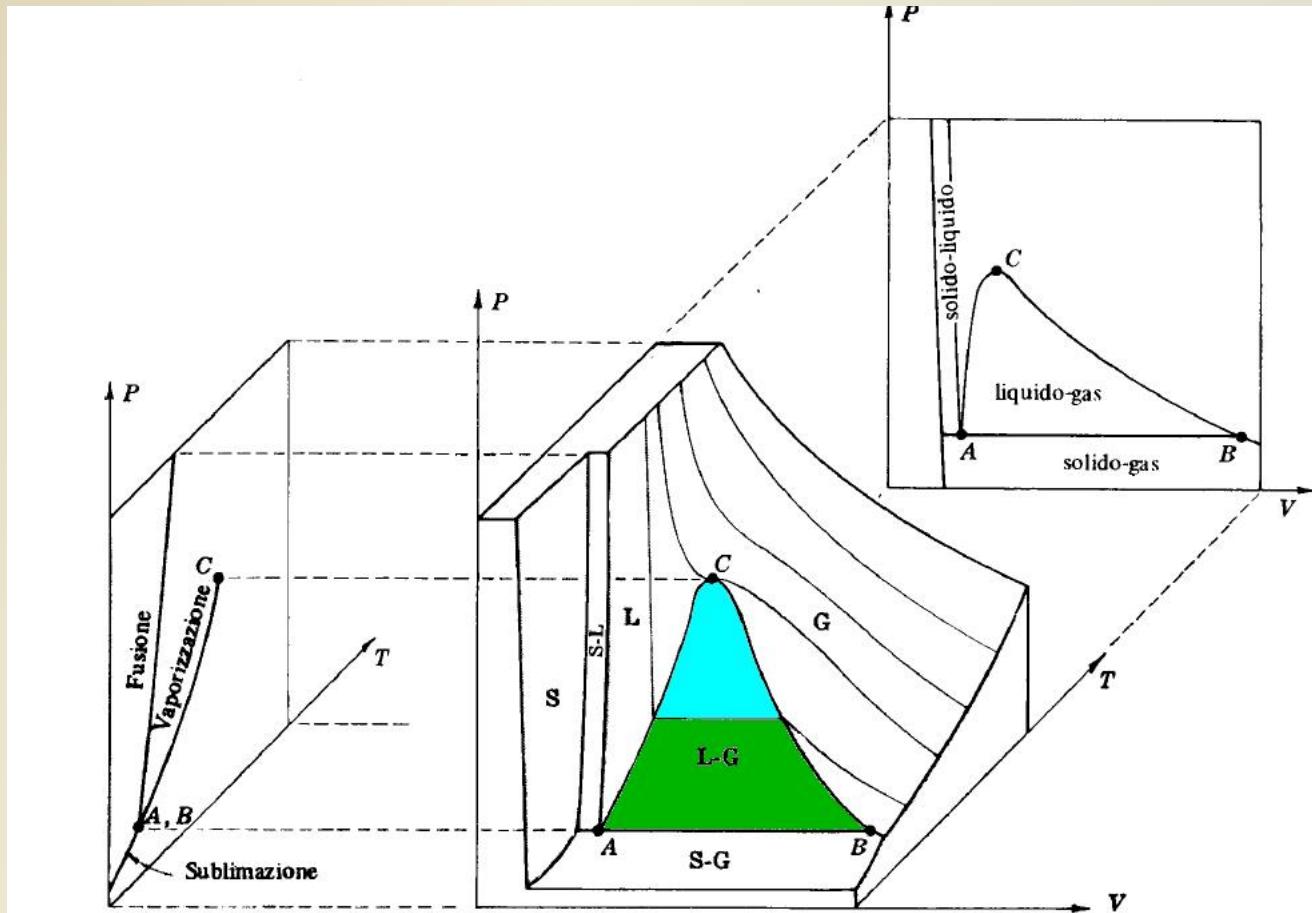
R.A.L. Jones, *Soft Condensed Matter*, Oxford Univ. Press 2002

# Thermodynamic Equilibrium



# Equilibrium

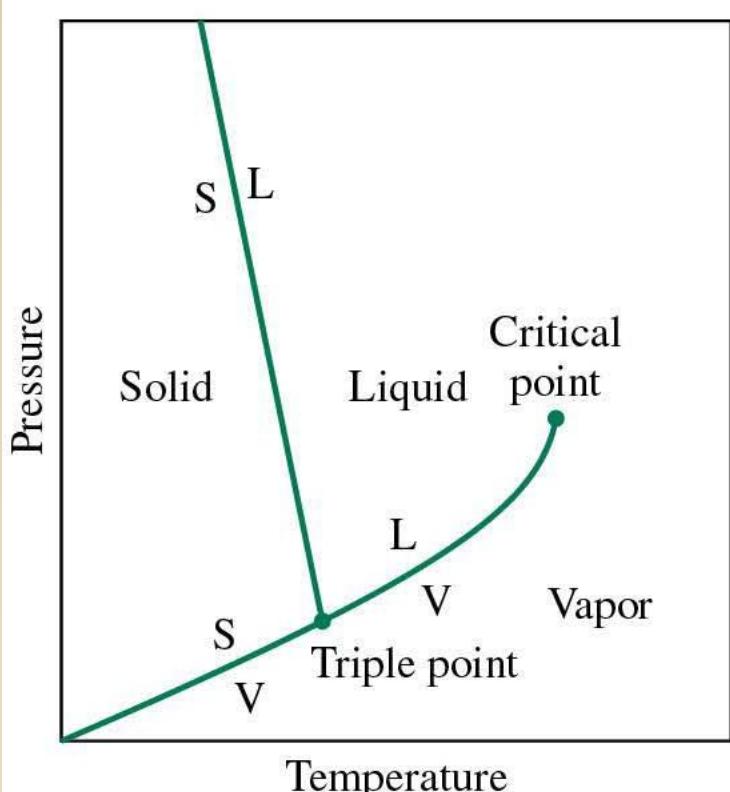
# PT and PV projections



# Equilibrium

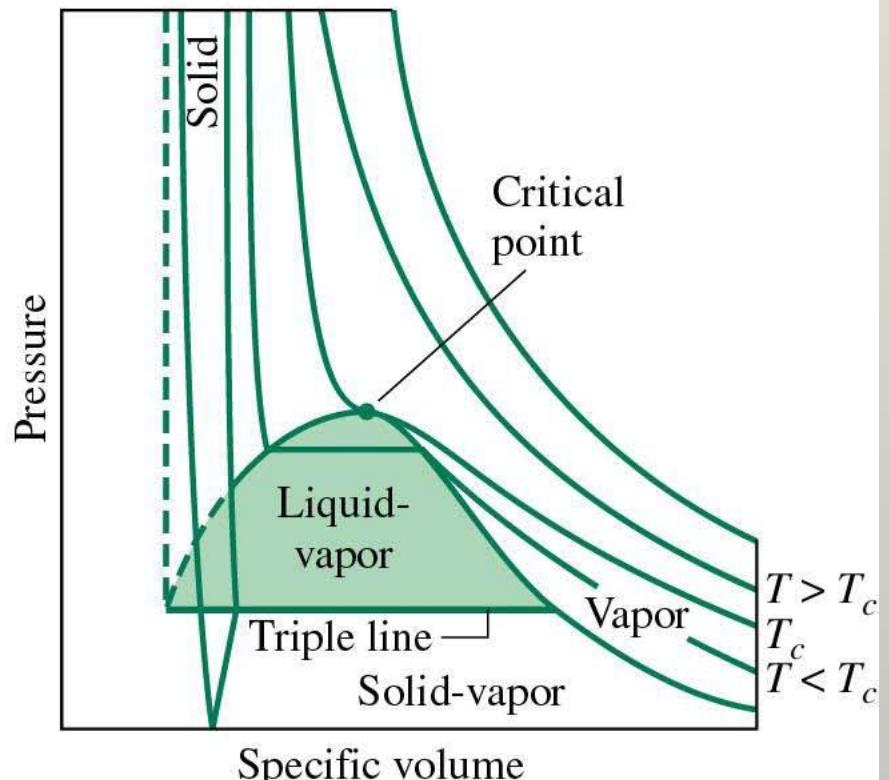
# Diagrams

P-T



(b)

P-V



(c)

Equilibrium surfaces for pure matter are defined by the

State Equation:  $f(V, P, T) = 0$

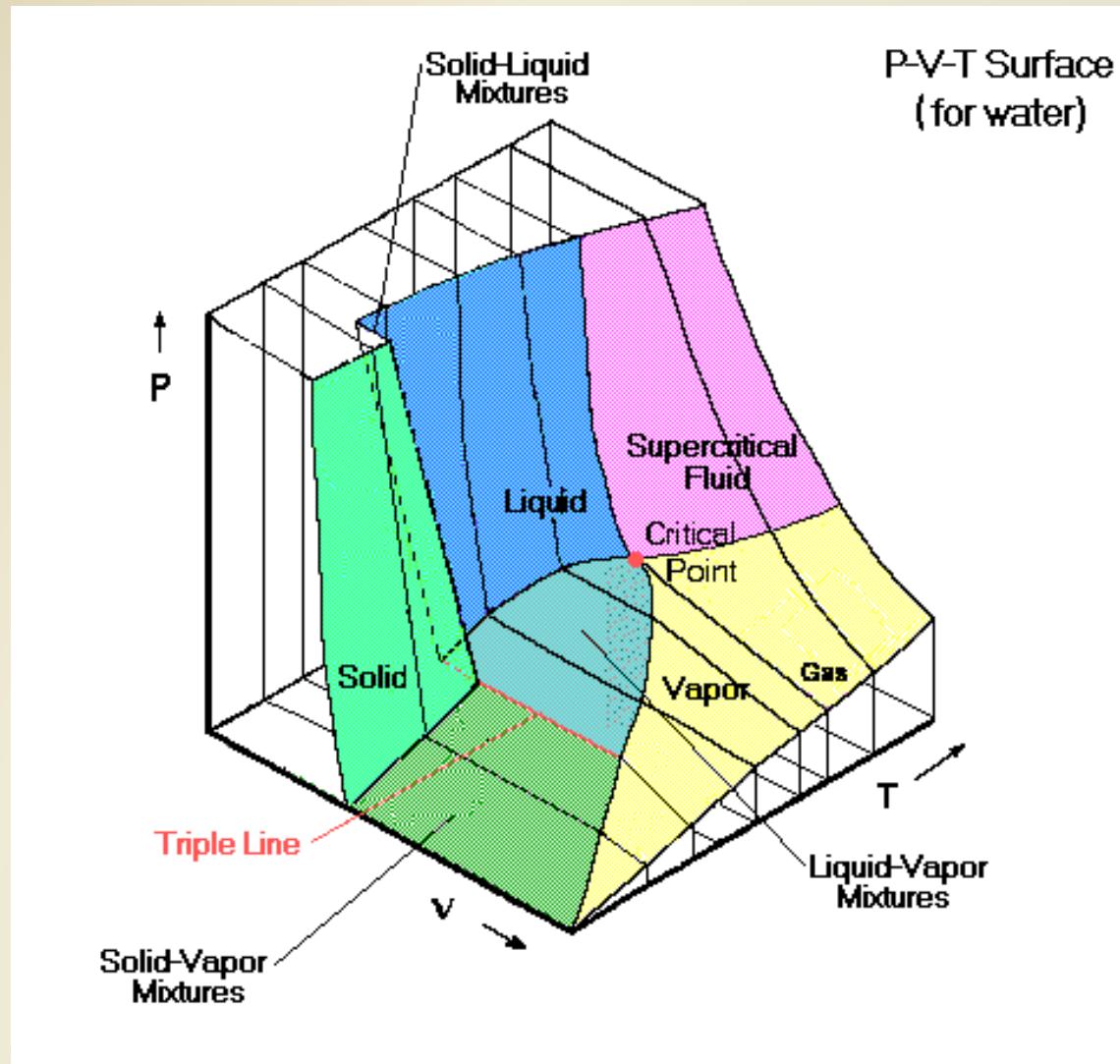
Gas ideale:  $P = R \frac{T}{V}$  ;  $R = \text{costante universale dei gas}$

Gas reale:  $P = R \frac{T}{V-b} - \frac{a}{V^2}$  *Eq. di Van der Waals*

$P = R \frac{T}{V-b} - \frac{a}{T^2 V (V+b)}$  *Eq. di Redlich/Kwong*

# Equilibrium

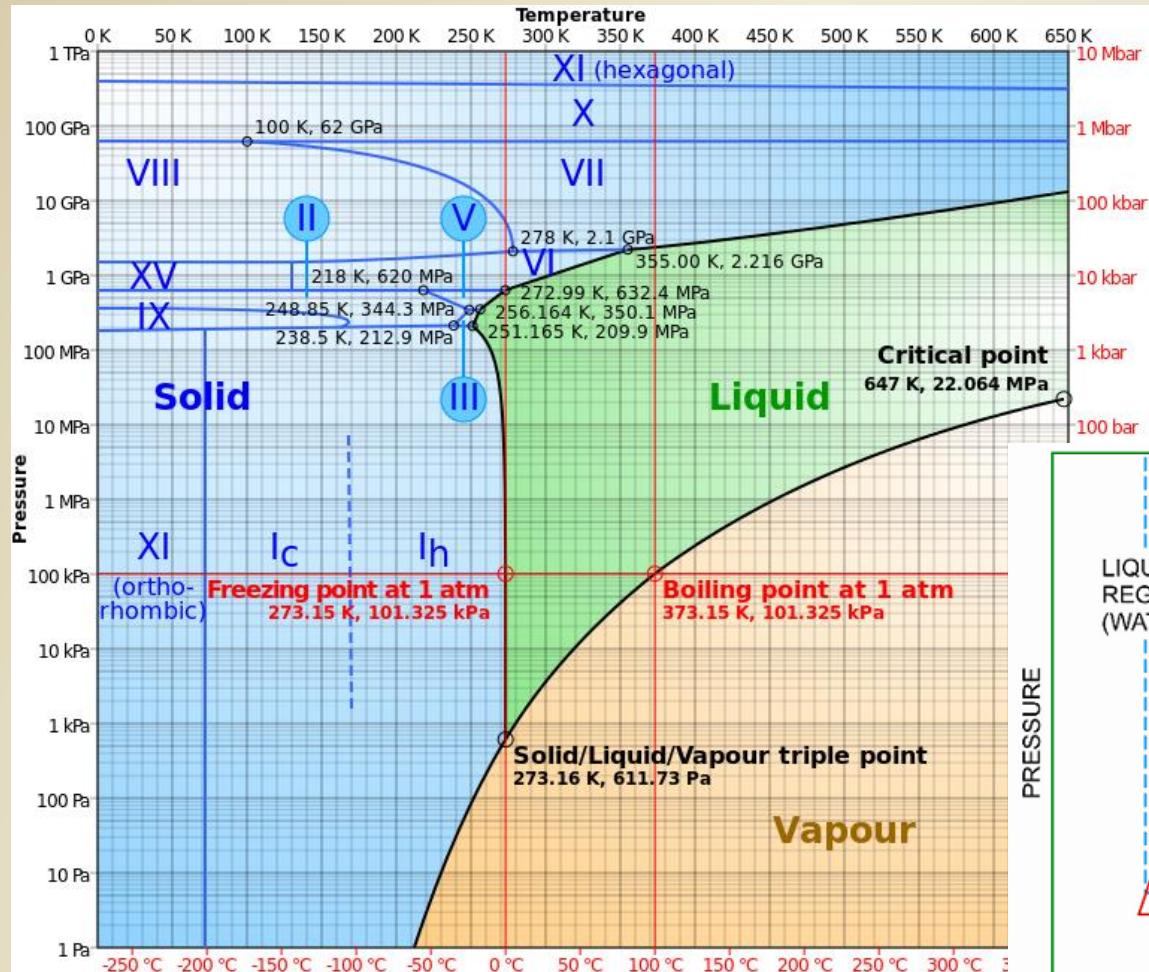
# Water



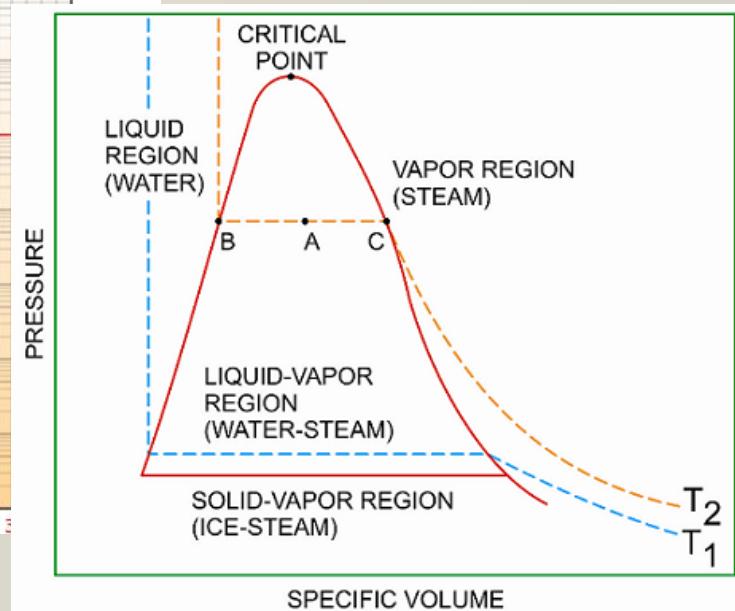
# Equilibrium

# Water

P-T

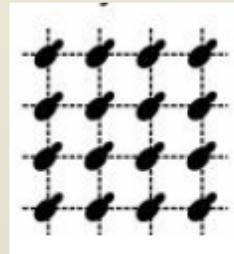
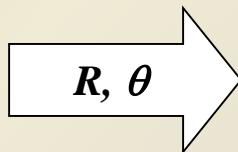
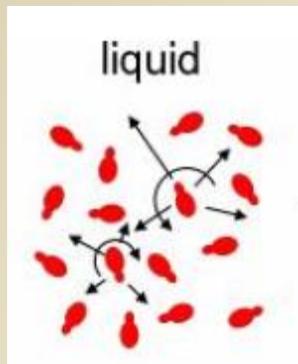


P-V



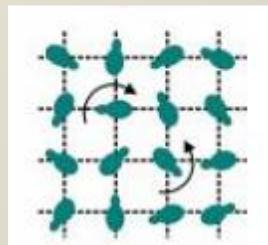
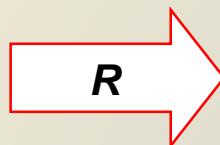
# Equilibrium

# Phase Tran. and Mesophases



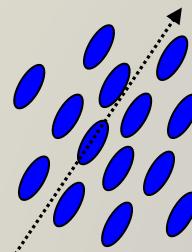
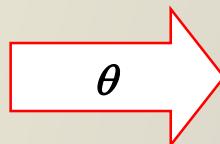
Ordered  
Crystal

Translational ordering



Plastic  
Crystal

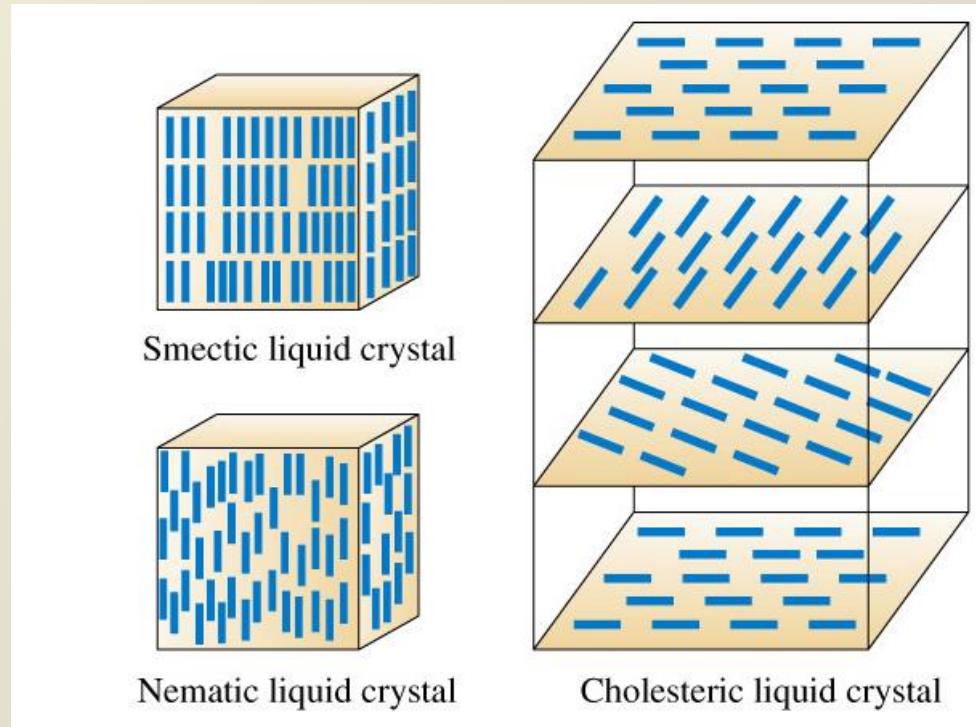
Orientational ordering



Liquid  
Crystal

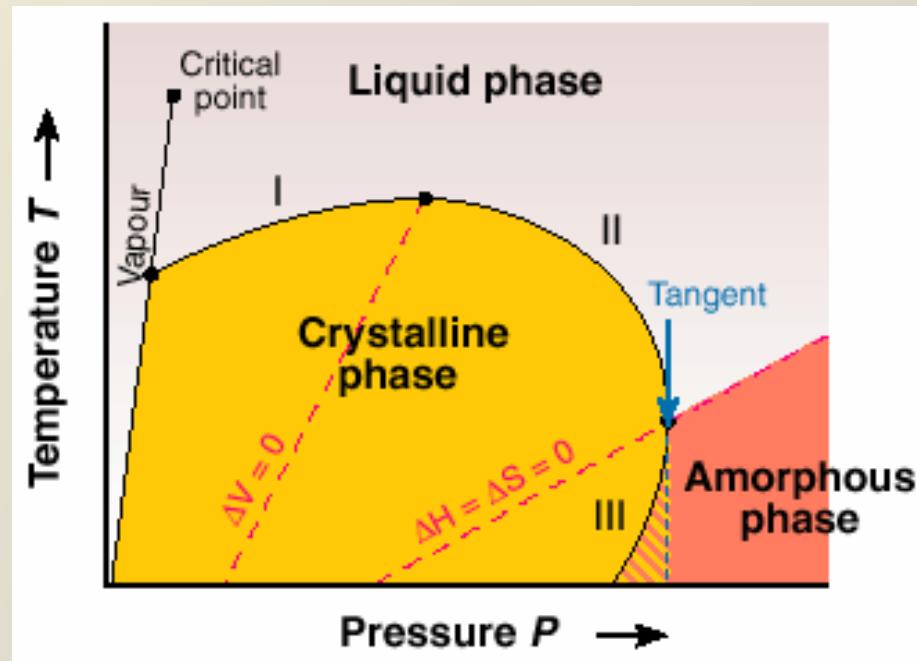
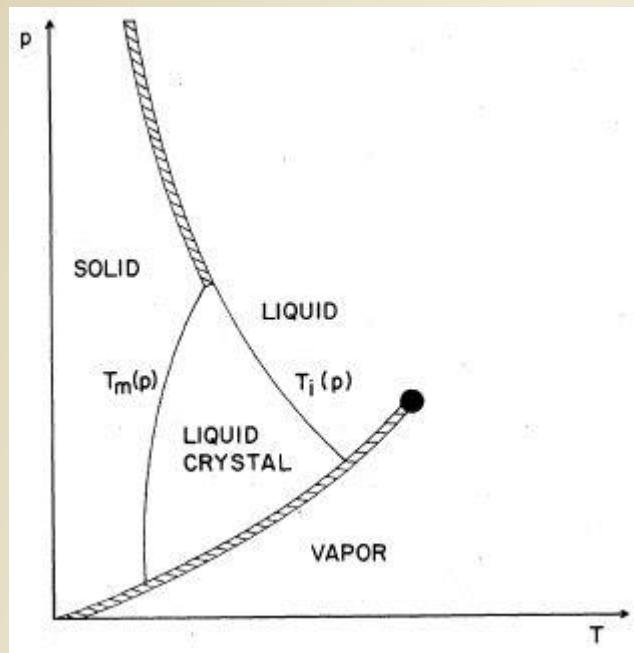
## Partial translational and/or orientational ordering

$R_i, \theta$



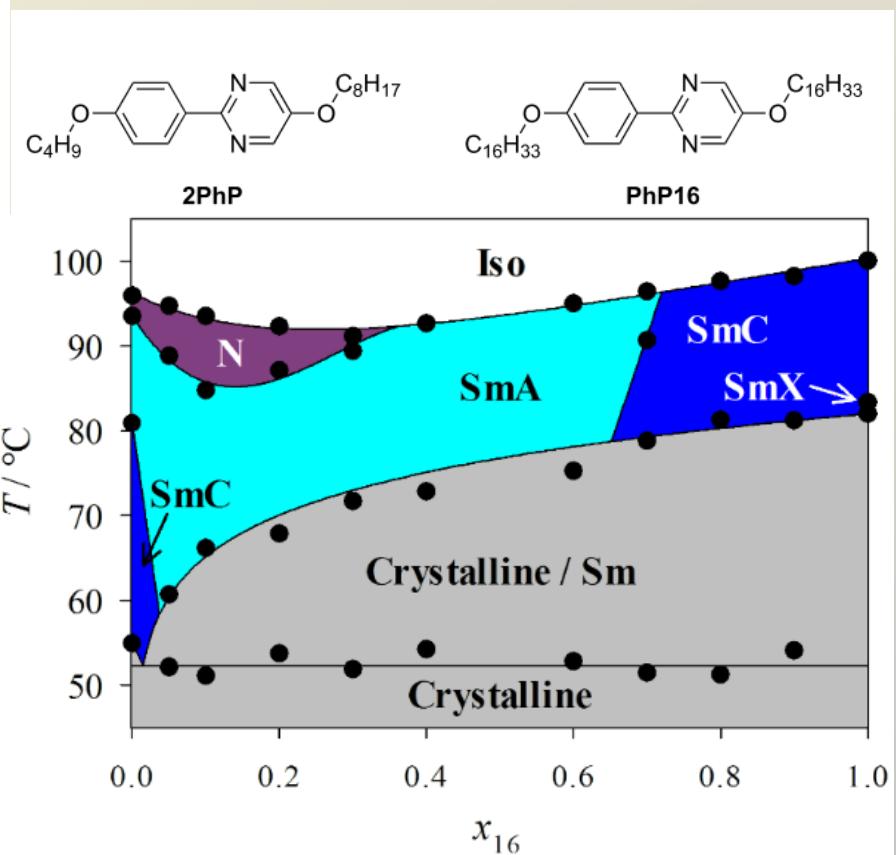
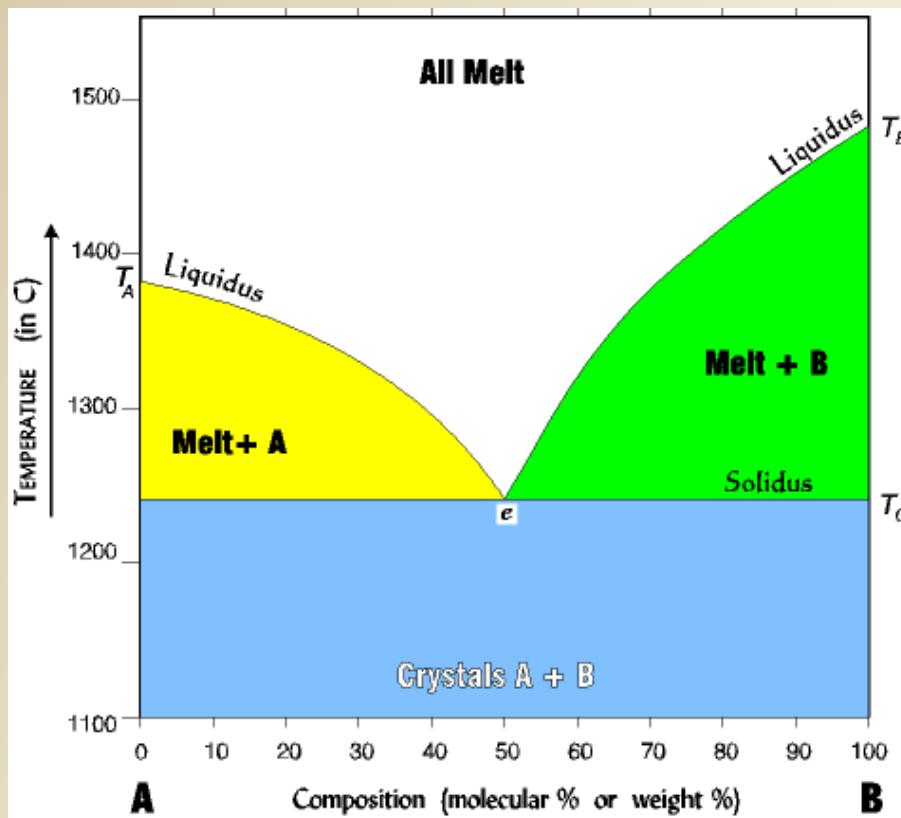
## Liquid Crystal thermotropic

Polymer



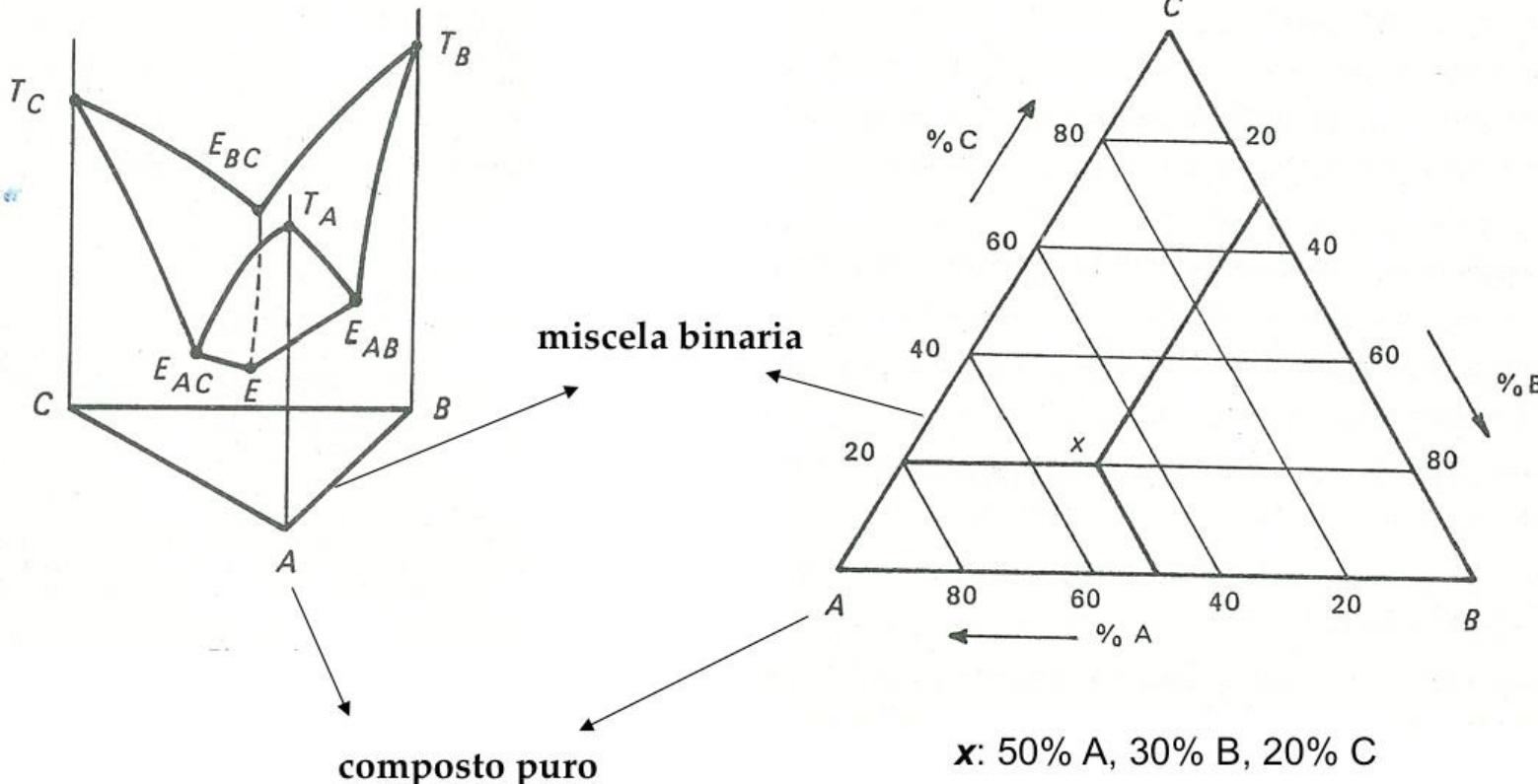
# Equilibrium

# two component systems



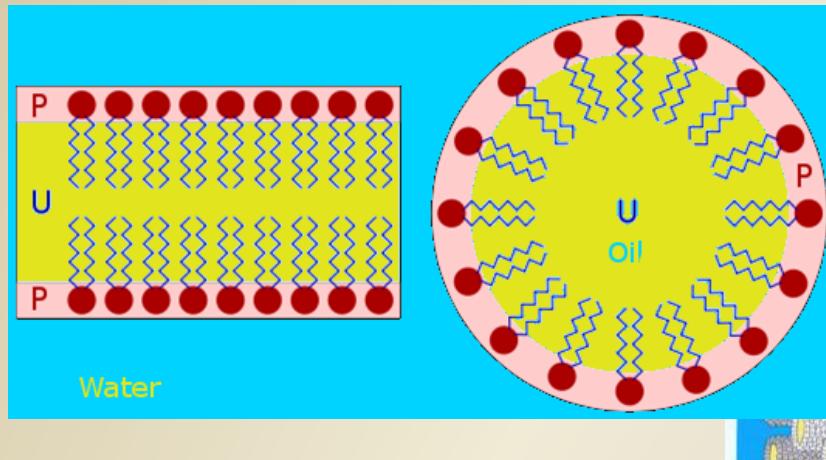
# Equilibrium

# three component systems

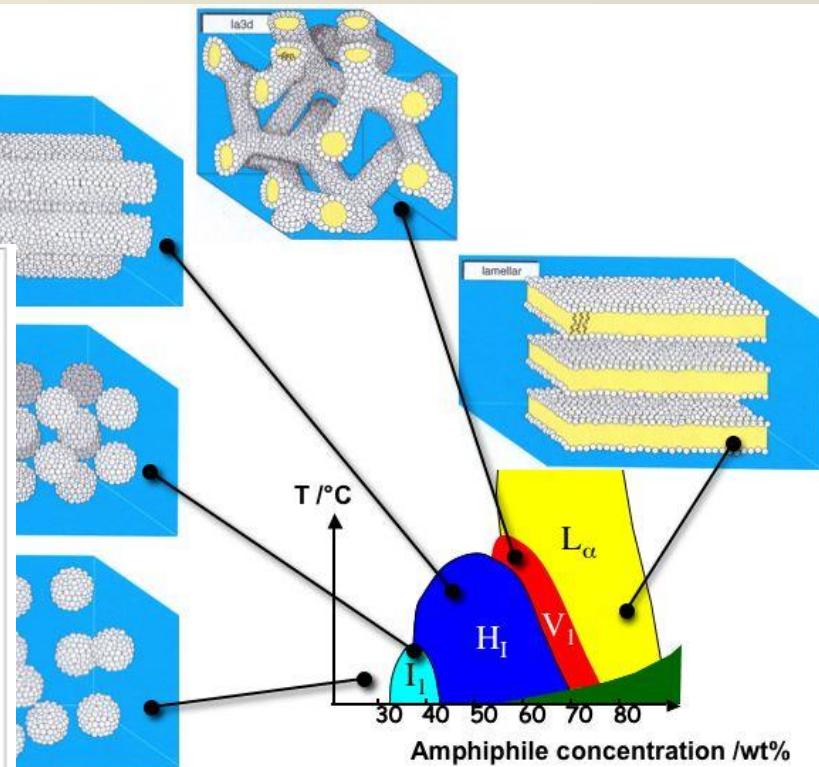
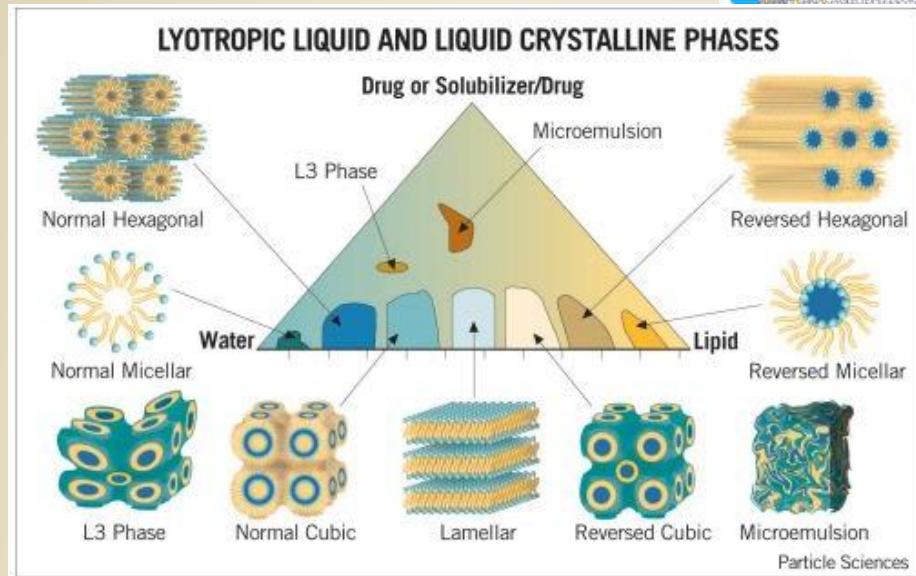


# Equilibrium

# three component systems



Amphiphilic Self-Assembly or  
Liquid Crystal Lyotropic

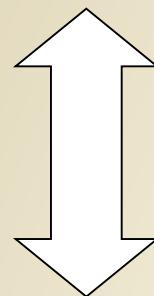
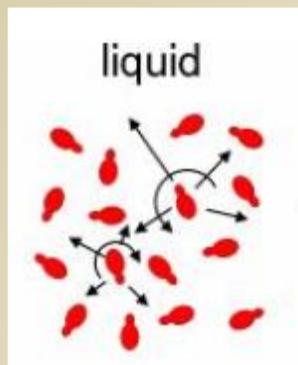


**L'Acqua che non congela  
.....Subito !**

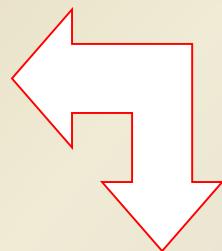
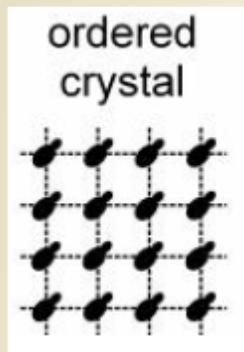
[www.youtube.com/watch?v=95GnYW6kgLs&feature=youtu.be](http://www.youtube.com/watch?v=95GnYW6kgLs&feature=youtu.be)

# Non-Equilibrium

# Supercooling and Glass

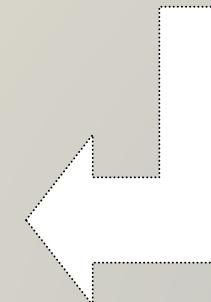
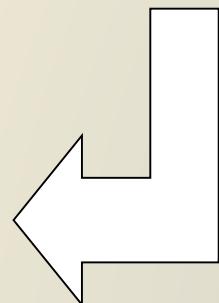
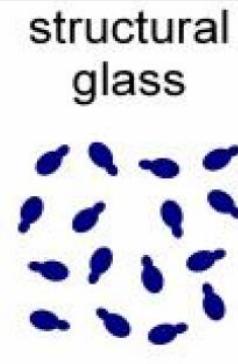
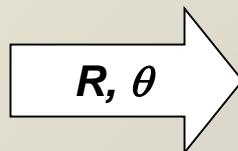
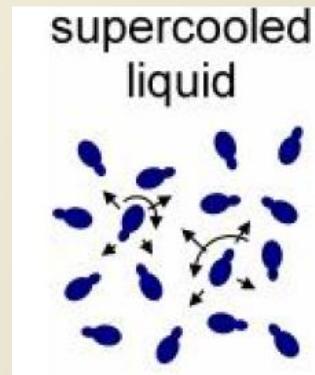


Slow  
Cooling



All liquids can be supercooled !

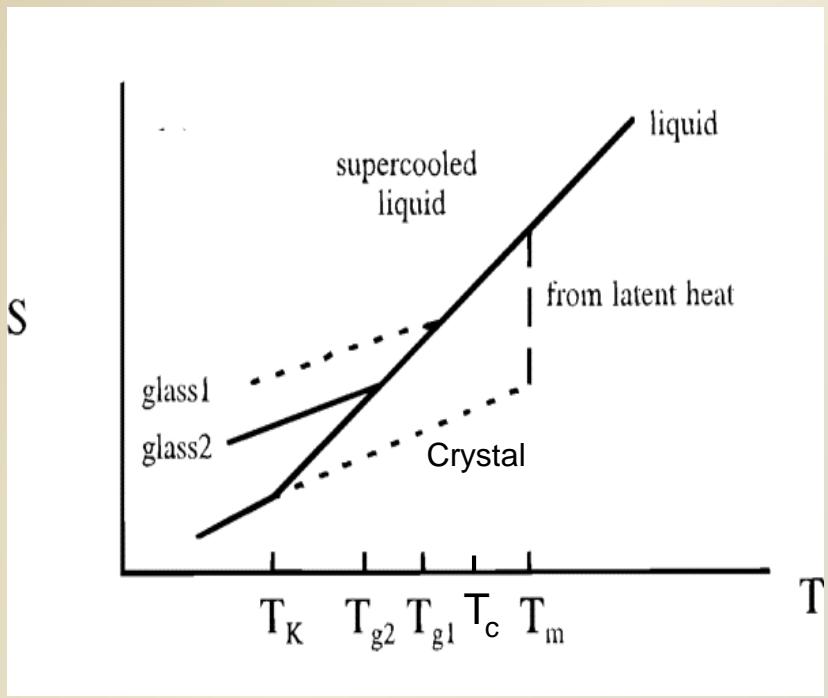
Fast Cooling



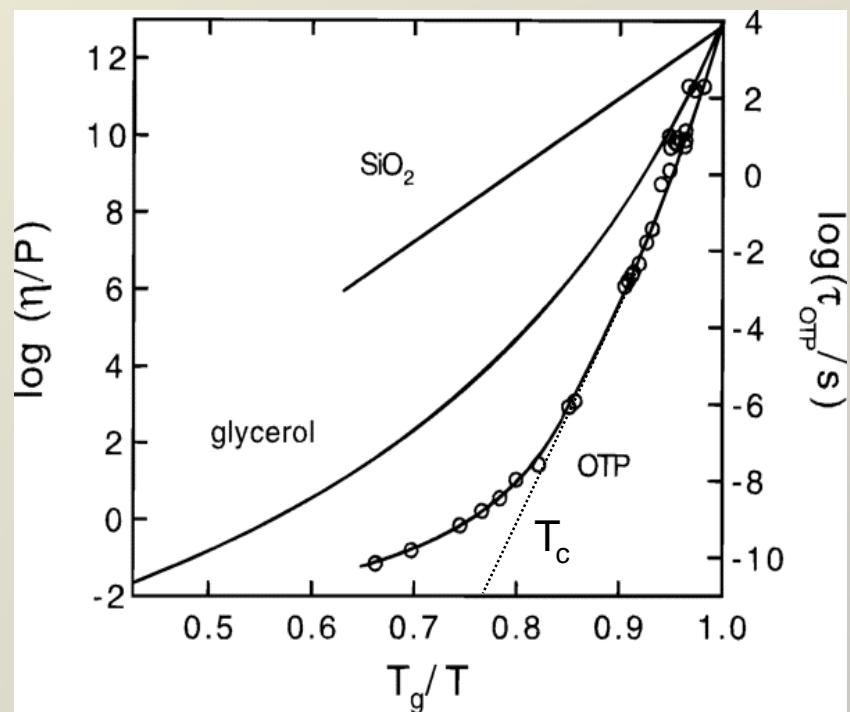
# Non-Equilibrium

# Supercooling and Glass

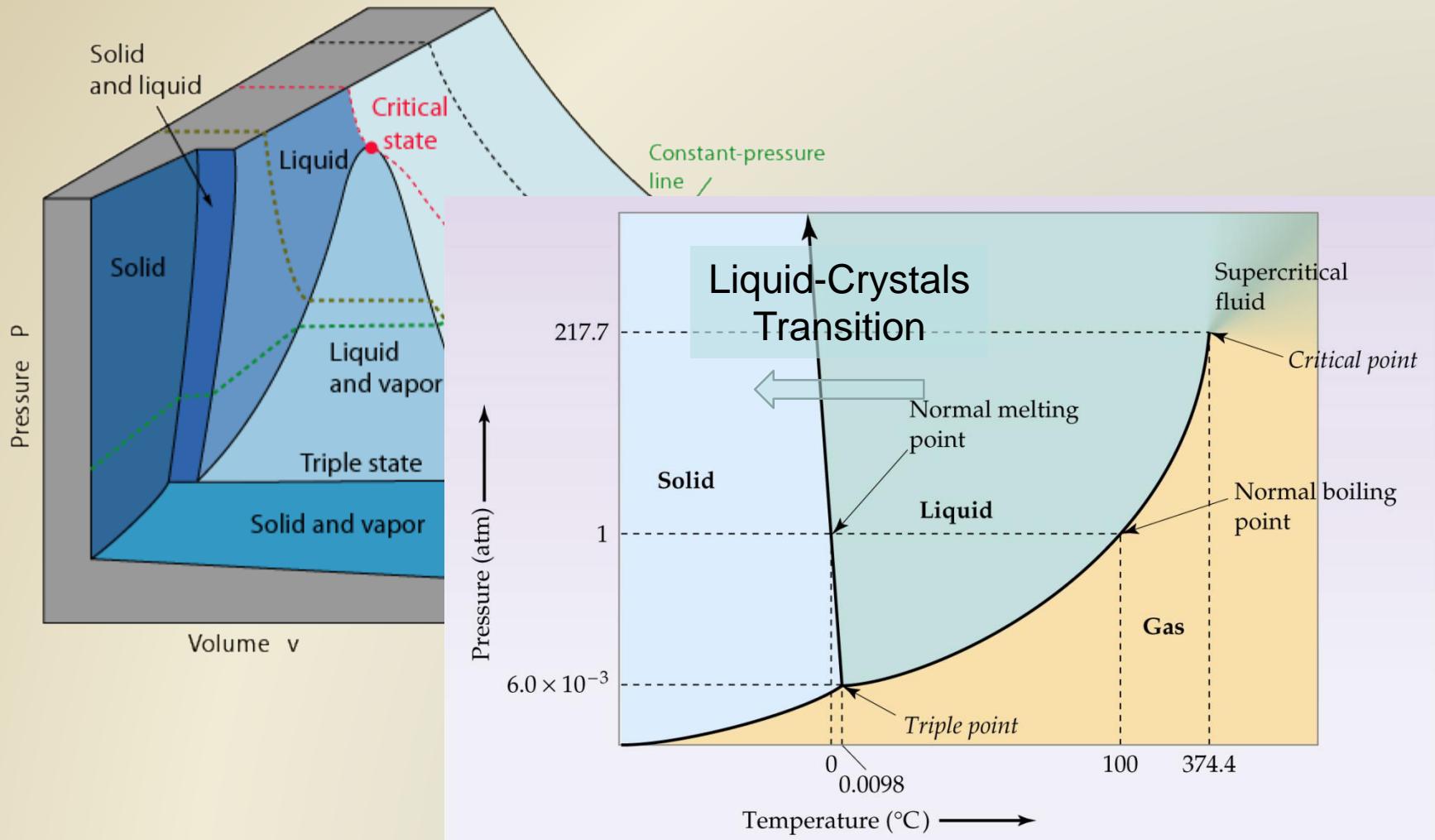
## Thermodynamics



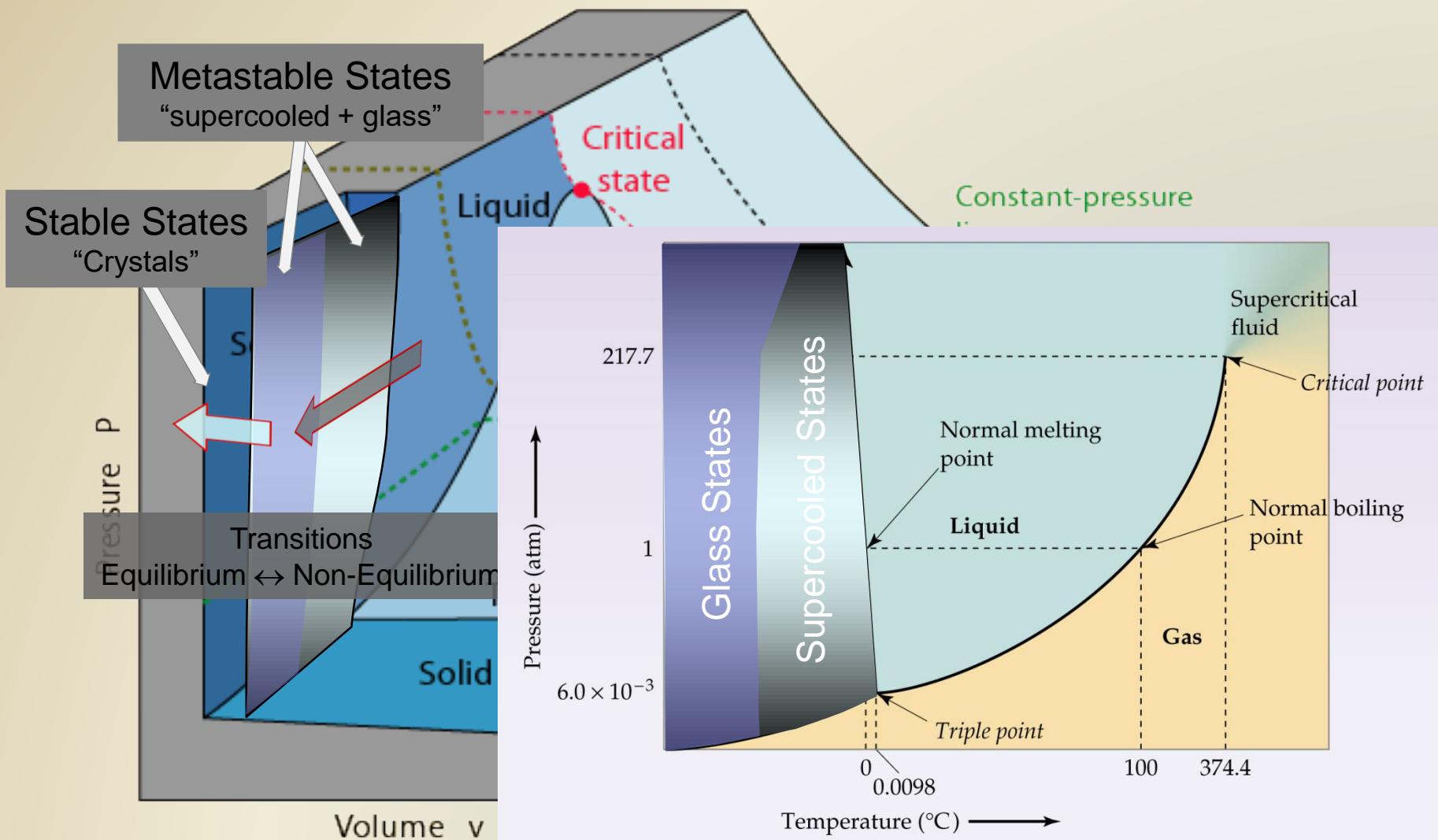
## Dynamics



# Equilibrium Phase Transitions



# Non-Equilibrium Transitions



# Non-Equilibrium → Equilibrium Transitions

## Nucleation Processes

Supercooled Water → Ice

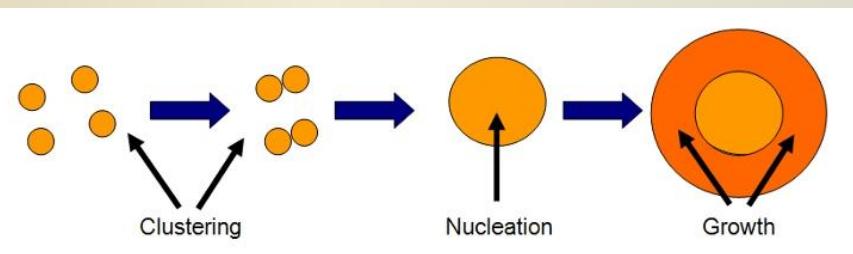
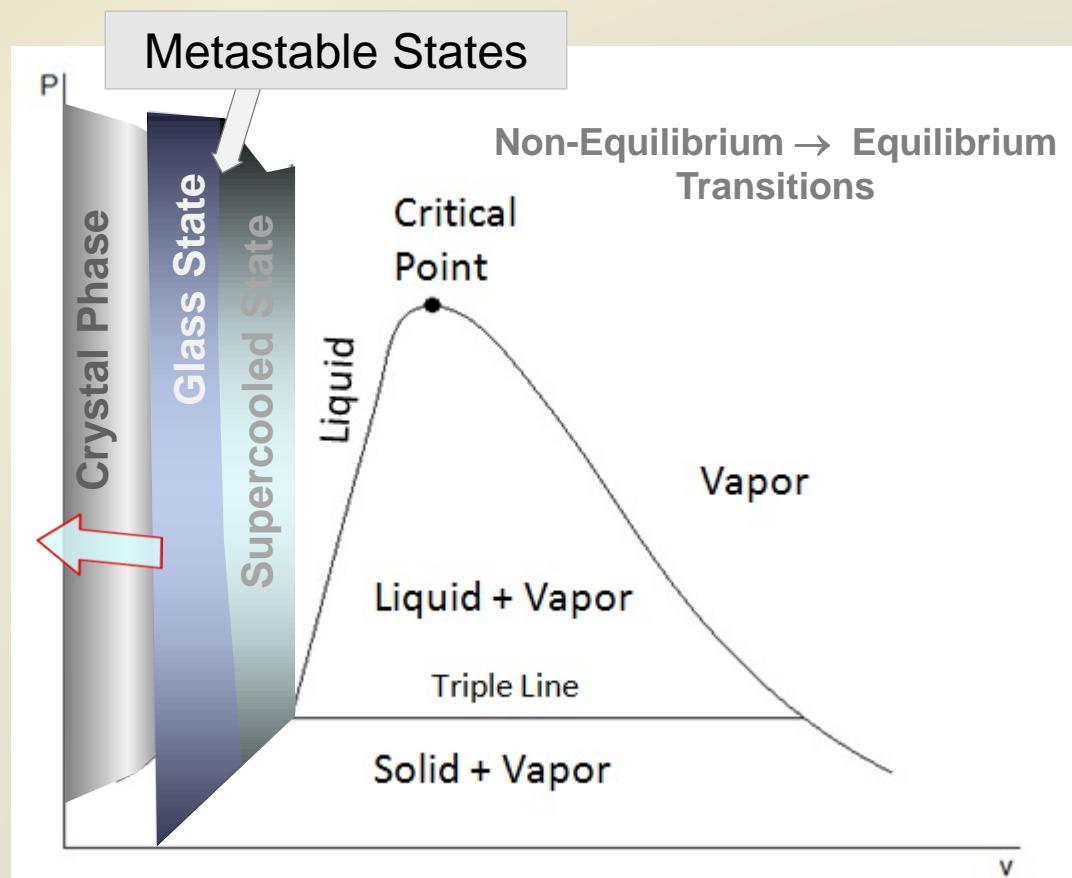
Supercooled Liquids → Crystals

## Aging Processes

Glass/Amorphous → Crystal

## Time Dependent Transitions

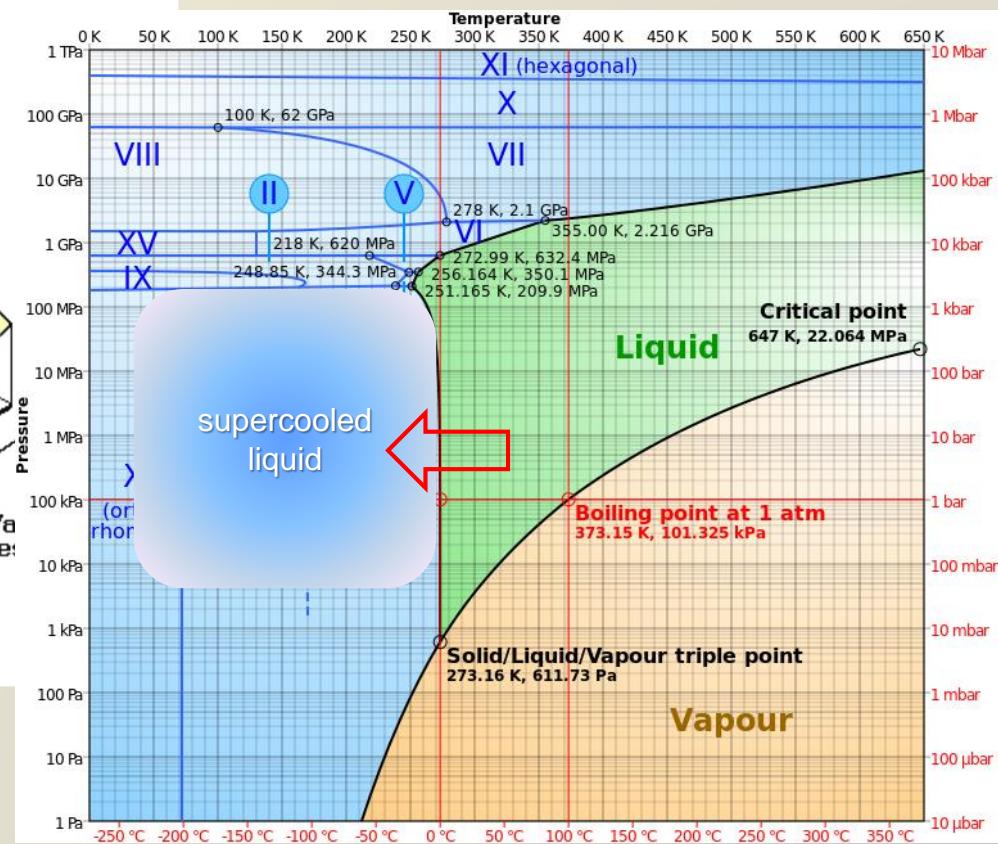
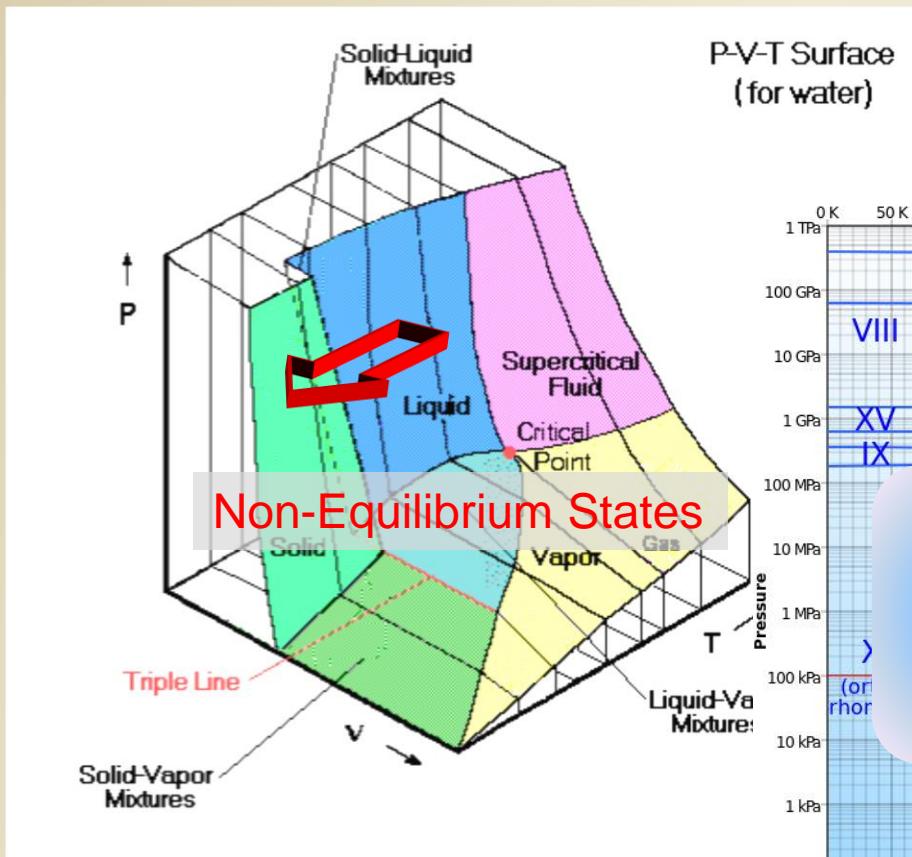
## Rare and random events



Different steps  
in the crystallization process

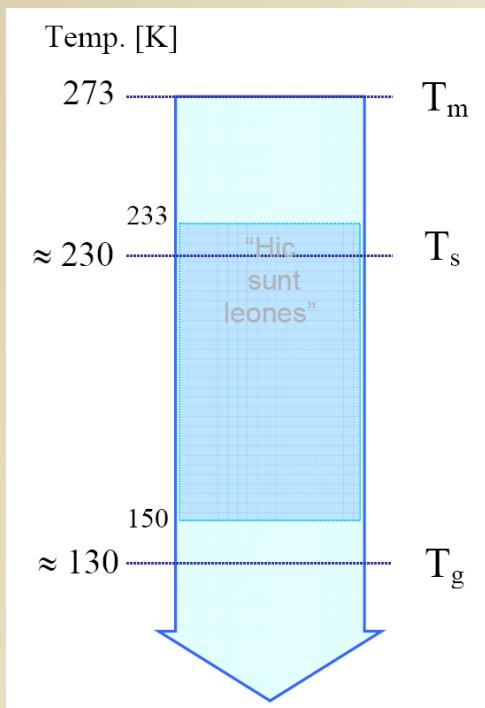
# Non-Equilibrium

# Supercooling Water



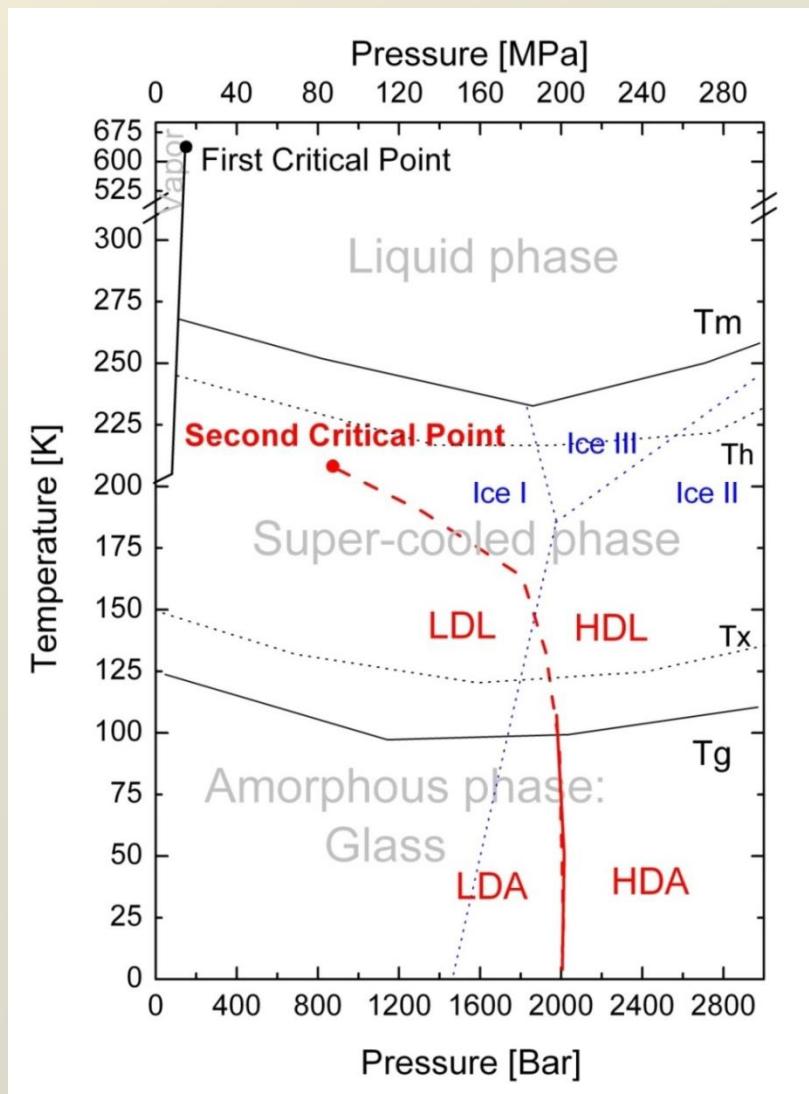
# Non-Equilibrium

# Water P-T Diagrams



**Supercooled**  $T = 273\text{-}230 \text{ K}$   
(nano-confinements, in bio)

**Glass**  $T \leq 150/130 \text{ K}$   
(cooling at  $10^6 \text{ K/sec}$ )



## First Manufactured Glass

Probably from the tomb of Thutmose III,  
Thebes, Egypt 18th Dynasty, around 1400 BC (British Museum)

## Silica (oxide) Glasses:

5000 B.C. First Glass from Fenici (Syria)

3500 B.C First Manufactured Glass from Egitto e Mesopotania)

100 A.C First blow glasses from Romans (Italia)



		SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	altri
		%	%	%	%
1450	A.Barovier (Venezia)	75	5	15	2 FeO <sub>3</sub>
1500	Cristalli di Boemia (Praga)	75	11	13	0.5
1675	Ravenscroft "Flint" (Londra)	65	3	7	21 PbO
1800	Franklin (USA) "CORNING"	85	1	1	5 TiO <sub>2</sub>
1800	Schott (Germania) "ZEISS"	80	0	4	13 B <sub>2</sub> O <sub>3</sub>

Sodic-calcium (finestre etc..), Thermal glasses (high temperature), Lead Glasses (TV and raggi x tube), Tempered Glasses (automobile ) etc..

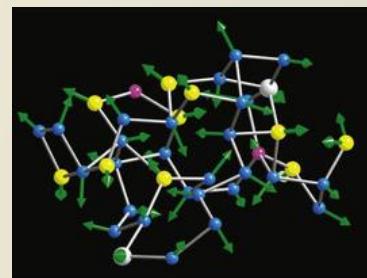
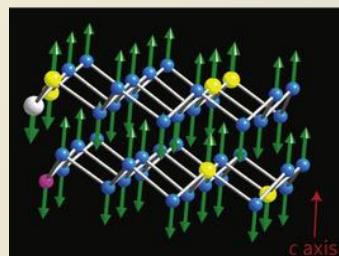
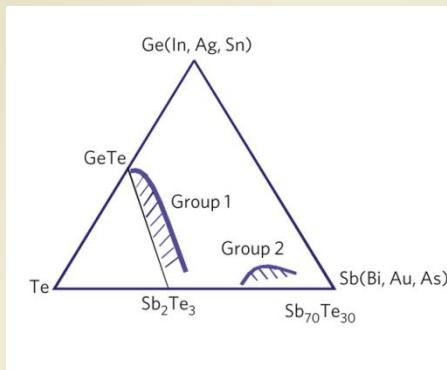
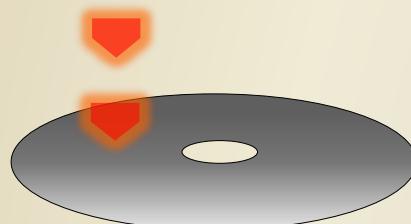
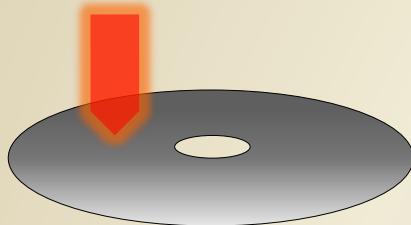
## Chalcogenide glasses:

GeAsSe

GeS, GeSI

GeSbTe

AgInSbTe



## Rewritable Optical Disc



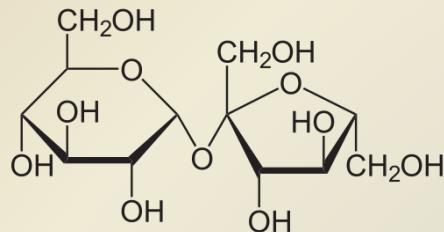
- During writing, the material is **first erased**, initialized into its crystalline state, with long, lower-intensity laser irradiation. The material heats up to its crystallization temperature, but not up to its melting point, and crystallizes in a **metastable** crystalline structure.
- Then the information is **written on** the crystalline phase, by heating spots of it with short (<10 ns), high-intensity laser pulses; the material locally melts and is quickly cooled, remaining in the **amorphous phase**.
- The amorphous phase has lower reflectivity than the crystalline phase, the bitstream can be recorded as "dark" amorphous spots on the crystalline background. A low laser **beam read** the spot using their different reflectivity.

## Organic glasses:

Methanol

Glycerol

Sucrose



## Polymer glasses:

**Polyethylene** (film and bags)  $-(CH_2-CH_2)_n-$

**Poly(vinyl chloride)** (pipe, plastic cover)  $-(CH_2-CHCl)_n-$

**Polystyrene** (toys and soft objects)  $-[CH_2-CH(C_6H_5)]_n-$



## Metallic glasses:

Metallic alloy obtained by **extremely rapid cooling**.

The first was produced at Caltech in 1960 ( $Au_{75}Si_{25}$ ).  
Alloy of 77.5% palladium, 6% copper, and 16.5% silicon was found to have critical cooling rate between 100 to 1000 K/s.

Samples of the new titanium-based metallic-glass composites showing their toughness and ductility