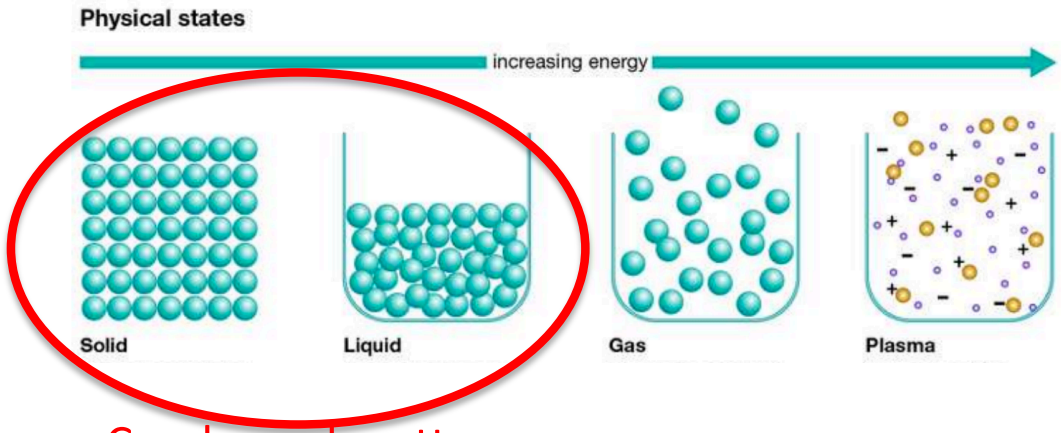
Lecture 12
Phase equilibria, phase transitions, phase diagrams and equations of state

Faselikevekter, faseoverganger, fasediagram og tilstandsligninger

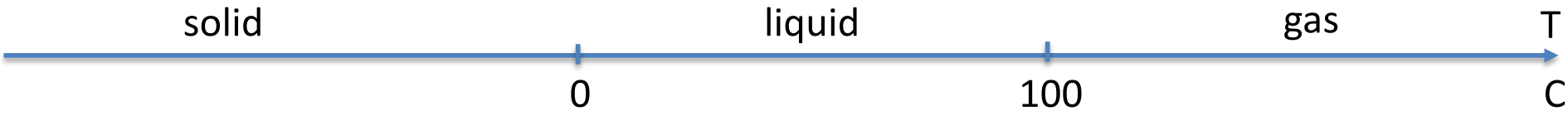
Phases of matter



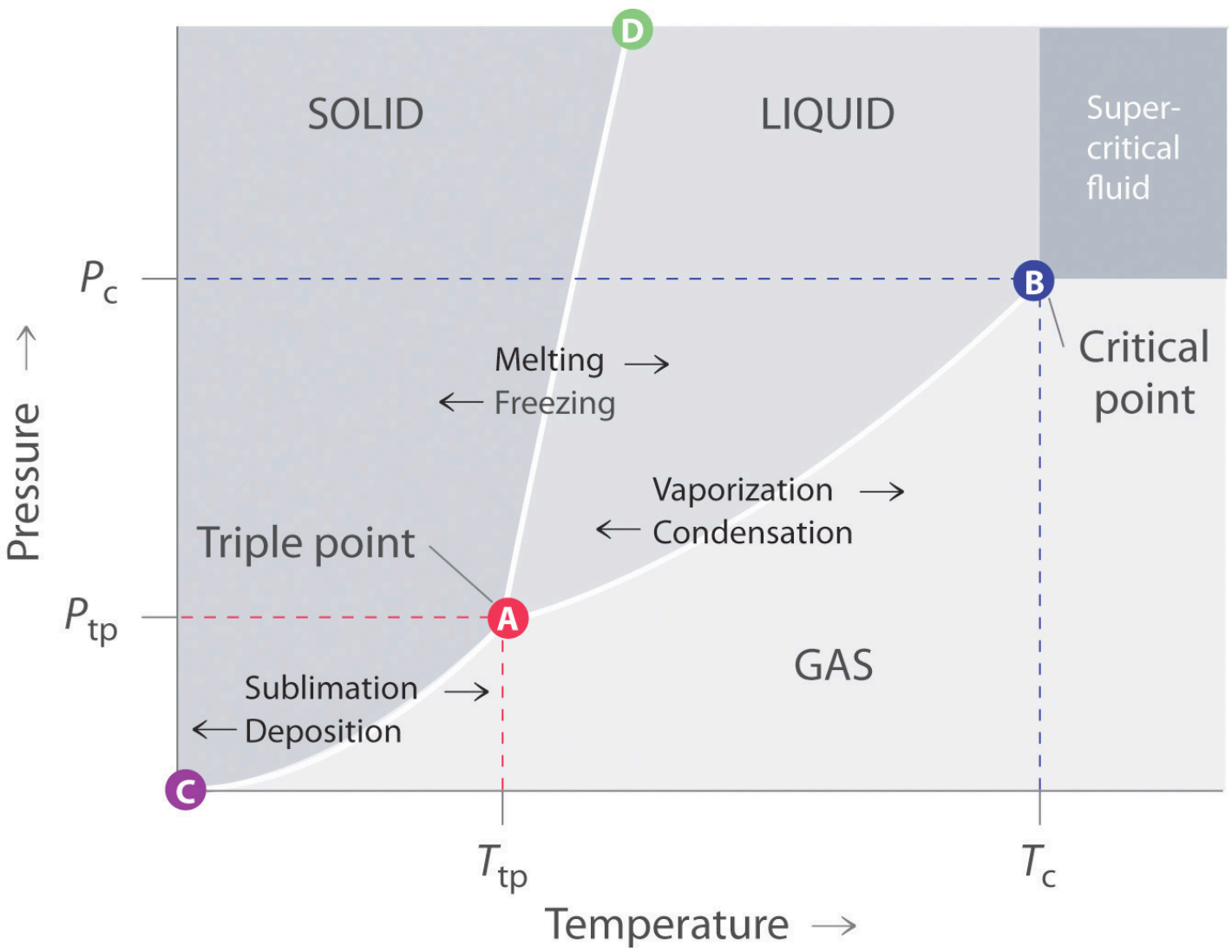
Condensed matter







Phase diagram P-T



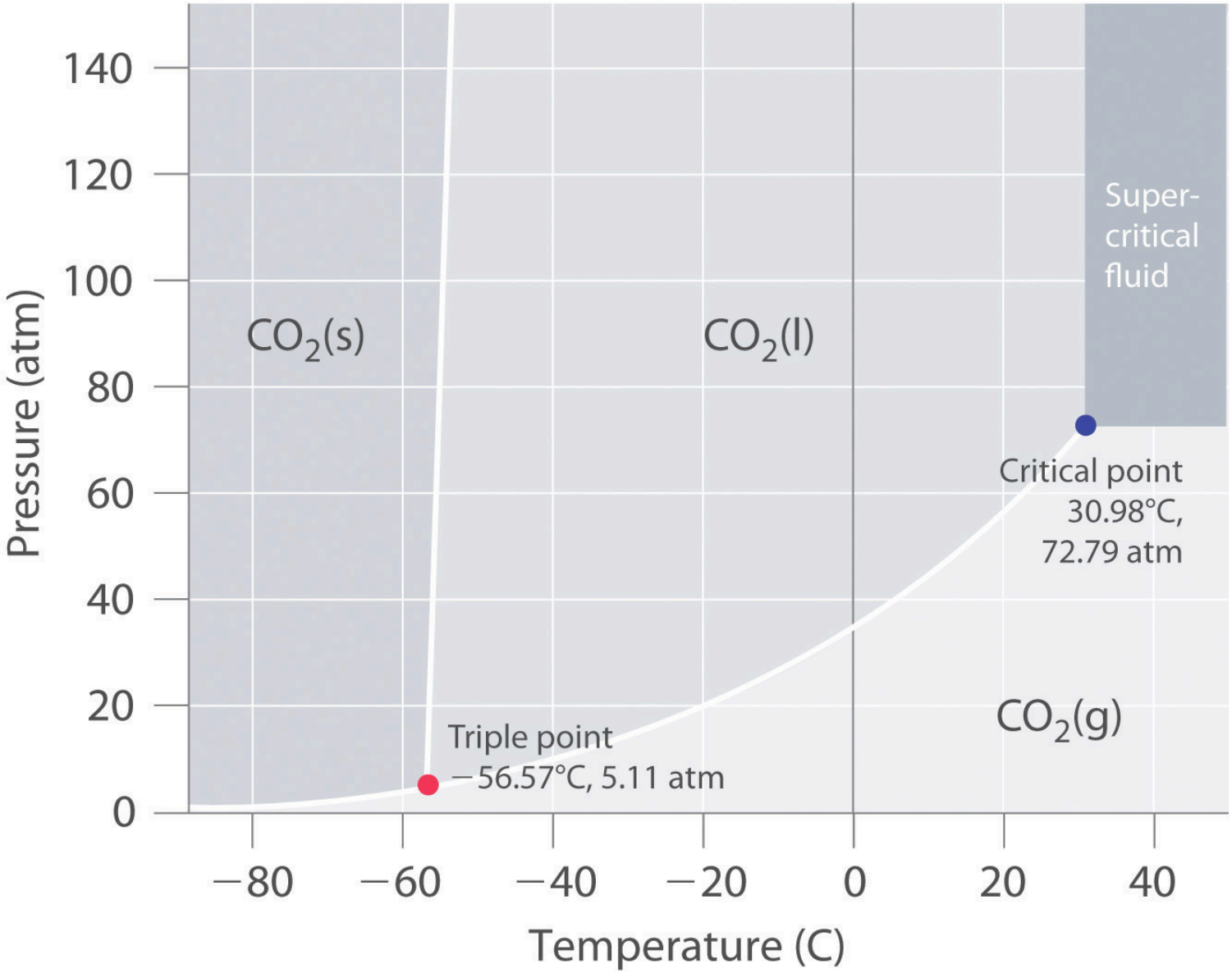
Coexistence lines

A-C solid– gas

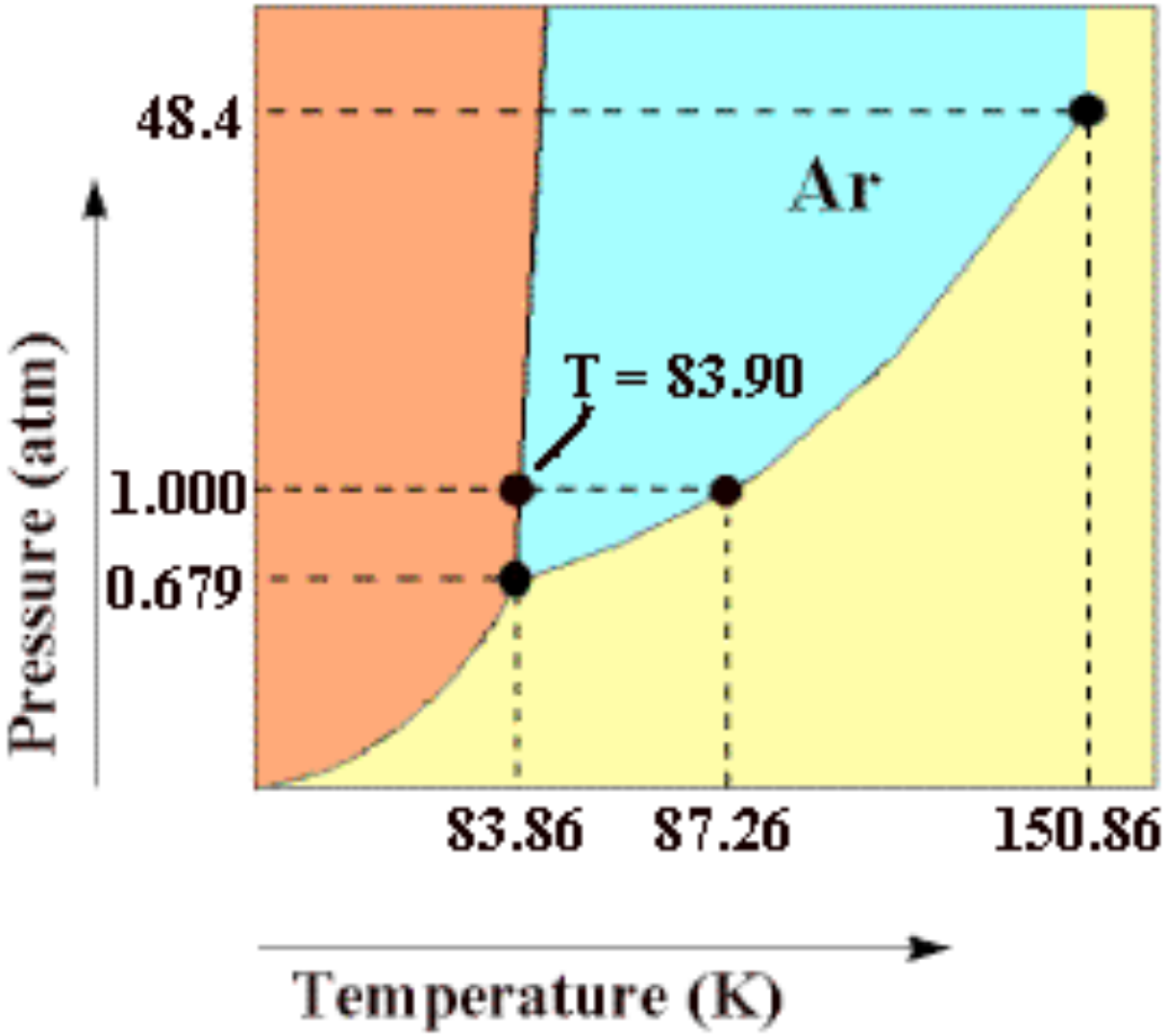
A-B Liquid – gas

A-D solid– liquid

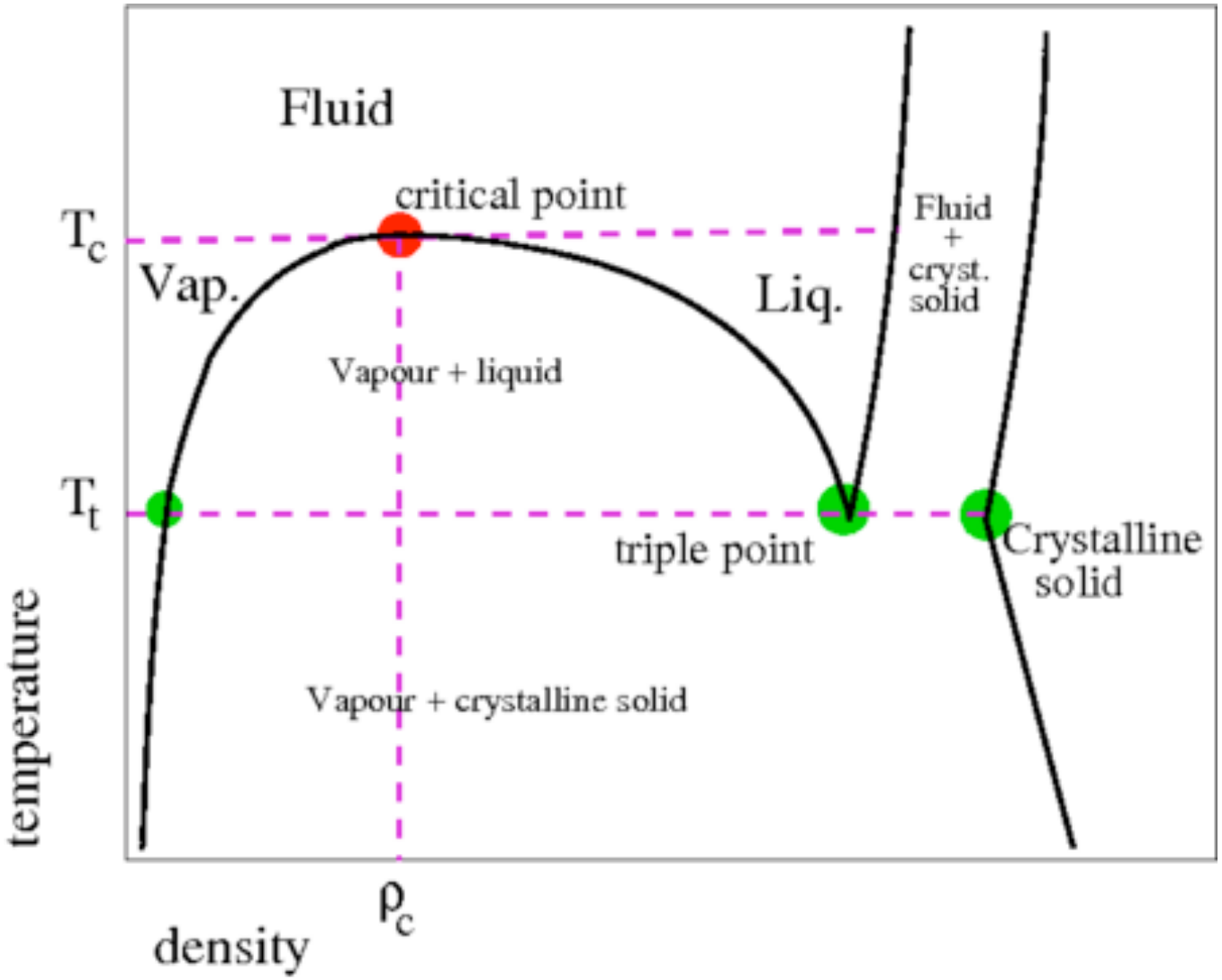
Phase diagram P-T for CO_2



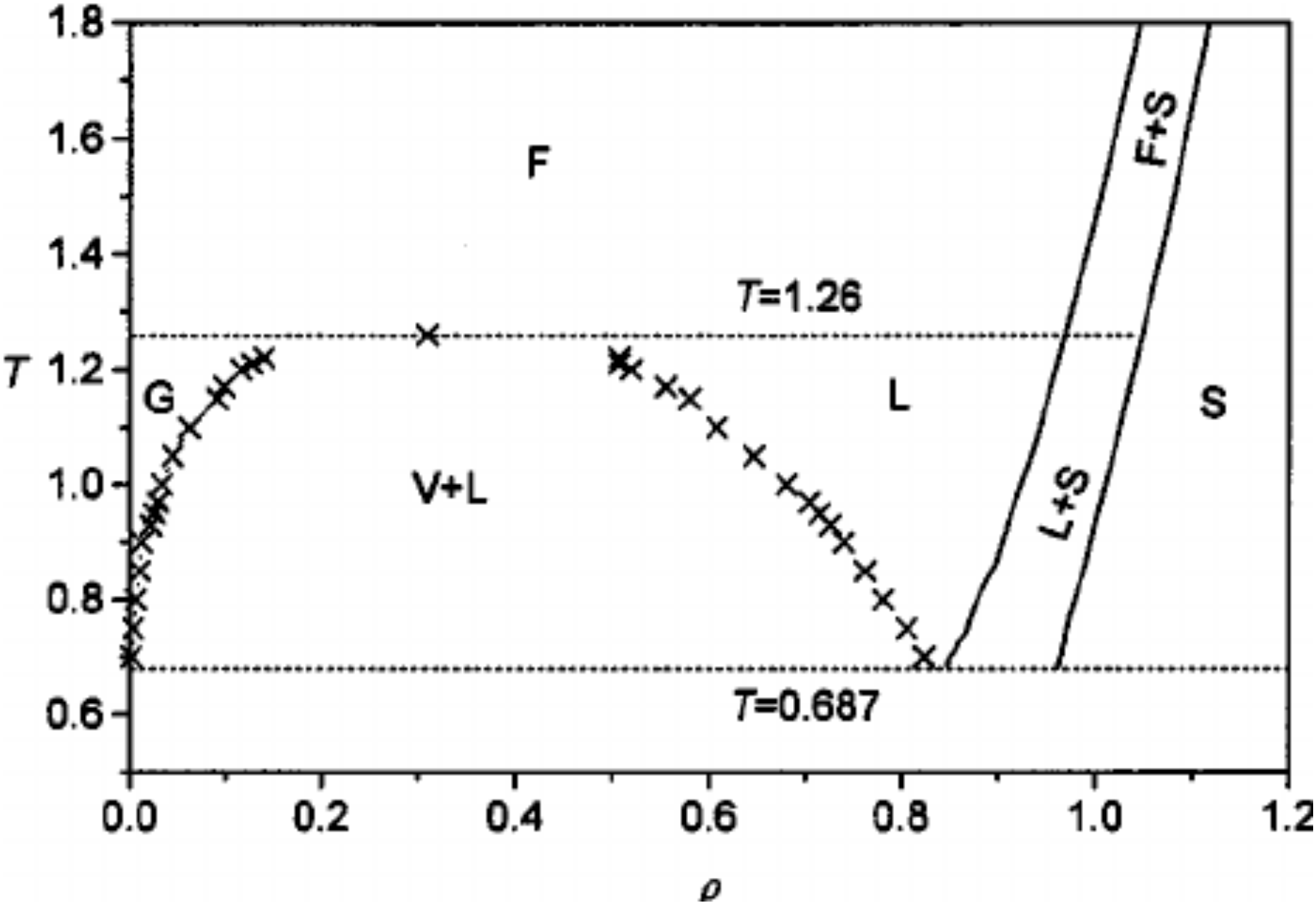
Phase diagram P-T, finding (T,P) of melting and vapourization



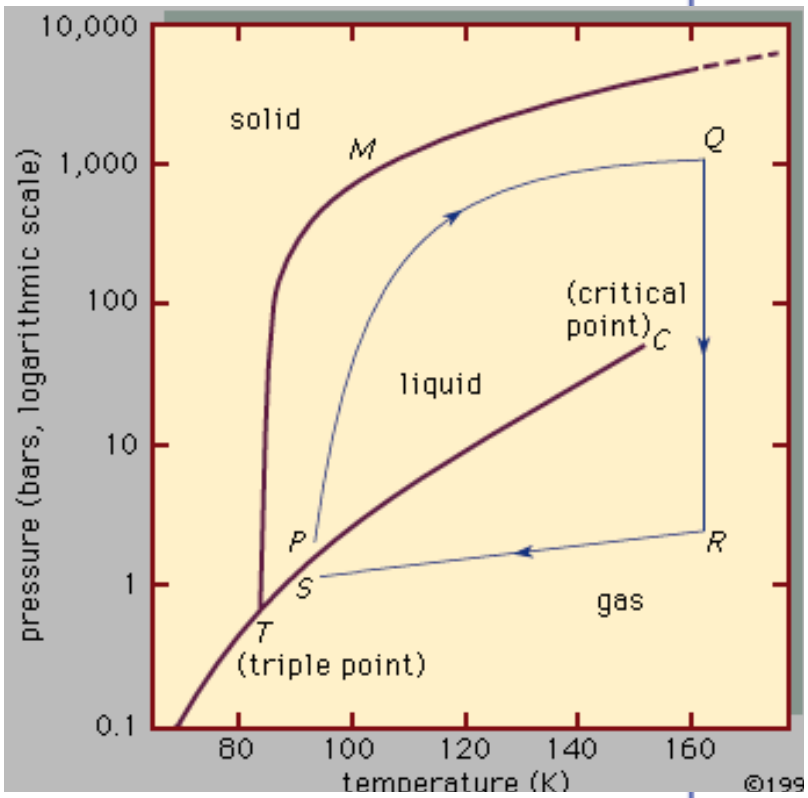
Phase diagram T-ρ



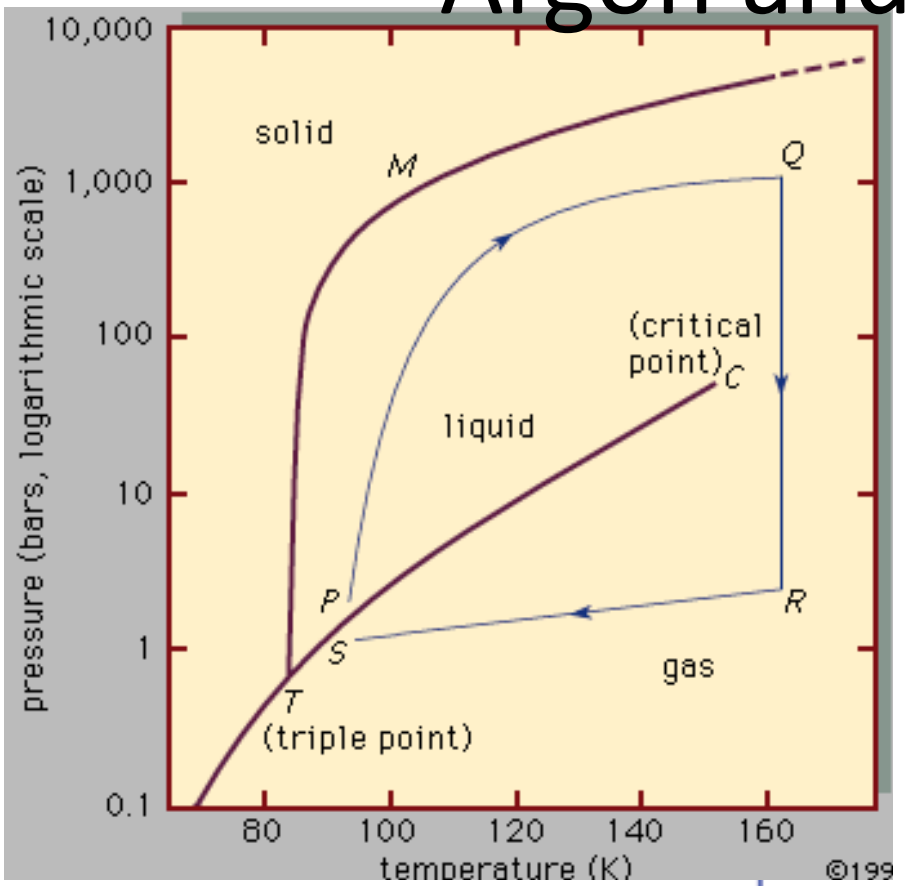
T-ρ Lennard-Jones phase diagram

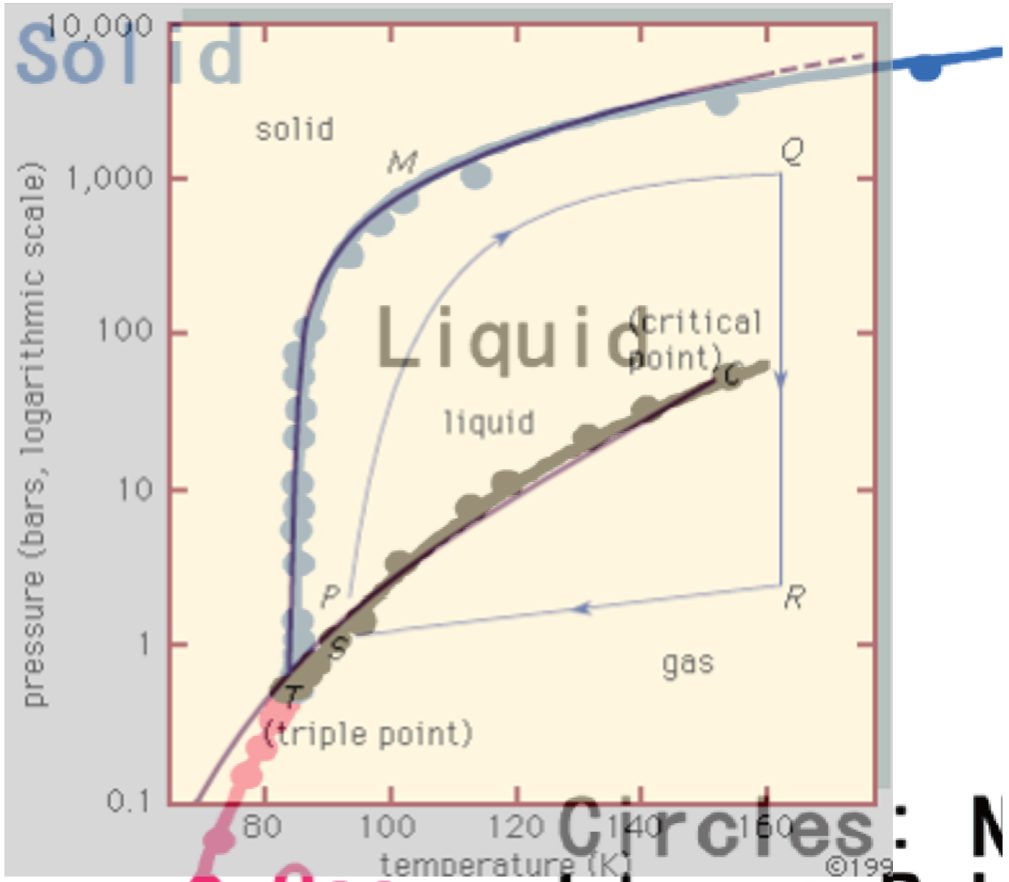


Argon and Lennard-Jones



Argon and Lennard-Jones





0. 001

0. 0001

10^{-5}

0

0. 5

1

1. 5

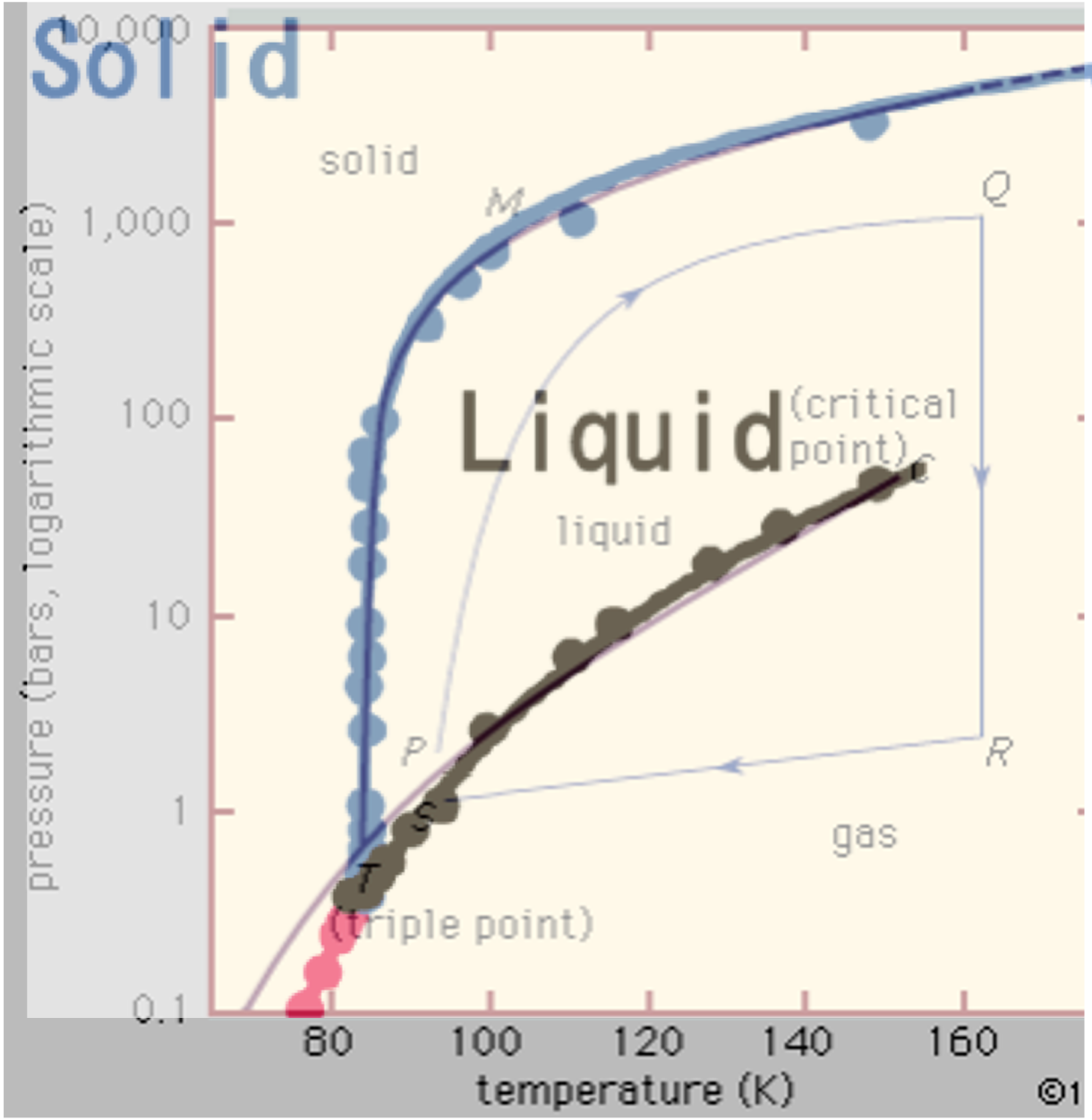
$T/(\varepsilon/k)$

Circles: N

Lines: Pub

Principle of corresponding states

Lennard-Jones and Argon



Two substances 1 and 2

The state of 1: $(T_1/T_{C1}, P_1/P_{C1})$

Corresponds to the state of 2: $(T_2/T_{C2}, P_2/P_{C2})$

Rescale by a unique state

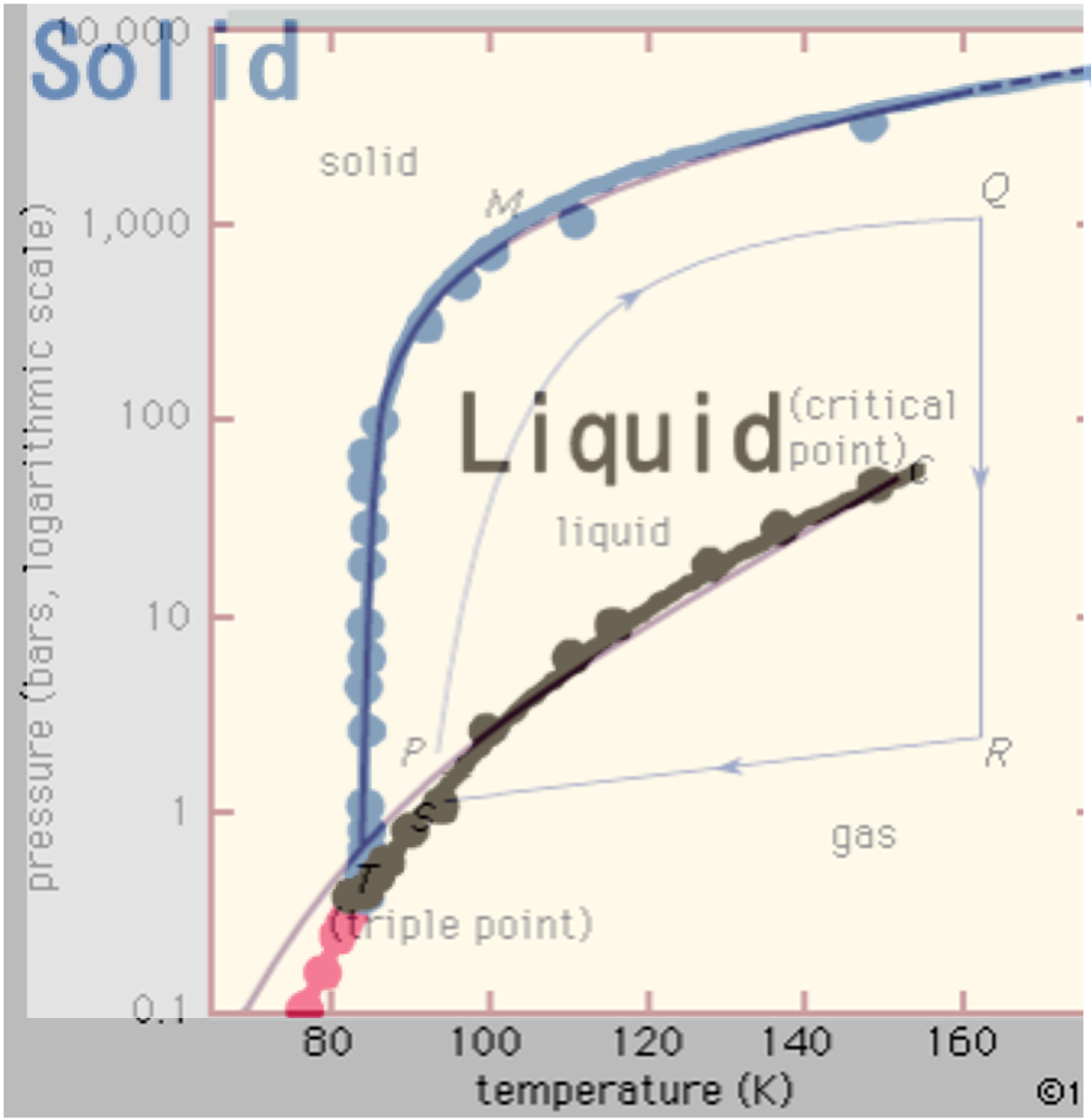
T_C, P_C, ρ_c

or

T_t, P_t, ρ_t

Principle of corresponding states

Lennard-Jones and Argon



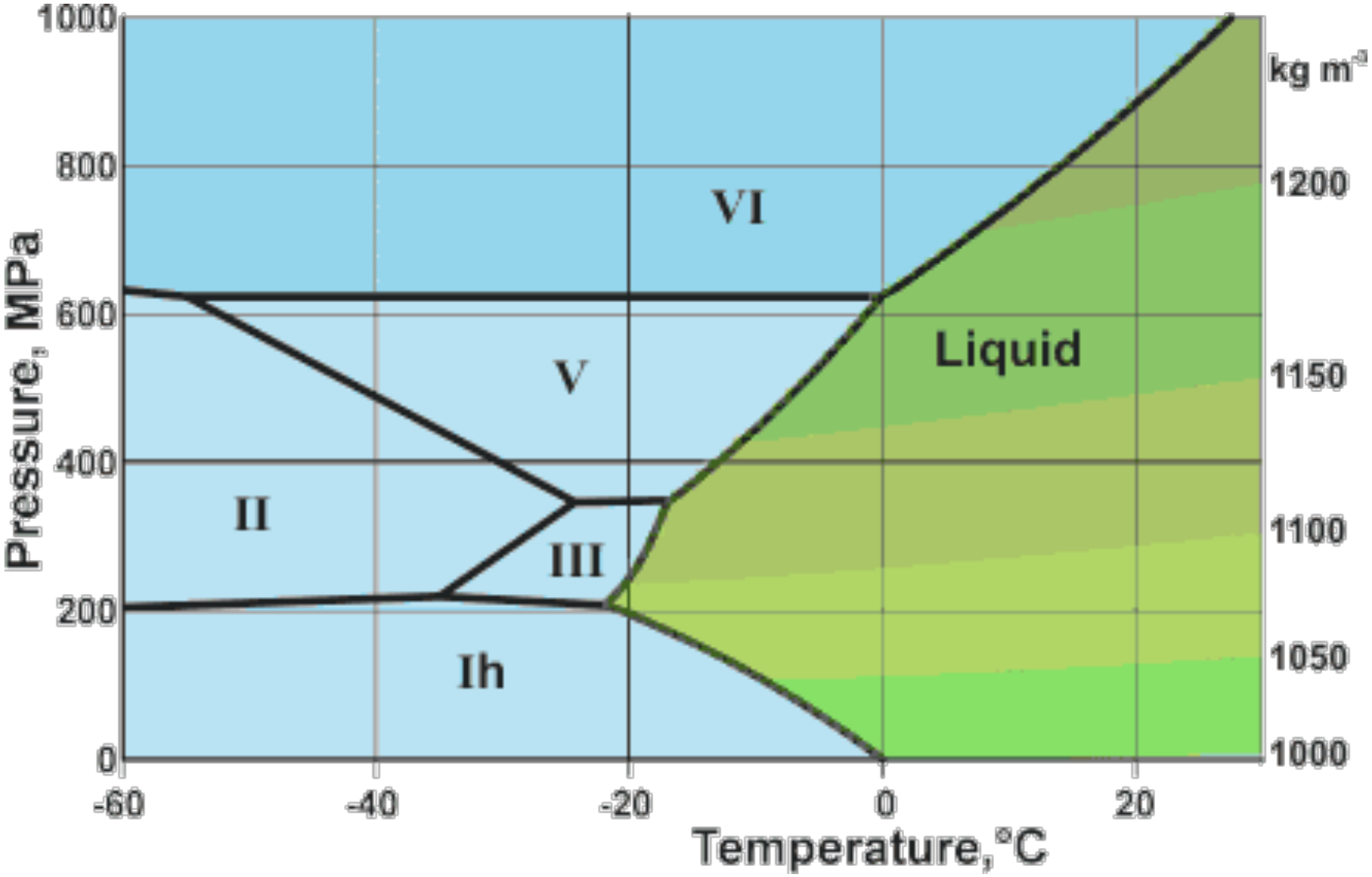
$T_{c,a}$=150.68 K
$P_{c,a}$=4.86 MPa

$T^*_{c,LJ} = kT_{c,LJ}/\varepsilon$=1.326
$P^*_{c,LJ} = P_{c,LJ}\,\sigma^3/\varepsilon$=0.128

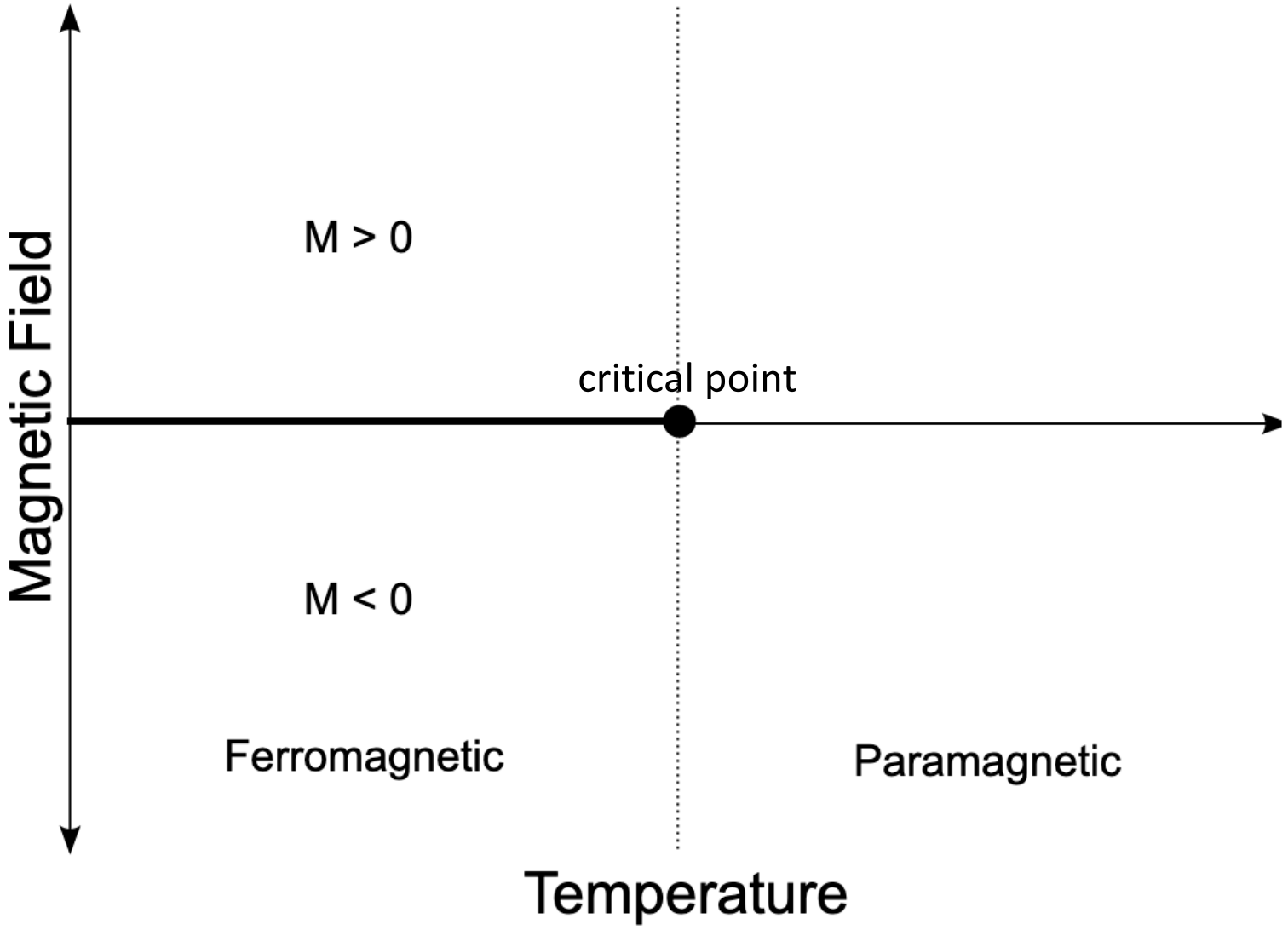
Principle of corresponding states:
$kT_{c,a}/\varepsilon$= k*150.68 K/ε =1.326
=> ε /k = 113.6 K

$P_{c,a}\,\sigma^3/\varepsilon$ = 4.86 σ^3/ 113.6 k
=> σ = 3.4 Å

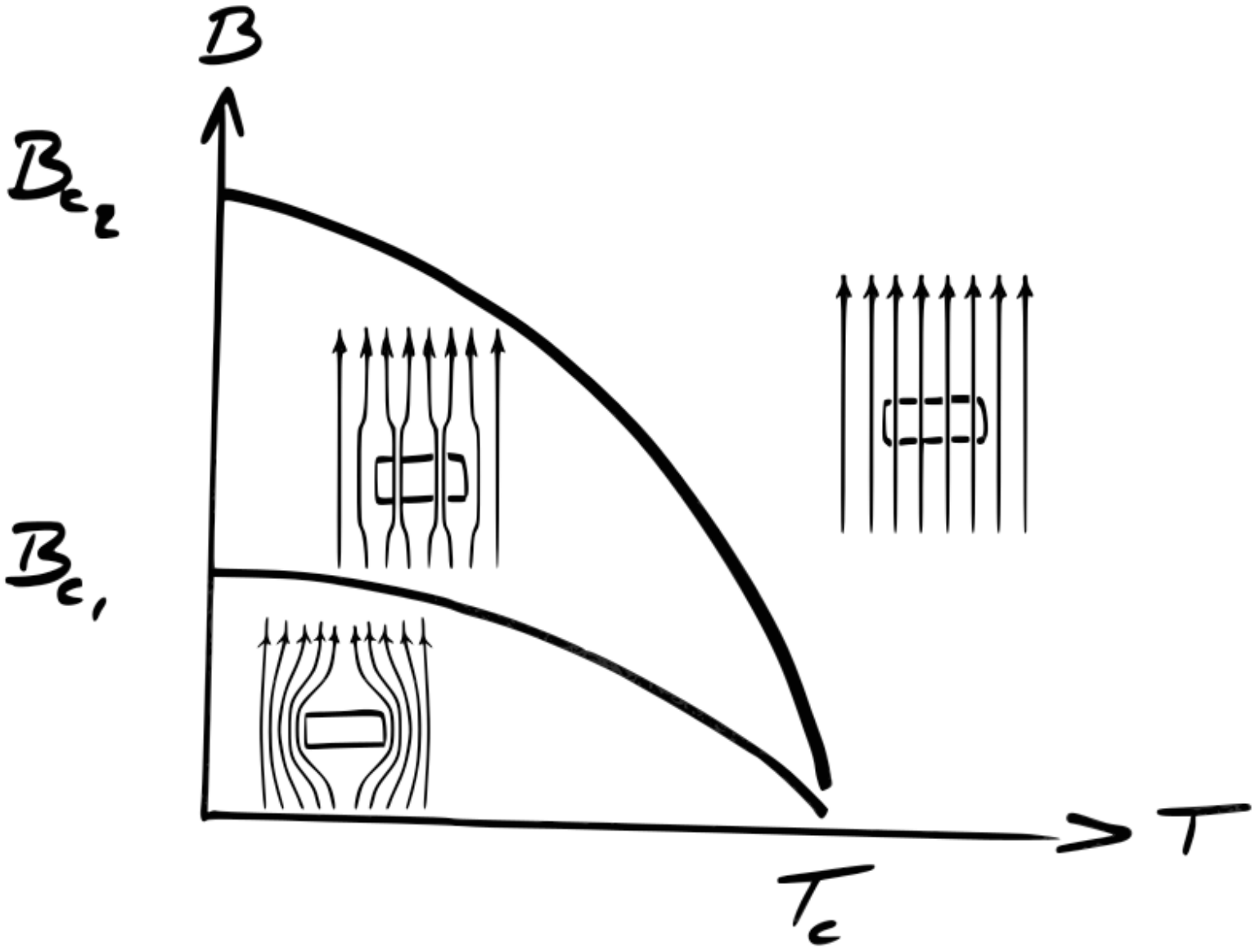
Mange faser: is



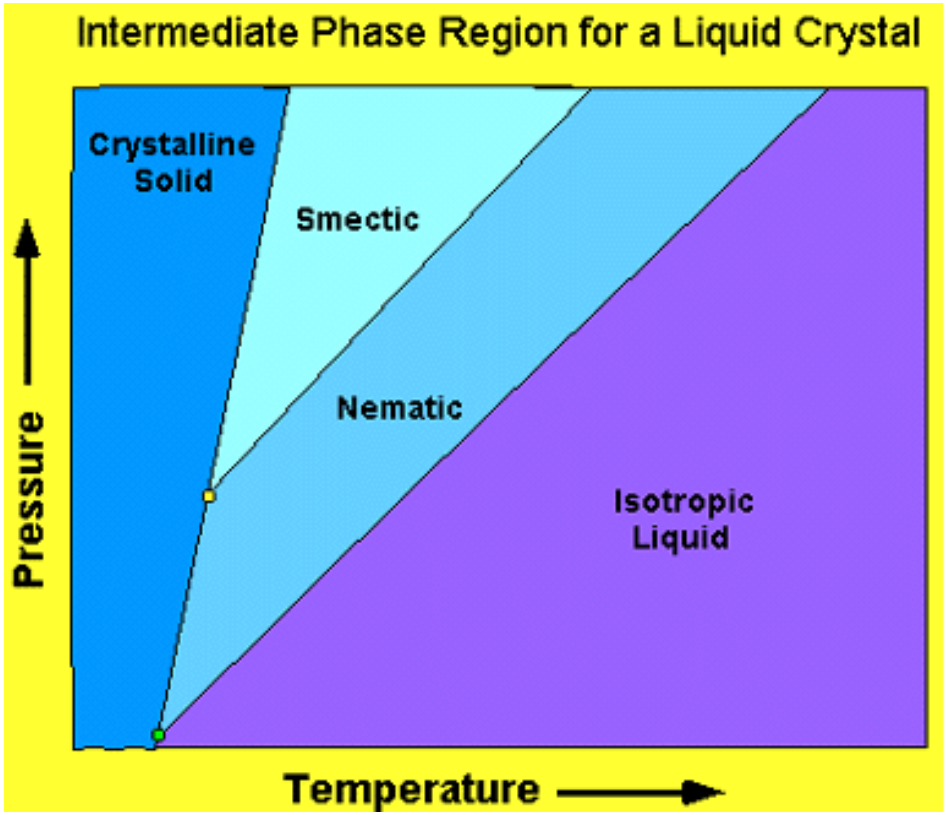
Ferromagnet

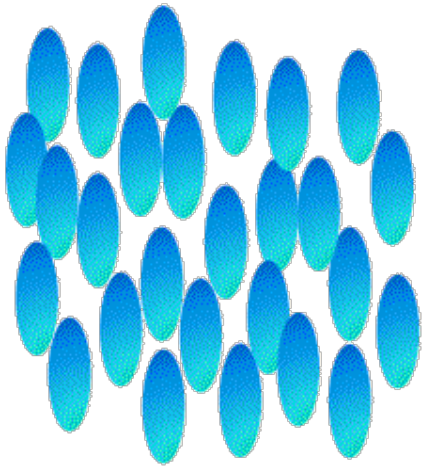


Superconductors

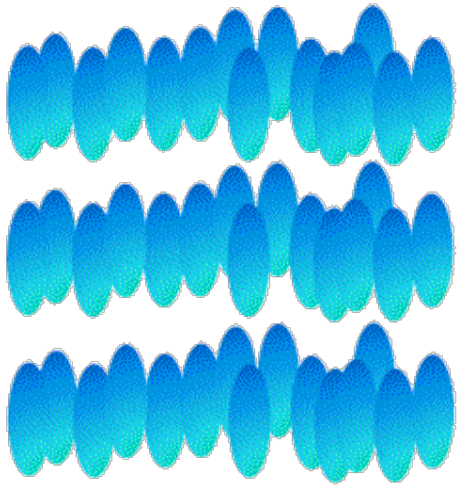


Liquid crystals

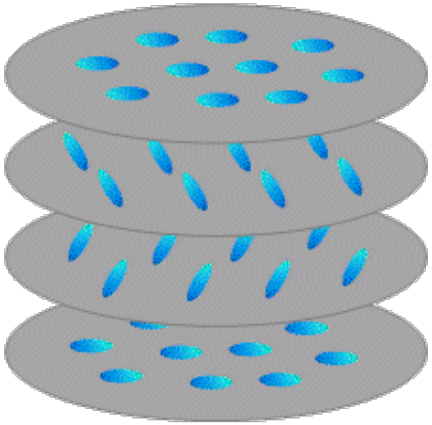




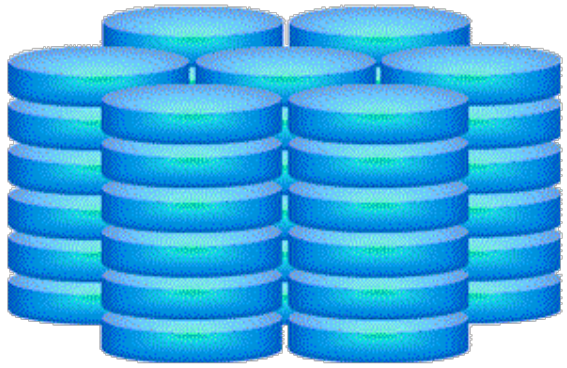
Nematic Phase



Smectic Phase

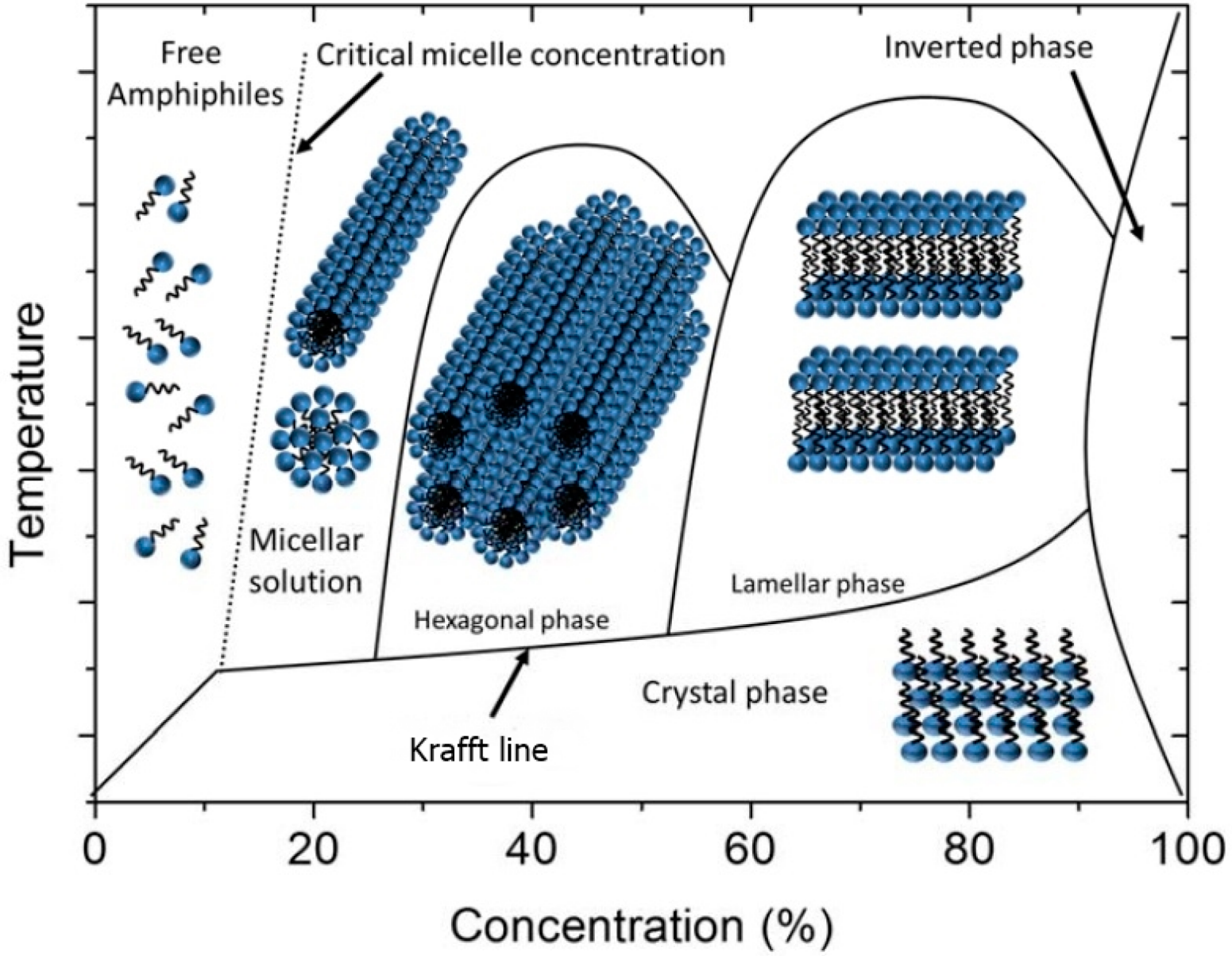


Cholesteric Phase
(Chiral Nematic Phase)



Discotic Phase
(Columnar Phase)

Self organization of amphiphiles



Frictional fluid flows

The only SFFs at our department:

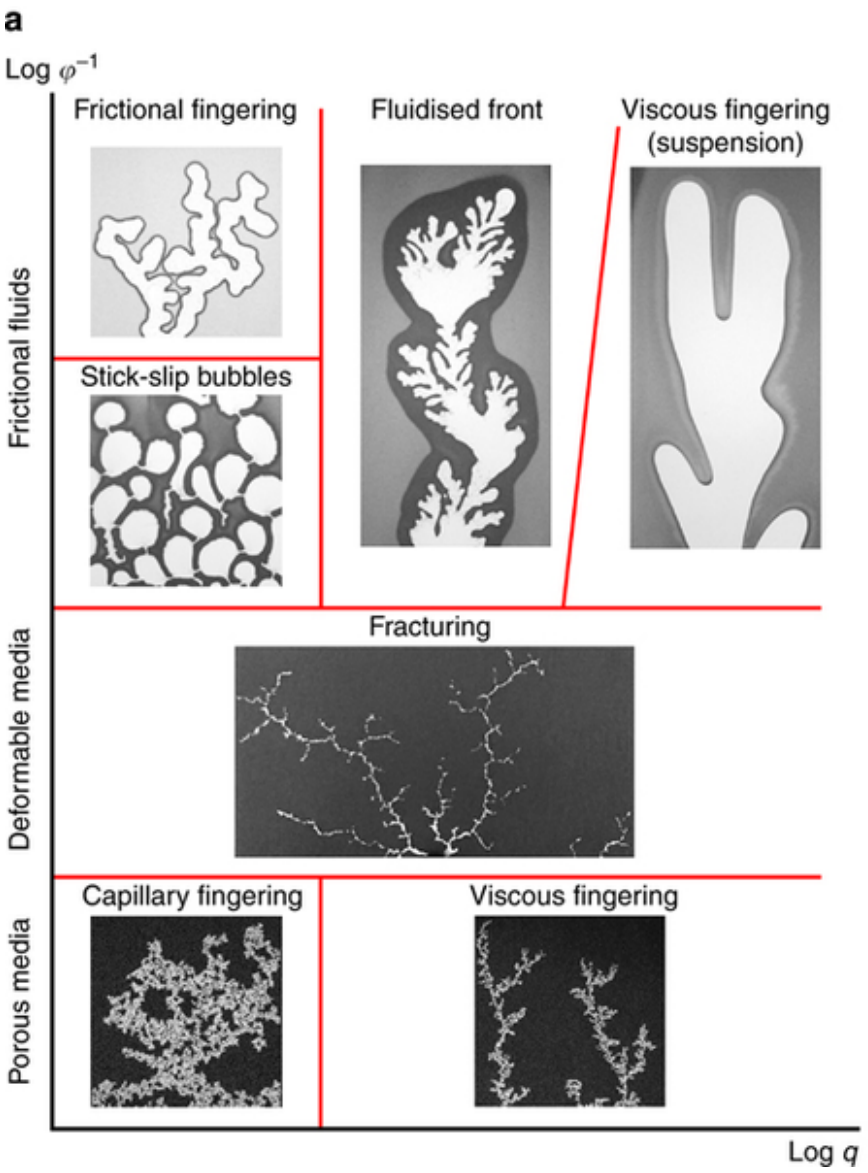
Norwegian Centre of Excellence

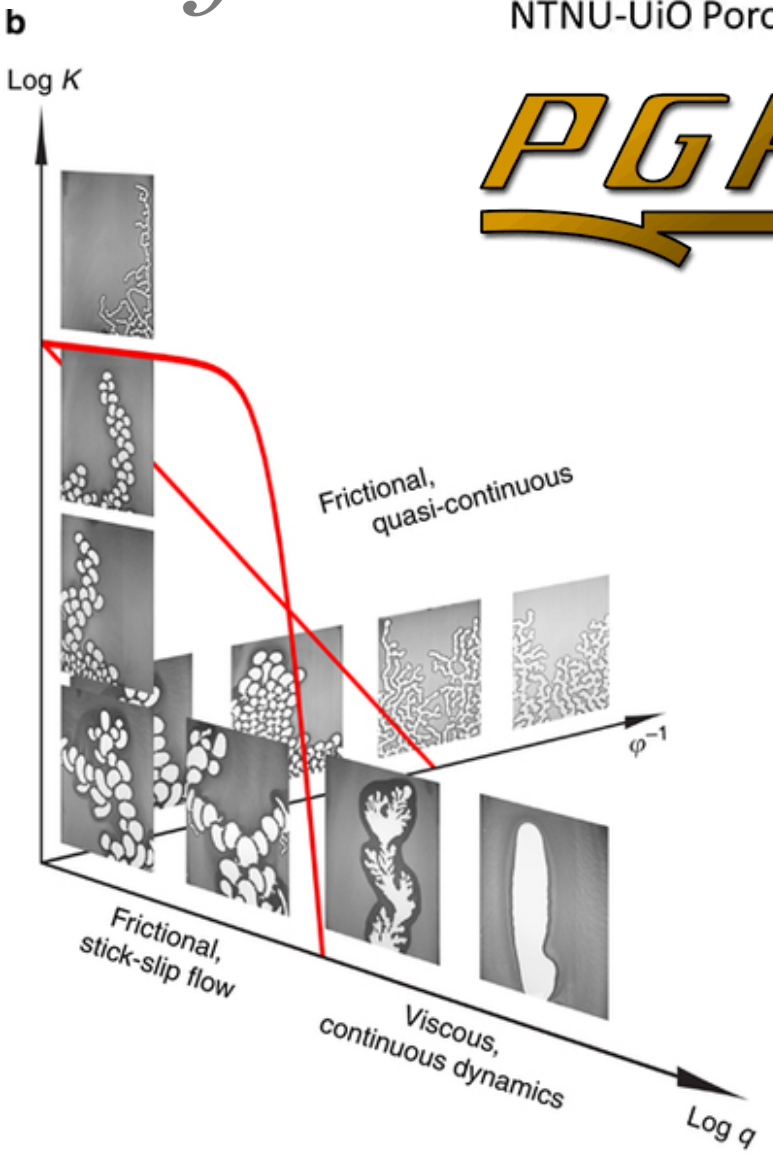


PoreLab

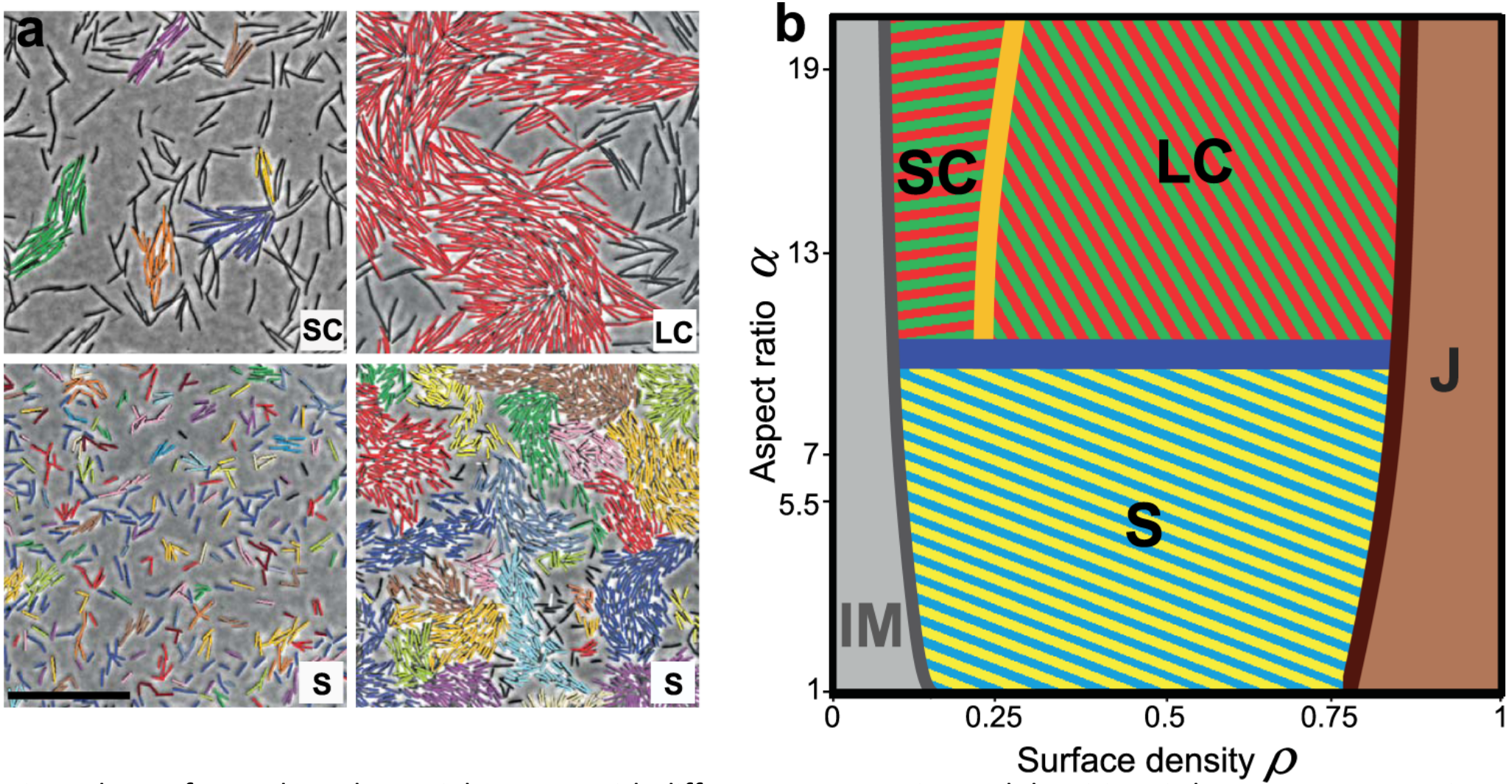
NTNU-UiO Porous Media Laboratory

PGP PHYSICS OF GEOLOGICAL PROCESSES





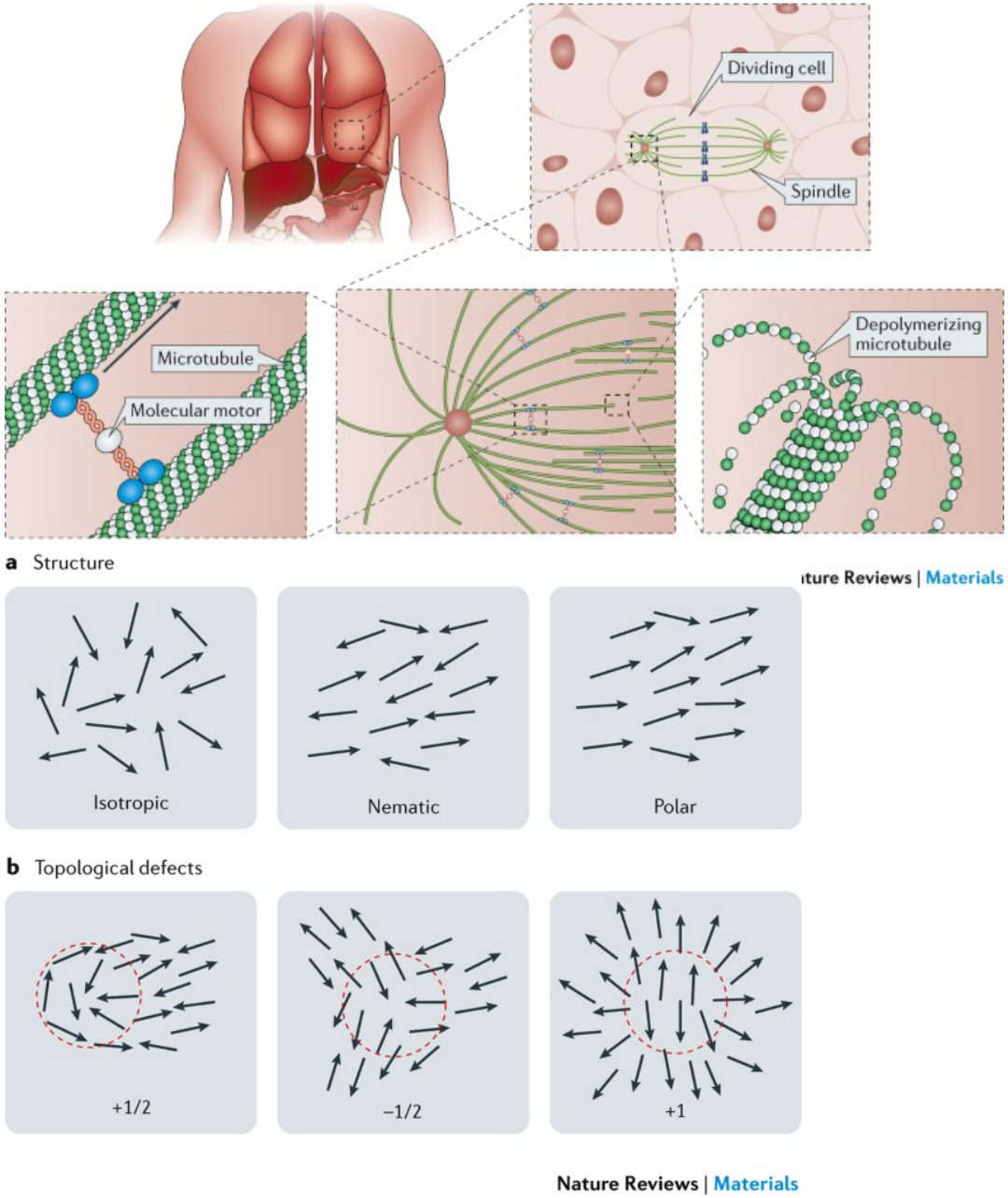
Active matter: Bacterial swarming



Snapshots of monolayer bacterial swarms with different aspect ratios and densities. Colors represent moving clusters. Scale bar 50 µm. For short cells (S phase), almost all cells are moving coherently. For long cells, spatial ordering into local (SC) or global (LC) clusters is apparent. **b** The inferred phase diagram as a function of aspect ratio (α) and surface density (ρ), showing five distinct phases: immotile (IM), swarming (S), small clusters (SCs), large clusters (LCs), and jammed (J).

nature reviews materials
Published: 20 July 2017

Active matter at the interface between materials science and cell biology





COVER Fluorescence microscopy image of a composite three-dimensional active nematic liquid crystal. Light-sheet microscopy reveals the structure and dynamics of disclination defects, which are fundamental features of nematic liquid crystals and other fluids with orientational order. See pages 1075 and 1120. Image: Ray Adkins

Condensed matter physics section host of the only SFFs at our department:

Topological defects



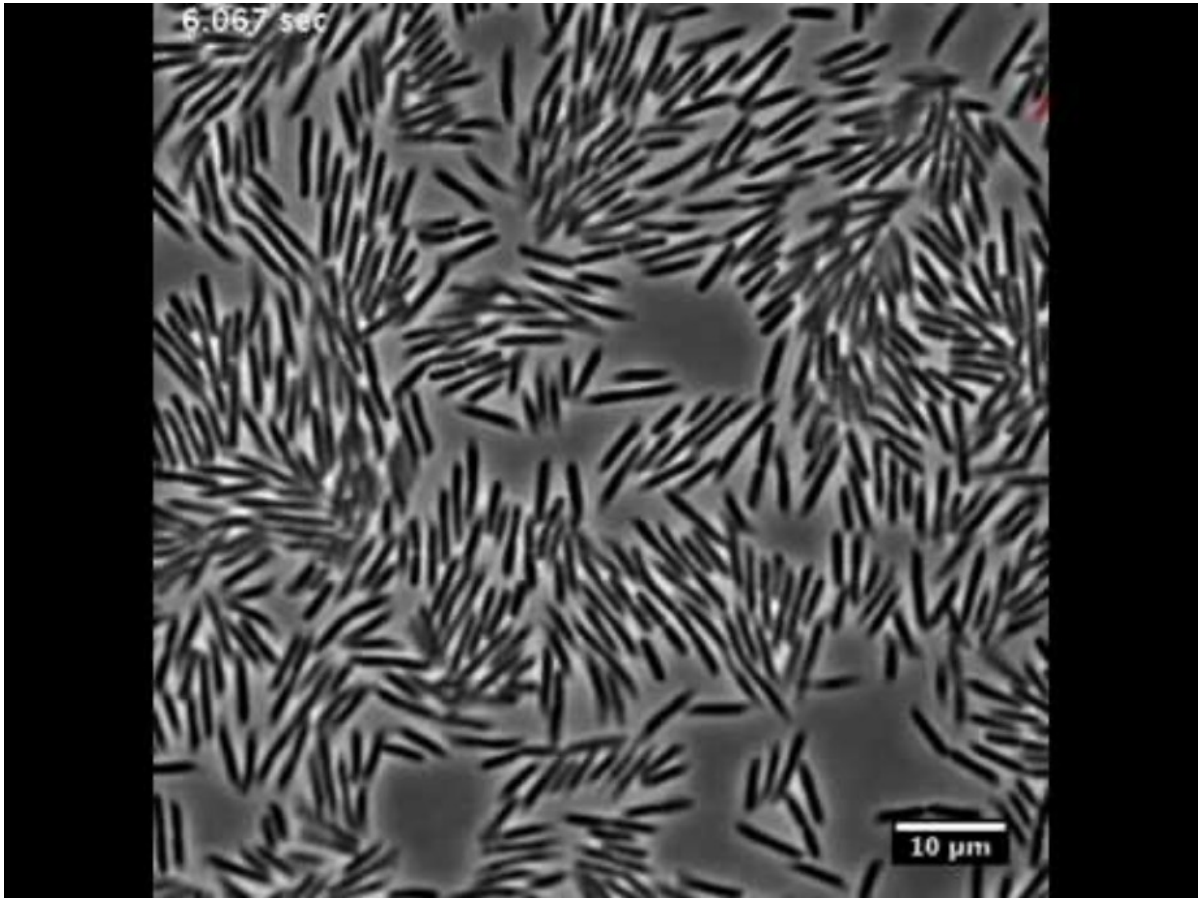
Norwegian Centre of Excellence

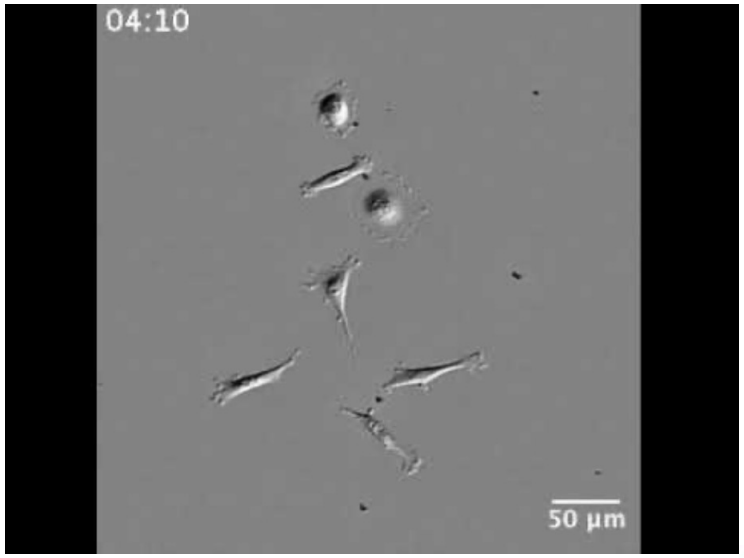
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PGP PHYSICS OF GEOLOGICAL PROCESSES

dynamics of interacting topological defects in ordered states, their collective effects on the large-scale properties

- Turbulence and vortex dynamics in superfluid Bose-Einstein condensates
- Plasticity and dislocation dynamics in crystalline matter
- Hydrodynamics of nematic active matter and its topological defects





The only SFFs at our department:

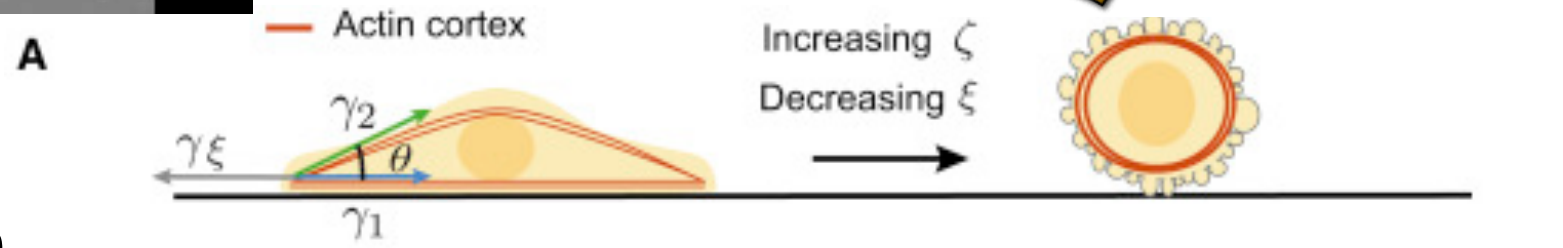
Norwegian Centre of Excellence

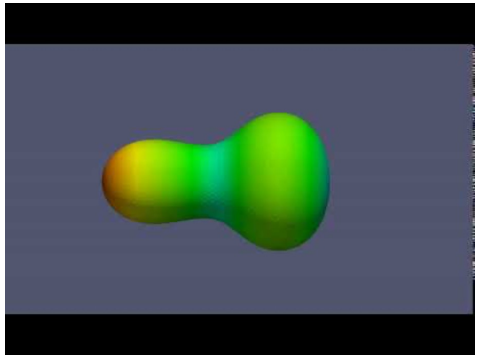


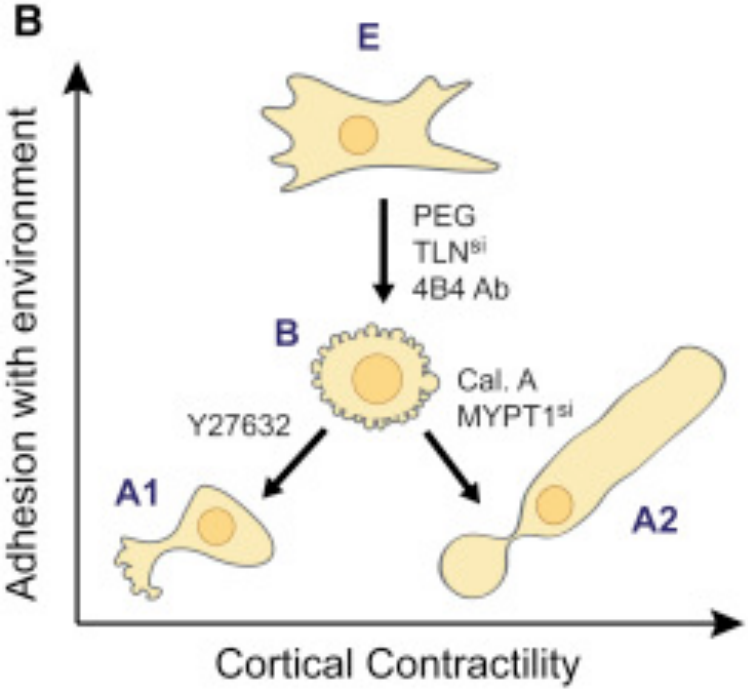
PoreLab
NTNU-UiO Porous Media Laboratory

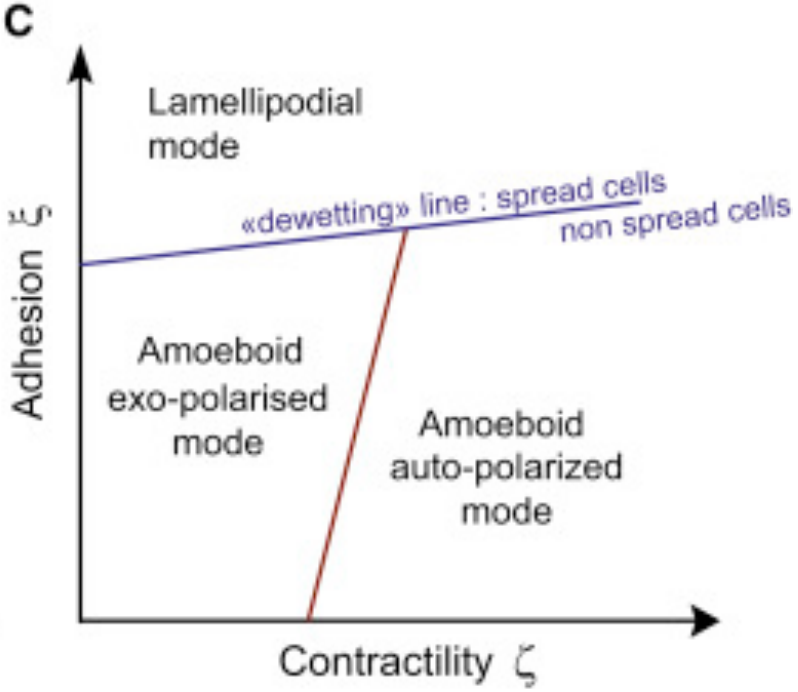
PGP PHYSICS OF GEOLOGICAL PROCESSES

Cell migration









Condensed matter physics section host to the only SFFs at our department:

Master programs:

Norwegian Centre of Excellence



PoreLab
NTNU-UiO Porous Media Laboratory

PGP PHYSICS OF GEOLOGICAL PROCESSES

MSc Physics, UiO:

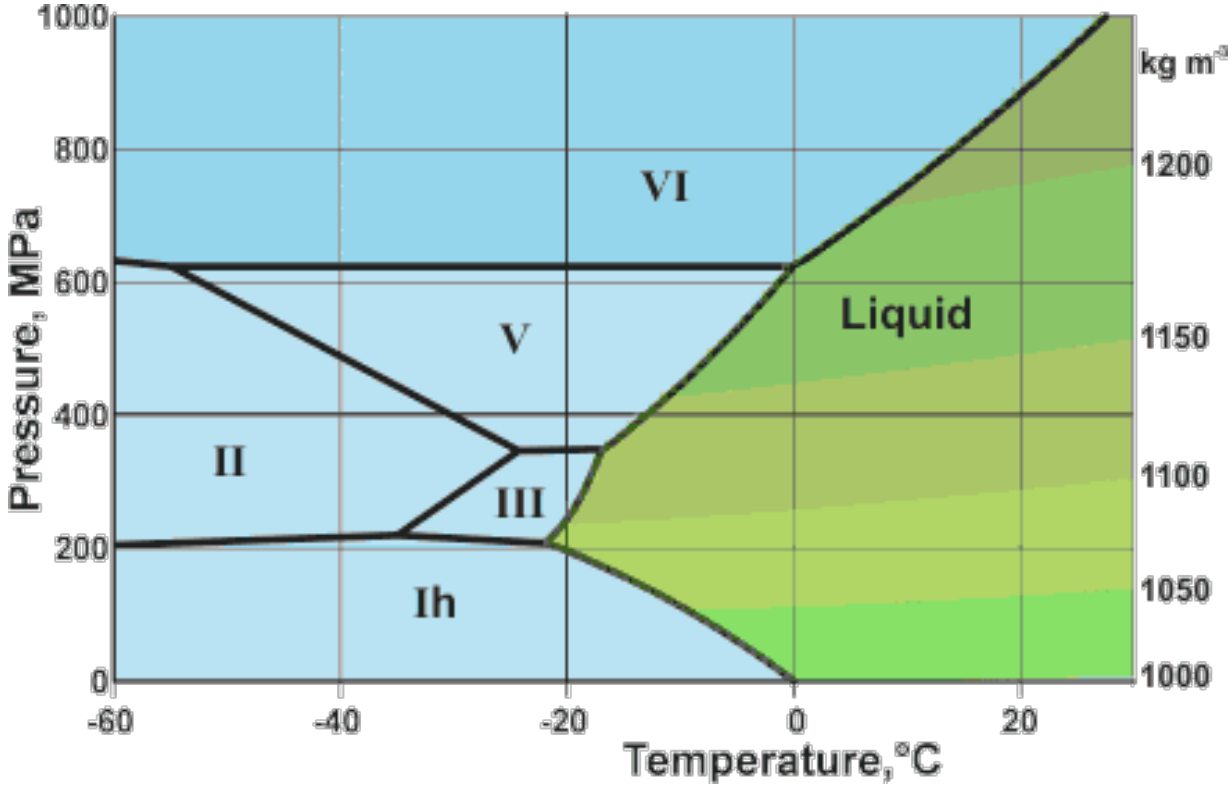
- **Materials, Nanophysics and Quantum Technology**
  - **Disordered and complex systems**
- **Biological and Medical Physics**
  - **Biological physics**

MSc Computational Science, UiO:

- **CS: Physics**

Phase coexistence lines

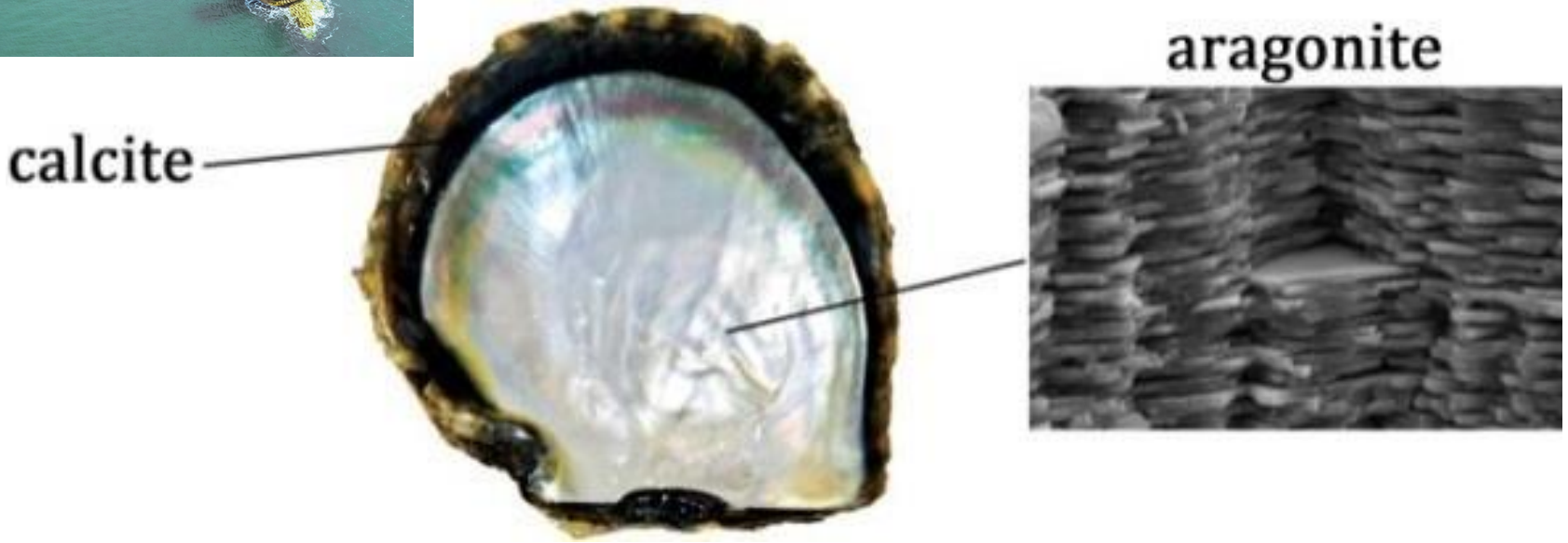
How can phase coexistence lines be determined?
What properties do coexistence lines have?
What data do we need?



calcite and aragonite







Calcite and Aragonite

$\Delta_f H$, $\Delta_f G$= Enthalpy, Gibbs free energy of formation. Energy to form one mole from elements

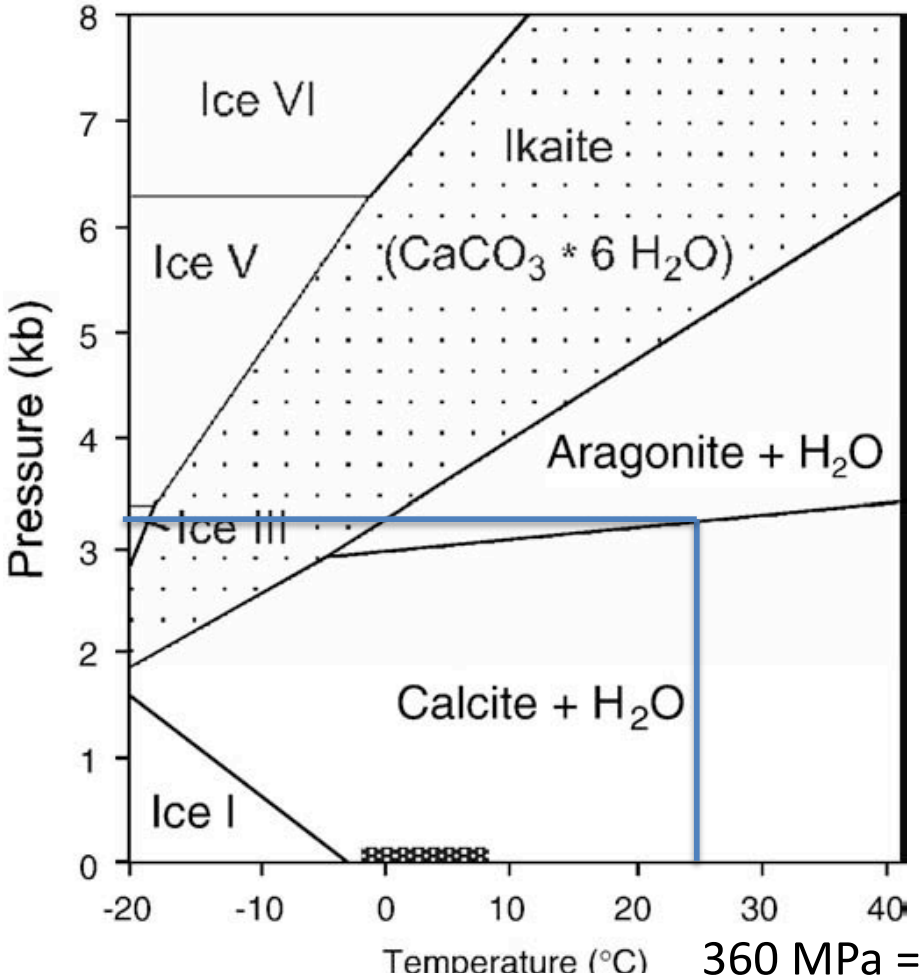
Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
Al (s)	0	0	28.33	24.35	9.99
Al_2SiO_5 (kyanite)	−2594.29	−2443.88	83.81	121.71	44.09
Al_2SiO_5 (andalusite)	−2590.27	−2442.66	93.22	122.72	51.53
Al_2SiO_5 (sillimanite)	−2587.76	−2440.99	96.11	124.52	49.90
Ar (g)					
C (graphite)	0	0	5.74	8.53	5.30
C (diamond)					3.42
CH_4 (g)					
C_2H_6 (g)					
C_3H_8 (g)					
C_2H_5OH (l)					58.4
$C_6H_{12}O_6$ (gl					
CO (g)					
CO_2 (g)					
H_2CO_3 (aq)	−699.65	−623.08	187.4		
HCO_3^- (aq)	−691.99	−586.77	91.2		
Ca^{2+} (aq)	−542.83	−553.58	−53.1		
$CaCO_3$ (calcite)	−1206.9	−1128.8	92.9	81.88	36.93
$CaCO_3$ (aragonite)	−1207.1	−1127.8	88.7	81.25	34.15
$CaCl_2$ (s)	−795.8	−748.1	104.6	72.59	51.6

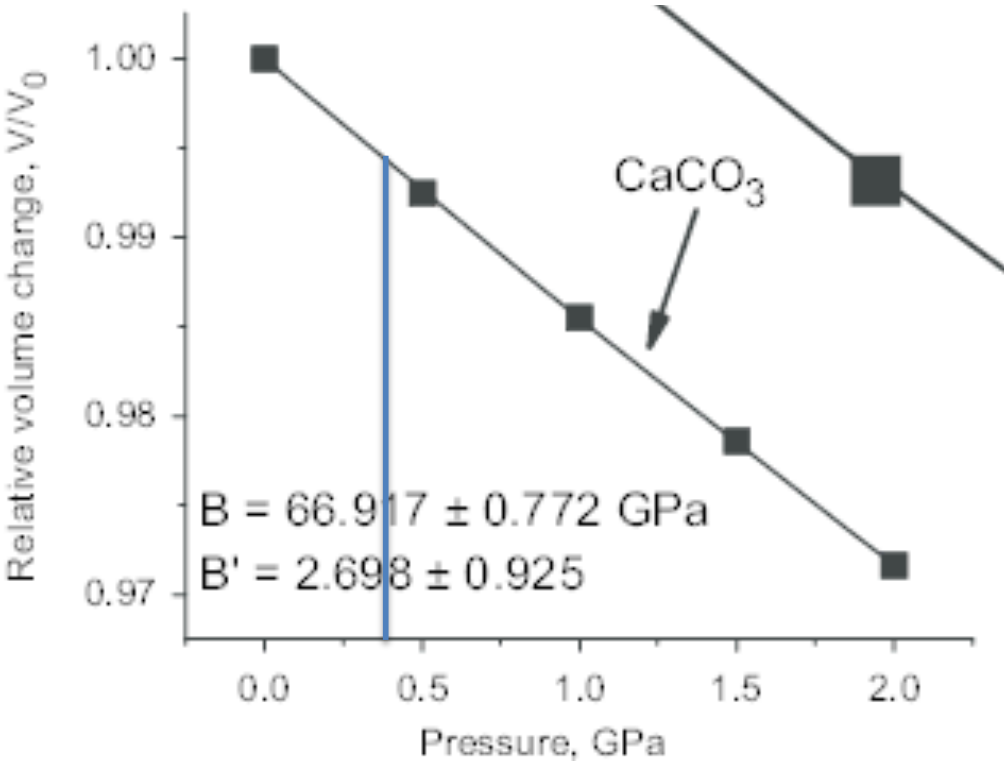
Is calcite or aragonite stable at 25C and 1 atmosphere?

At what pressure is aragonite stable?

- $\Delta_f G_C - \Delta_f G_A$ = -1 kJ/mol
- $dG = VdP - SdT + \mu dN$
- $\Delta G_C - \Delta G_A = (V_C - V_A)\Delta P$
- $\Delta_f G_C - \Delta_f G_A + \Delta G_C - \Delta G_A = 10^3 + 2.78 * 10^{-6} \Delta P = 0$
- ΔP = 360 MPa

Kalsitt og aragonitt





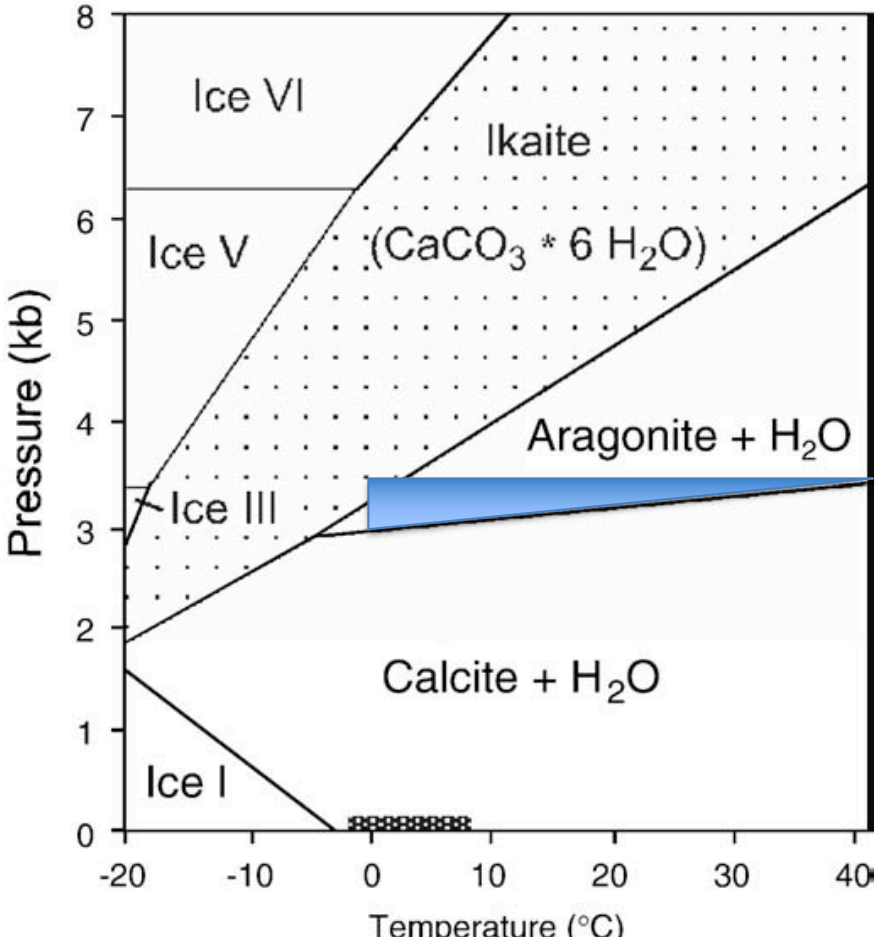
360 MPa = 0.36 GPa = 3.6 kbar

Density of the Earth's crust: 2600kg/m^3, => z = - p/(rg) = 14km

Clausius-Clapeyron relation

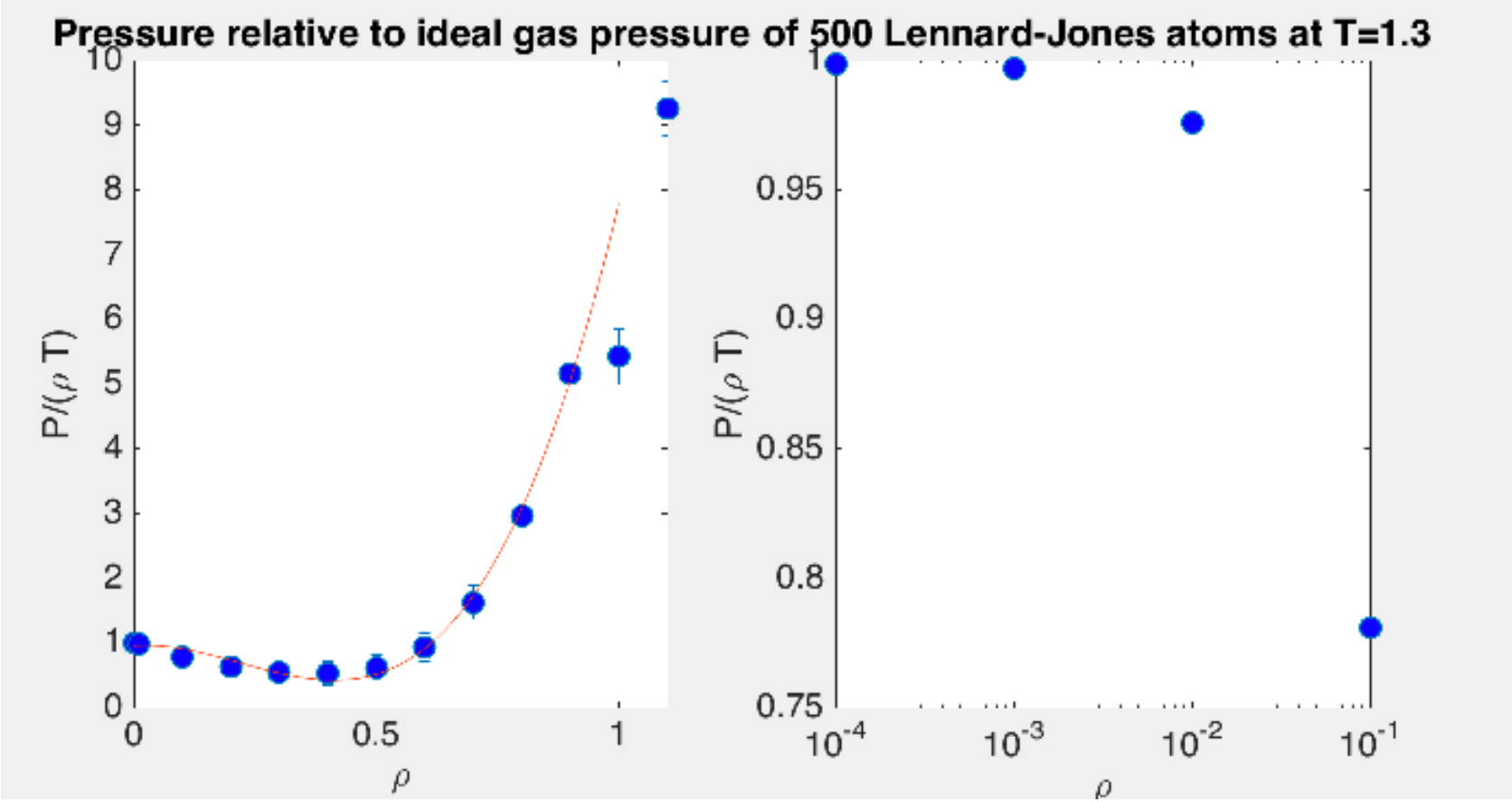
- $dG = VdP - SdT$
- => The shape of a coexistence line in a PT-diagram is determined by V and S
- $G_A = G_B$ at the coexistence line
- $dG_A = dG_B$ to stay on the line
- $-S_A dT + V_A dP = -S_B dT + V_B dP$

- => $dP/dT = (S_A - S_B)/(V_A - V_B) = \Delta S/\Delta V$
- $dP/dT = \Delta H/(T\,\Delta V) = L/(T\,\Delta V)$
- ΔS = 92.9-88.7 J/K = 4.2 J/K
- ΔV = 36.93-34.15 cm^3 = 2.8 cm^3
- dP/dT = 1.5 MPa/K = 0.015 kb/K = 0.6 kb/ 40 K



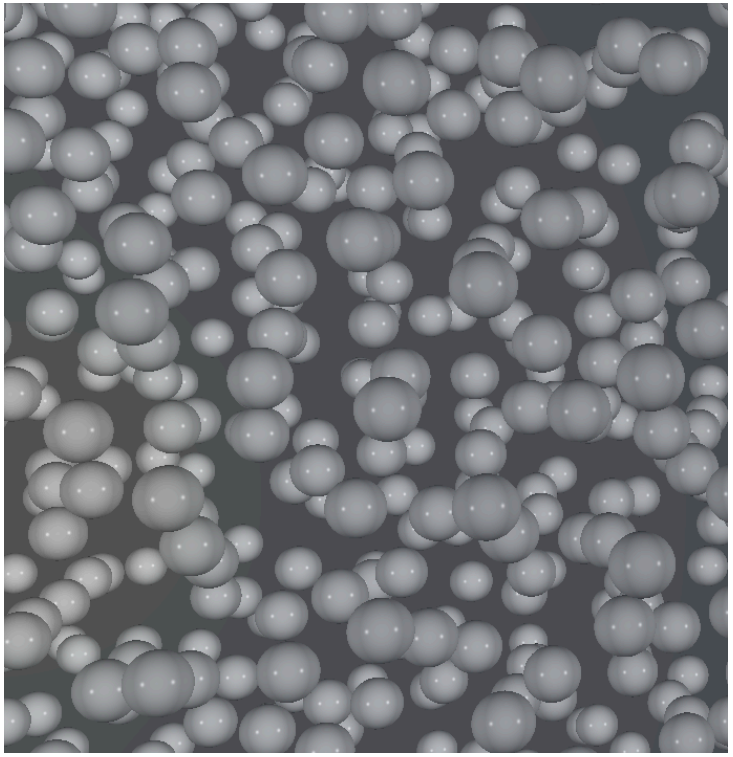
Equations of state

- **Ideal gas**: PV=NkT, $P^*=\rho^*T^*$
- **Virial equation:** $P^*/(\rho^*T^*) = 1 + B\rho^* + C\rho^{*2} + D\rho^{*3} + \ldots$



Equations of state

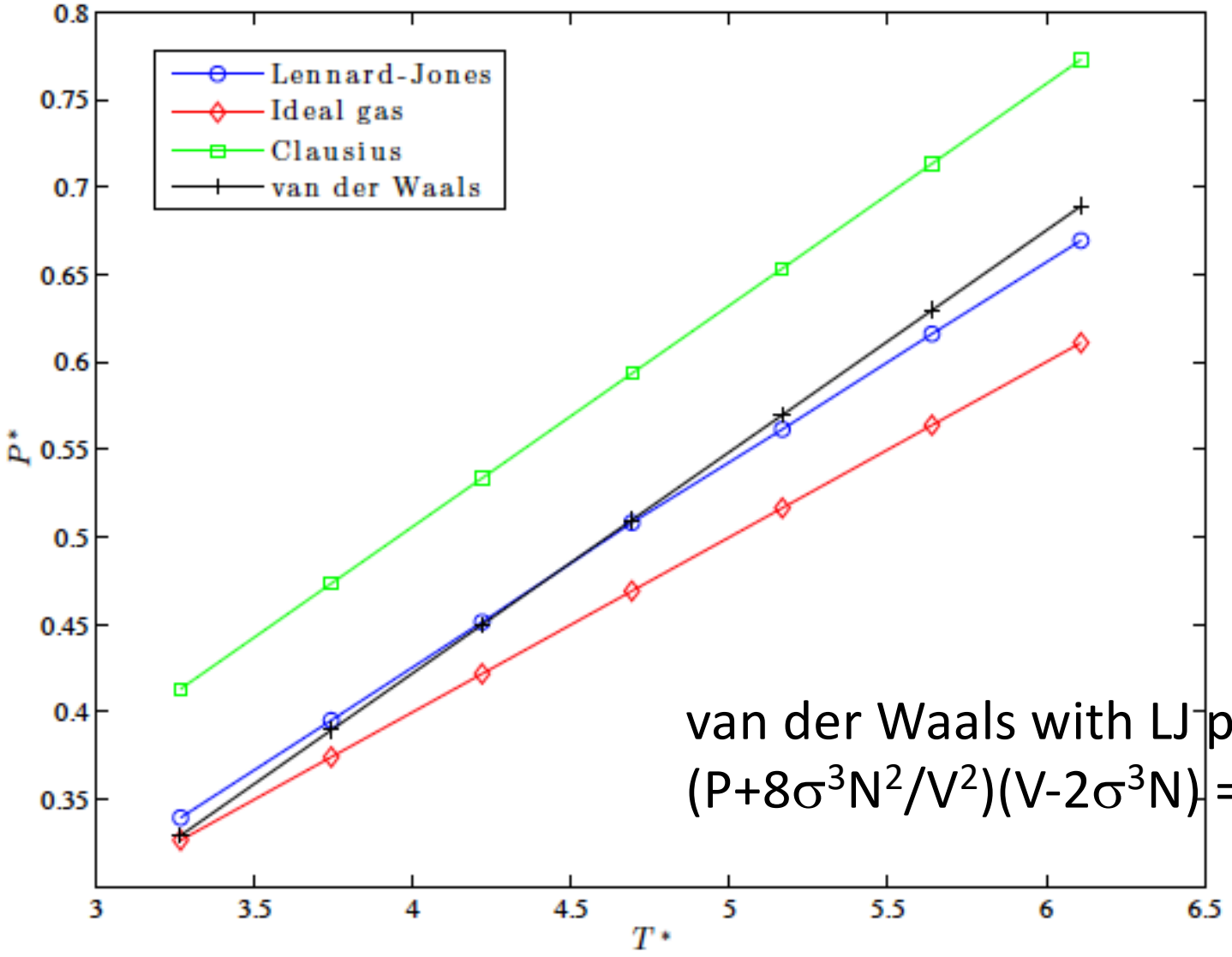
- **Ideal gass**: $PV=NkT, \quad P^*=\rho^*T^*$
- **Virial equation** $P^*/(\rho^*T^*) = 1 + B\rho^* + C\rho^{*2} + D\rho^{*3} + \ldots$
- **Clausius:** $P\,(V-Nb) = NkT$
- Nb: smallest possible volume
- $b \sim (\text{molecular diameter})^3 \sim V_c/(3N) \sim 2\sigma^3$



Equations of state

- **Ideal gass**: $PV=NkT, \quad P^*=\rho^*T^*$
- **Virial equation** $P^*/(\rho^*T^*) = 1 + B\rho^* + C\rho^{*2} + D\rho^{*3} + \ldots$
- **Clausius:** $P\,(V-Nb) = NkT$
- Nb: smallest possible volume
- $b \sim (\text{molecular diameter})^3 \sim V_c/(3N) \sim 2\sigma^3$
- **van der Waals:** $(P+aN^2/V^2)(V-Nb) = NkT$
- aN^2/V^2: Short range attractive forces
  - potential energy of one molecule $U \sim N/V$
  - potential energy til alle molecule $U \sim N^2/V$
  - Pressure $P = dU/dV = -aN^2/V^2$
- $a \sim 3P_cV_c^2 \sim 8\sigma^3$

Equations of state



van der Waals with LJ parameters:

$(P+8\sigma^3N^2/V^2)(V-2\sigma^3N) = NkT$

- $T' = T/T_c$, $P' = P/P_c$, $V' = V/V_c$
- vdW: $(p'+3/V'^2)(V'-1/3) = 8T'/3$

