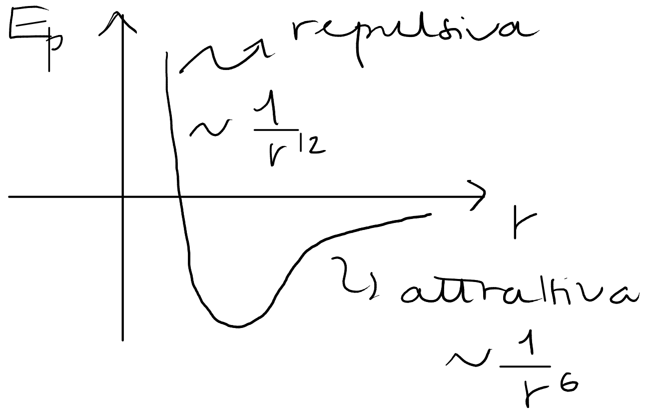
## 2. Equazione di stato di van der Waals

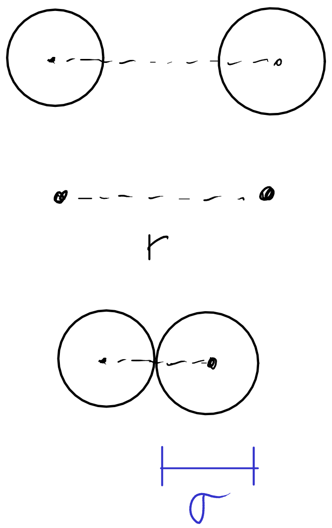
Effetto delle interazioni intermolecolari

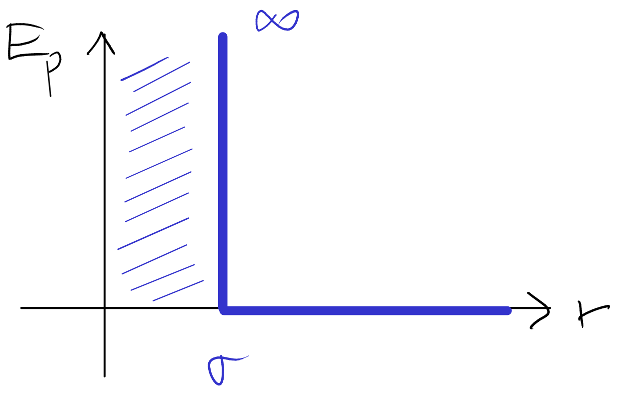
Approccio empirico / fenomenologico




### a. Repulsione intermolecolare

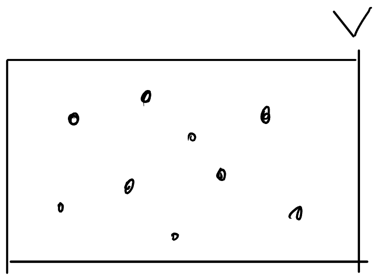
Sfera dura

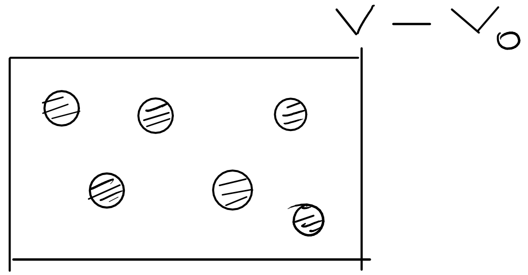



$$E_p(r) = \begin{cases} 0 & r > \sigma \\ \infty & 0 < r \leq \sigma \end{cases}$$

$$PV = nRT \rightarrow P(V - V_0) = nRT$$




$V_0 \sim n$

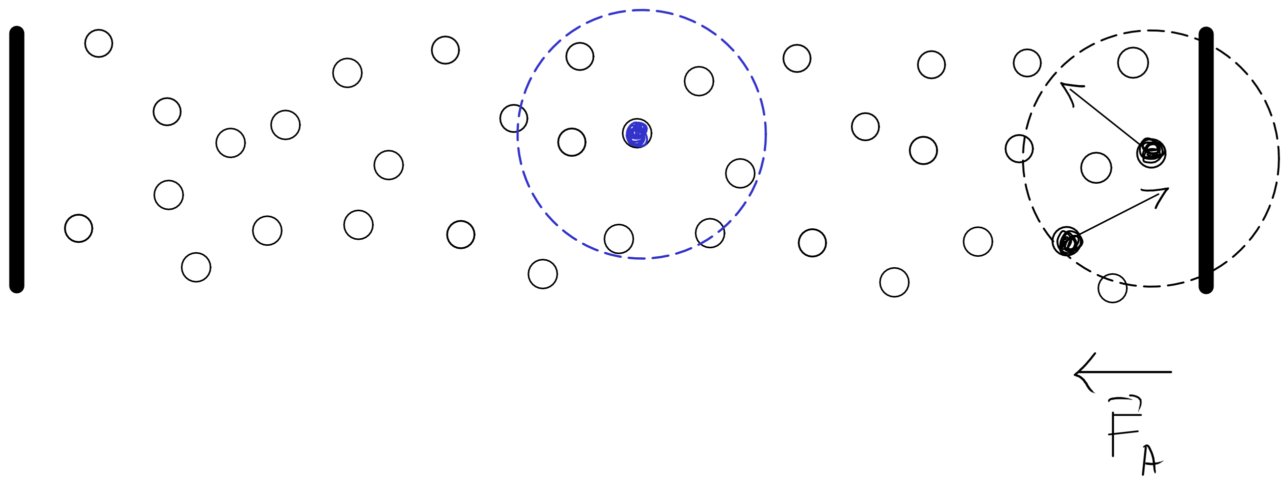
$V_0 = b n$

↑ "covolume"

$$\Rightarrow \quad P(V - nb) = nRT$$

es: traccia questa eq. di stato nel diagramma (P, V)

b. Attrazione intermolecolare a corto raggio




$$P = \frac{nRT}{V-nb} - P_A \qquad (P_A > 0)$$

$$P_A \sim \left(\frac{n}{V}\right)^2 \qquad P_A = a\left(\frac{n}{V}\right)^2$$

$$P = \frac{nRT}{V-nb} - a\left(\frac{n}{V}\right)^2$$

$$P + a\left(\frac{n}{V}\right)^2 = \frac{nRT}{V-nb}$$

$$\left(P + a\frac{n^2}{V^2}\right)(V-nb) = nRT$$

eq. di stato di van der Waals

$\downarrow$ $P$ $\qquad$ $\downarrow$ $V$ $\qquad$ $nRT$

↗ repulsione – "volume escluso"

↘ attrazione

Dimensioni di a, b :

$$[n][b] = [V] \rightarrow [b] = \frac{[V]}{[n]} \qquad SI: \frac{m^3}{mol} \qquad \frac{l}{mol} = x \frac{m^3}{mol} \; ?$$

$$[a]\frac{[n]^2}{[V]^2} = [P] \rightarrow [a] = \frac{[P][V]^2}{[n]^2} \qquad SI: \frac{Pa \cdot m^6}{mol^2} \qquad \frac{bar \cdot l^2}{mol^2} = y \frac{Pa \cdot m^6}{mol^2} \; ?$$

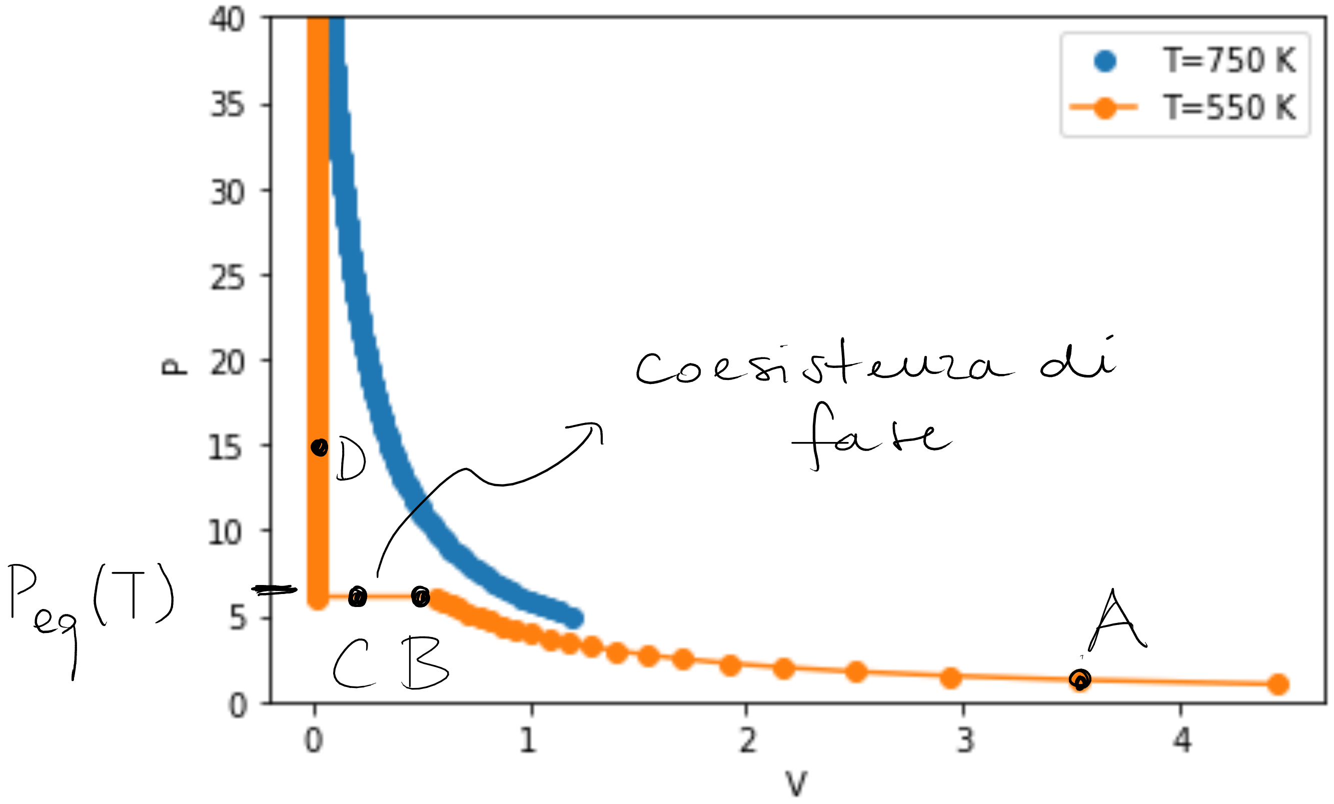
$$1\,l = 1(dm)^3 = (10^{-1} m)^3 = 10^{-3} m^3 \qquad 10^5\, Pa \cdot (10^{-3} m^3)^2 = 10^5 \times 10^{-6} \cdot Pa \cdot m^6 = 10^{-1}\, Pa \cdot m^6$$

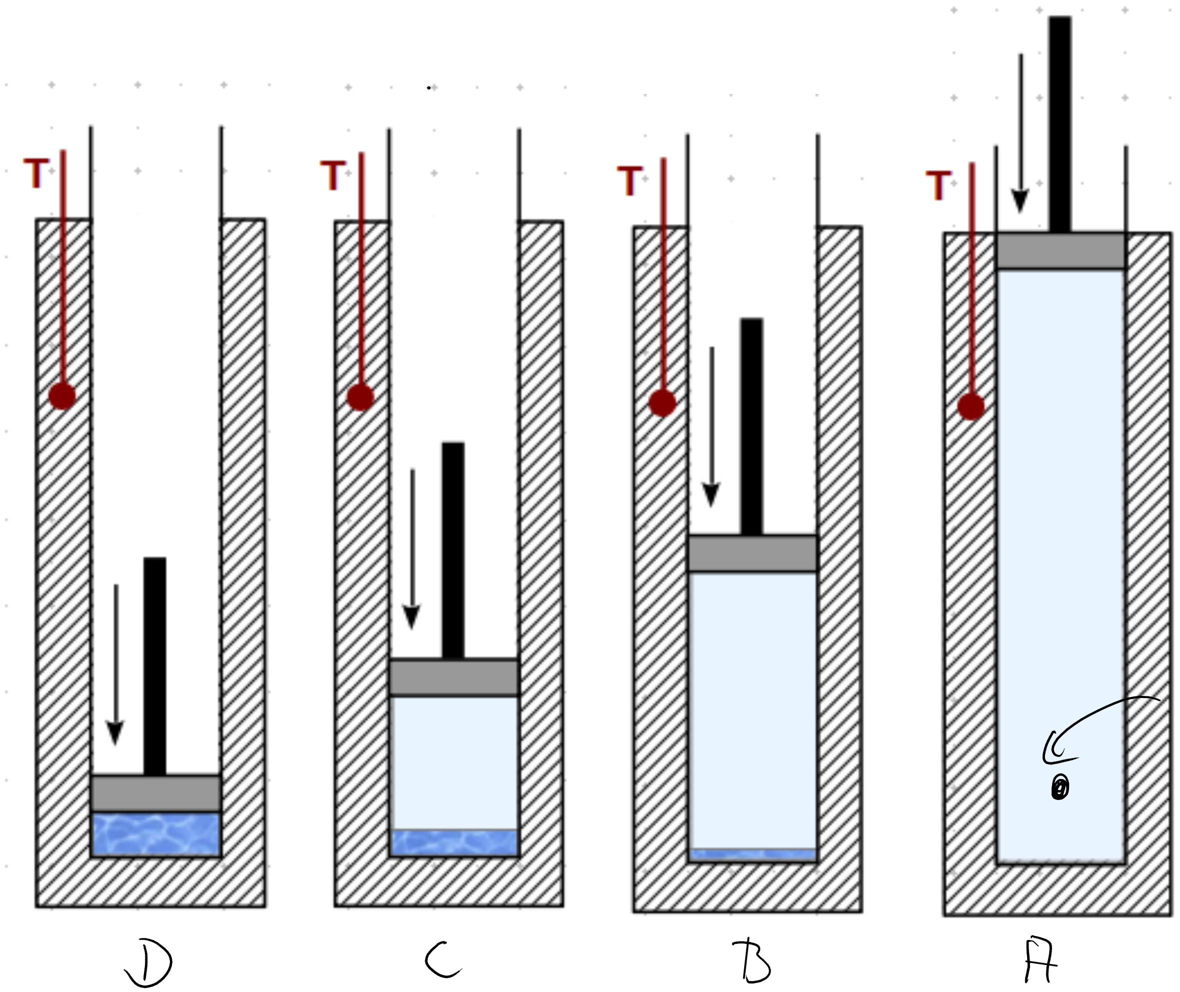
$$x = 10^{-3} \qquad y = 10^{-1}$$

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

# Coesistenza di fase

Fase: stato della materia caratterizzato da proprietà fisiche omogenee

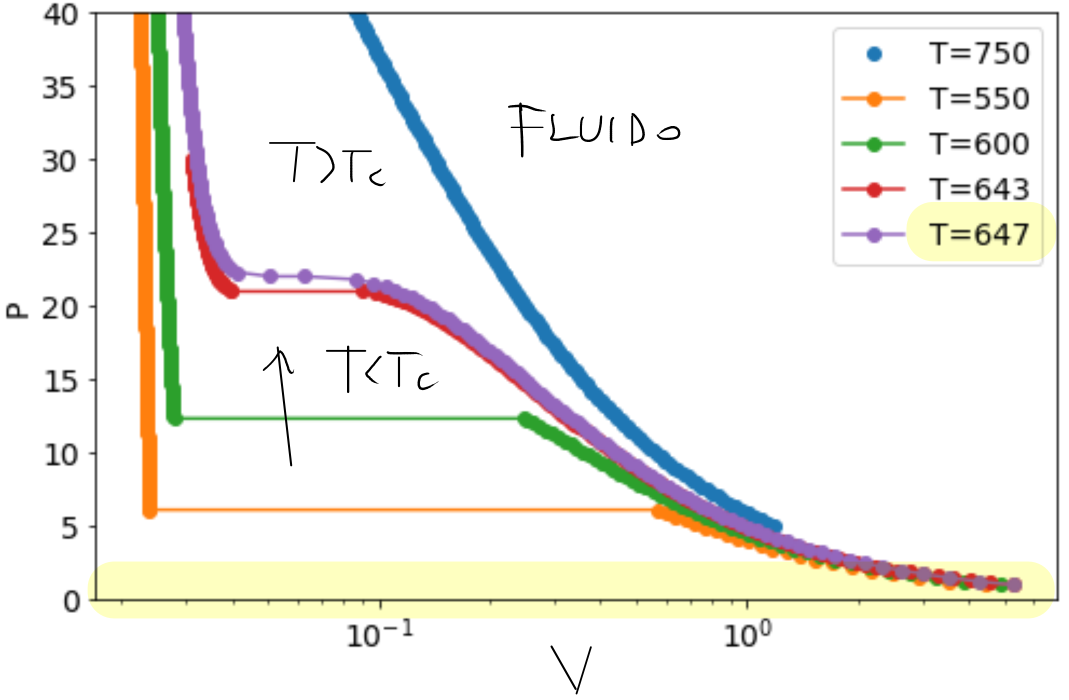


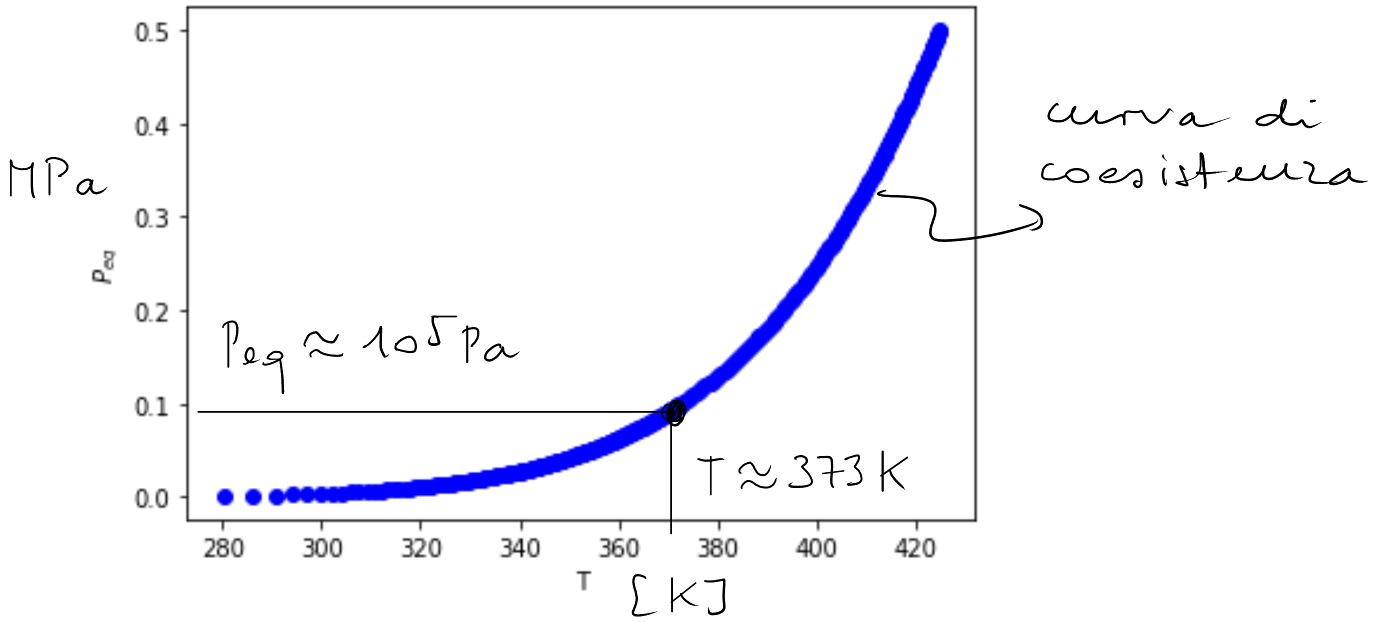



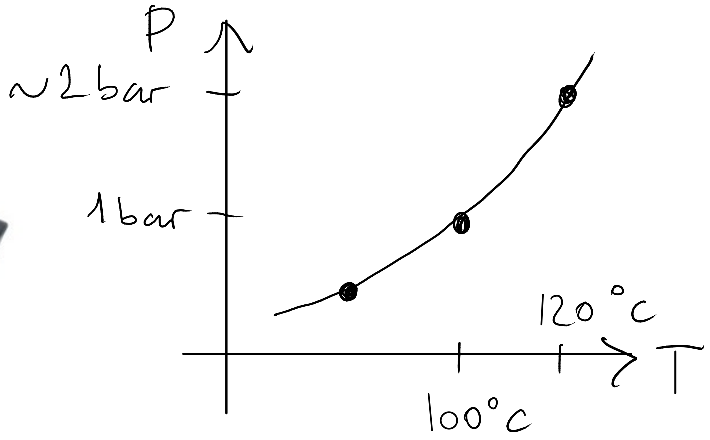

Due fasi in contatto tra loro coesistono se ciascuna rimane in condizioni di equilibrio termodinamico

$P_{eq}$ = pressione di coesistenza

$T_c \approx 647$ K ($H_2O$) temperatura critica



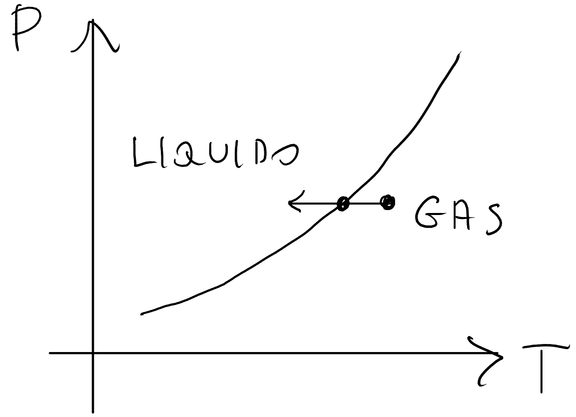
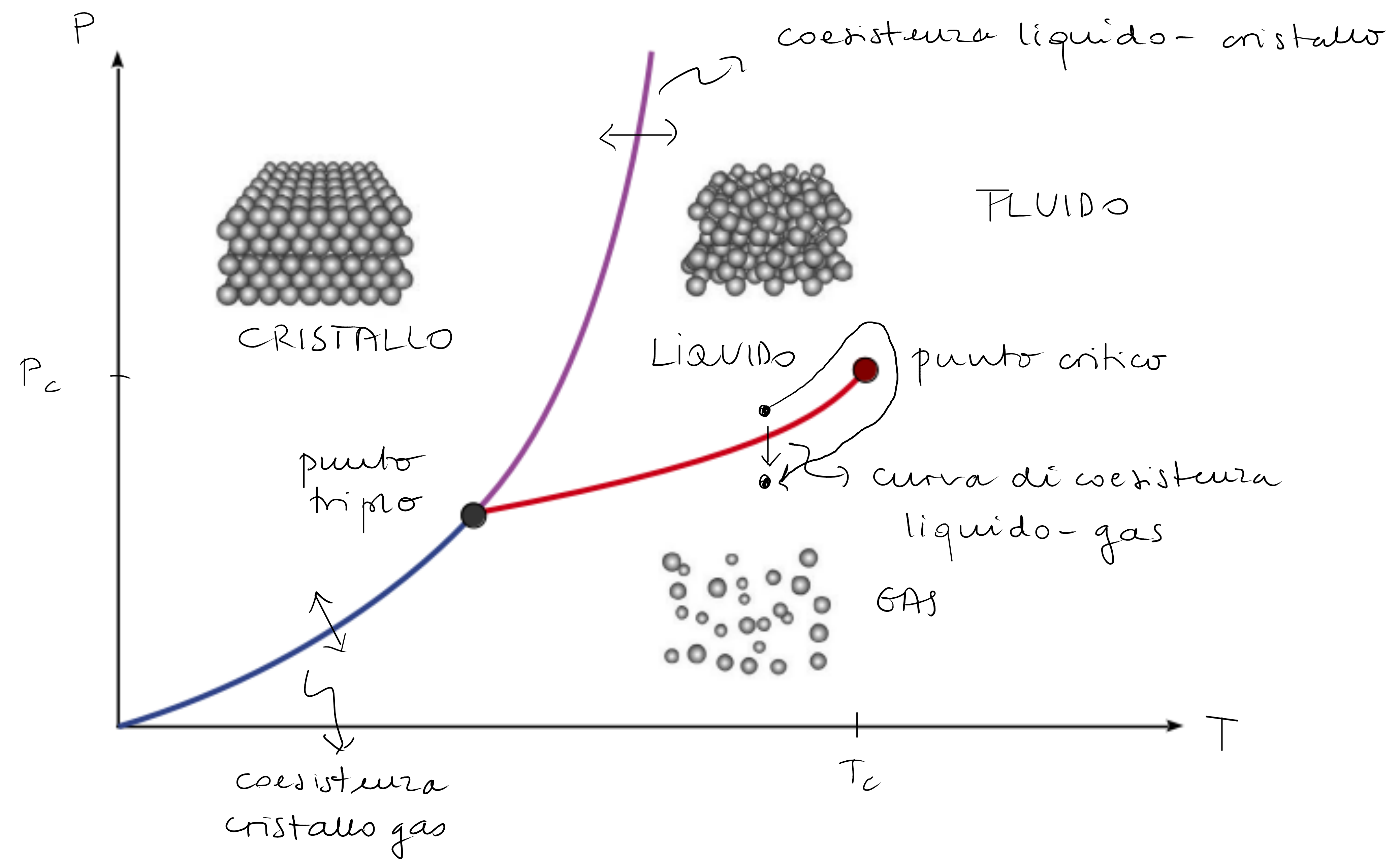



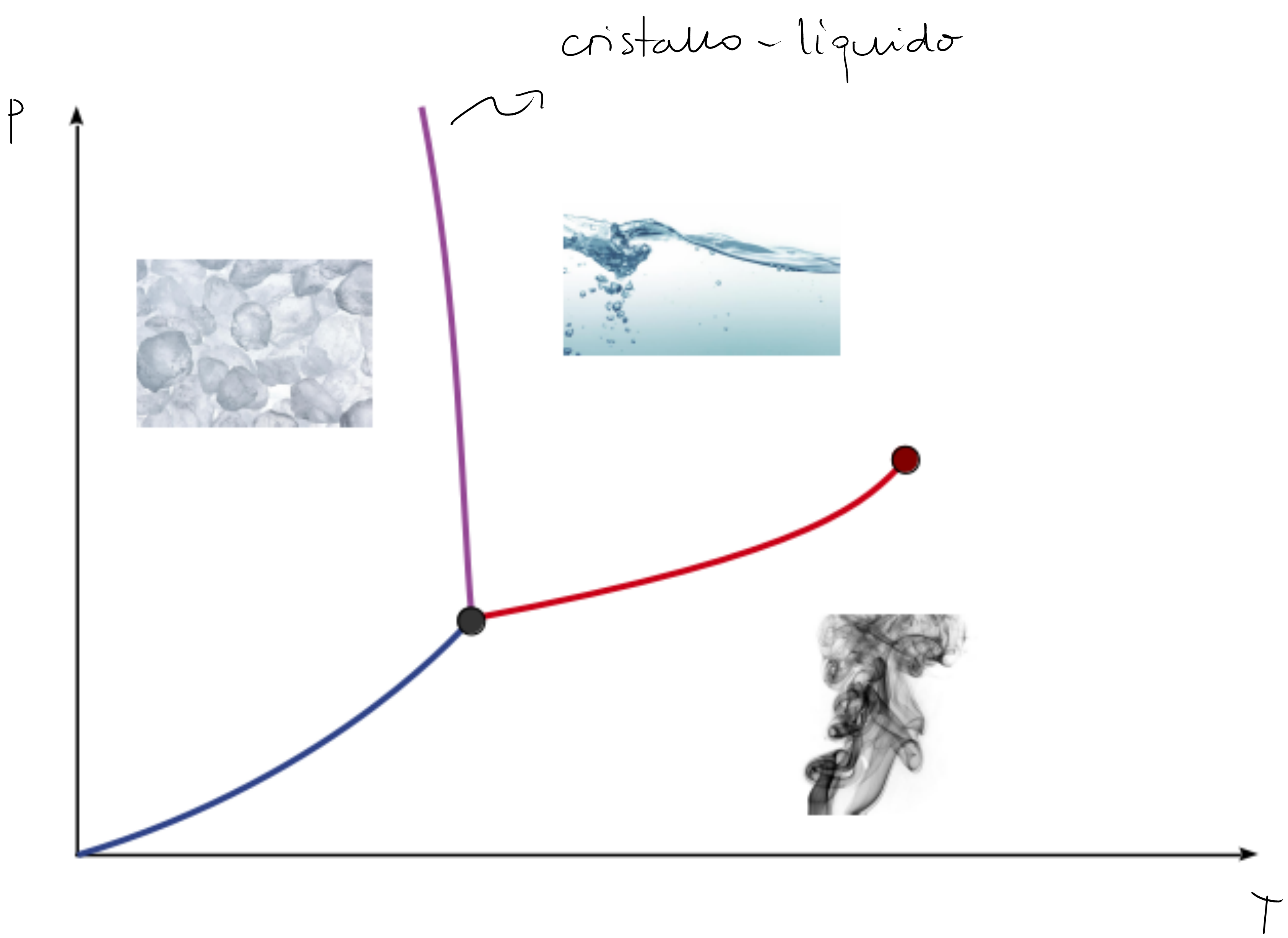
Diagramma di fase di materiali "normali"

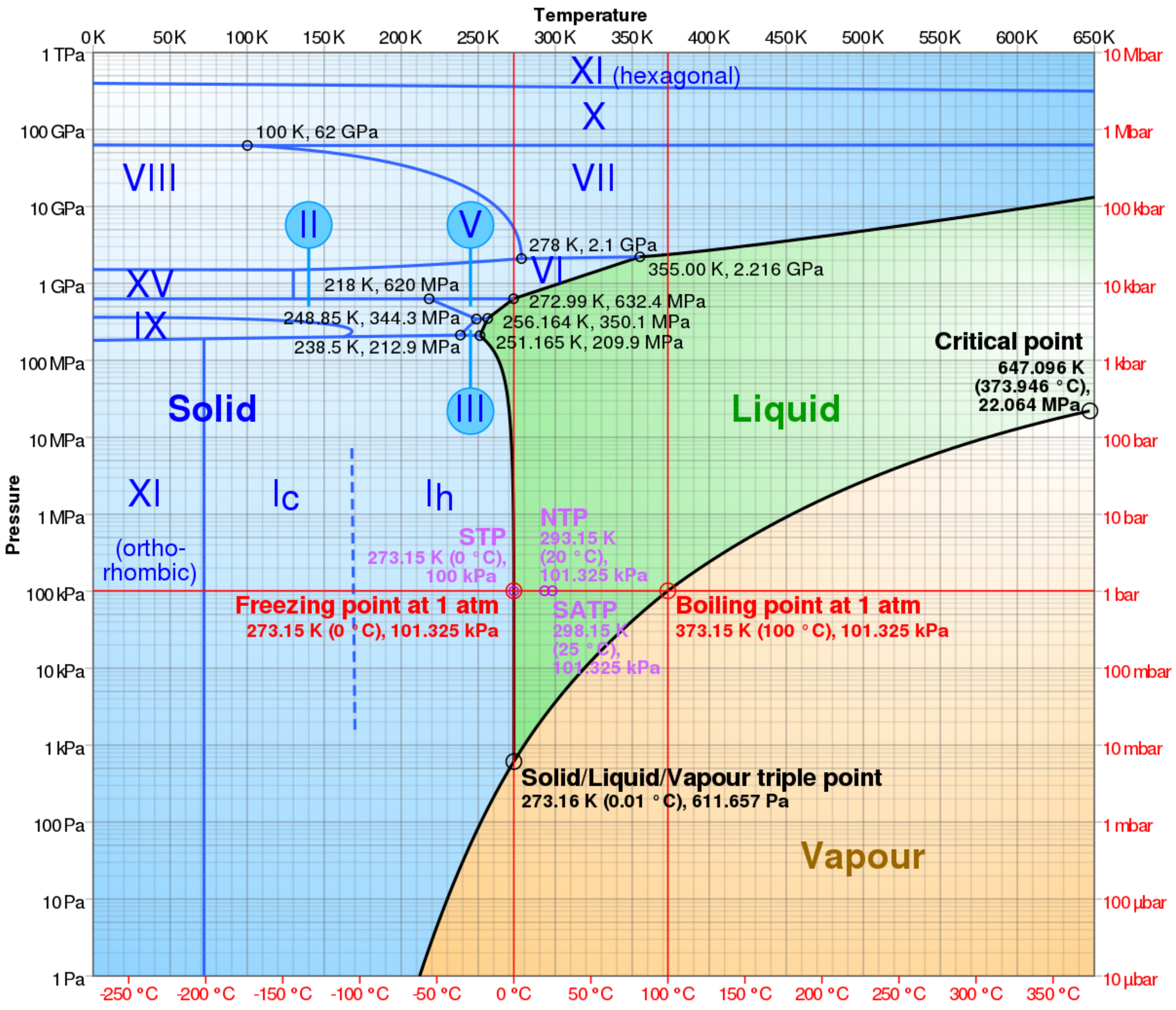


# Diagramma di fase dell'acqua

→ anomalie dell' $H_2O$

$\rho_{crist} < \rho_{liq}$





Temperature
0 K
50 K
100 K
150 K
200 K
250 K
300 K
350 K
400 K
450 K
500 K
550 K
600 K
650 K
Pressure
1 TPa
100 GPa
10 GPa
1 GPa
100 MPa
10 MPa
1 MPa
100 kPa
10 kPa
1 kPa
100 Pa
10 Pa
1 Pa
10 Mbar
1 Mbar
100 kbar
10 kbar
1 kbar
100 bar
10 bar
1 bar
100 mbar
10 mbar
1 mbar
100 µbar
10 µbar
-250 °C
-200 °C
-150 °C
-100 °C
-50 °C
0 °C
50 °C
100 °C
150 °C
200 °C
250 °C
300 °C
350 °C
XI (hexagonal)
X
VII
VIII
100 K, 62 GPa
II
V
278 K, 2.1 GPa
355.00 K, 2.216 GPa
XV
VI
218 K, 620 MPa
272.99 K, 632.4 MPa
IX
248.85 K, 344.3 MPa
256.164 K, 350.1 MPa
238.5 K, 212.9 MPa
251.165 K, 209.9 MPa
Critical point
647.096 K
(373.946 °C),
22.064 MPa
Solid
III
Liquid
XI
(ortho-
rhombic)
Ic
Ih
STP
273.15 K (0 °C),
100 kPa
NTP
293.15 K
(20 °C),
101.325 kPa
Freezing point at 1 atm
273.15 K (0 °C), 101.325 kPa
SATP
298.15 K
(25 °C),
101.325 kPa
Boiling point at 1 atm
373.15 K (100 °C), 101.325 kPa
Solid/Liquid/Vapour triple point
273.16 K (0.01 °C), 611.657 Pa
Vapour