

Limiti di validità

$$PV = nRT$$

$$p = \frac{nRT}{V}$$

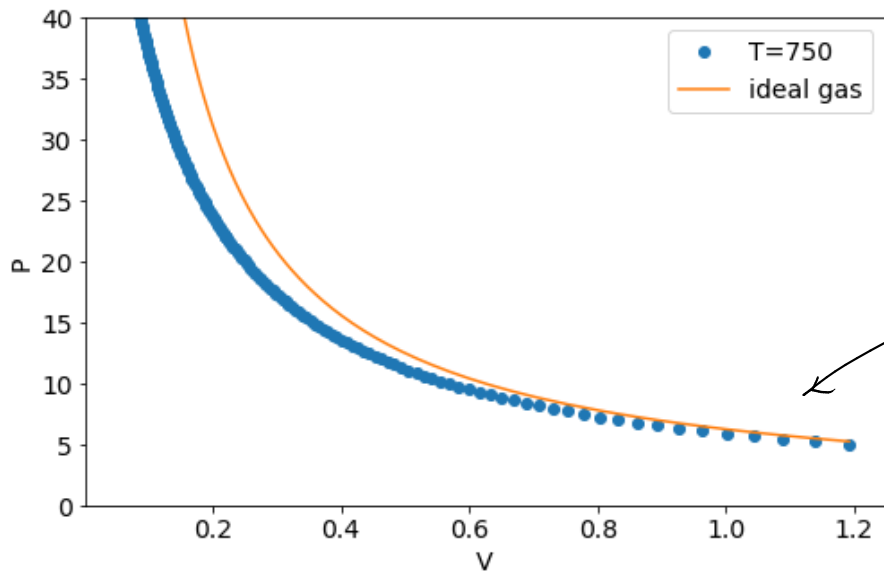
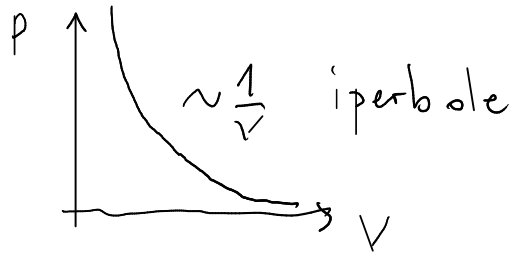
→ cost se $T = \text{cost}$; eq. stato $f(P, T, \rho) = 0$

$$f(P, T, N, V) = 0$$

$$1\text{l} = 1\text{dm}^3 = (10^{-1}\text{m})^3 = 10^{-3}\text{m}^3$$

$$\frac{PV}{nRT} - 1 = 0$$

$$\uparrow$$
$$n = N/N_A$$



Scala log-log : $P \sim V^{-1}$

$$\log P \sim \log V^{-1} = -\log V$$

regime diluito :
buon accordo

pendenza -1

Non ci sono parametri liberi!

2. Equazione di stato di van der Waals

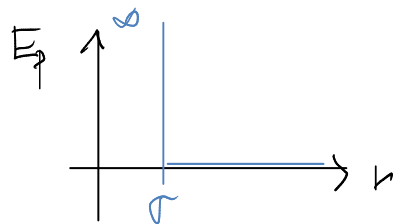
↗ modello micro → fisica statistica

↘ fenomenologia \square

$$PV = nRT$$

a. repulsione a corto raggio tra molecole

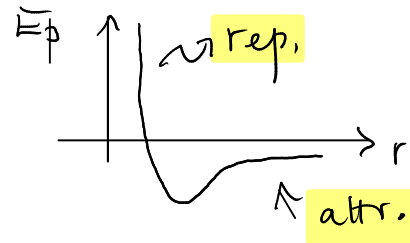
\sim sfere dure di diametro σ



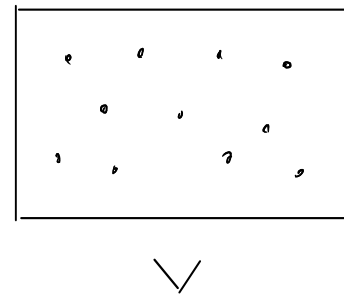
$$E_p(r) = \begin{cases} \infty & r \leq \sigma \\ 0 & r > \sigma \end{cases}$$

volume accessibile

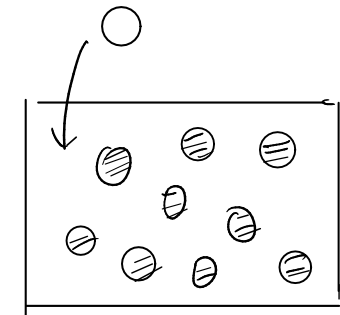
Descrivo meglio interazione tra molecole:



es. Lennard-Jones



→



→

$$V - V_0$$

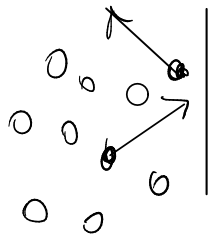
↑

volume occupato dalle molecole

$V_0 \equiv nb \leftarrow$ volume proprio o covolume

$$\rightarrow P(V - nb) = nRT$$

b. attrazione tra molecole



$$P = \frac{nRT}{V-nb} - P_A$$



\Rightarrow riduce la pressione sulle pareti

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

\rightarrow eq. di stato vdW

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

a \rightarrow SI: $\text{Pa} \cdot \text{m}^6 / \text{mol}$

$$[a] \frac{[n]^2}{[V]^2} = [P]$$

b \rightarrow SI: $\frac{\text{m}^3}{\text{mol}}$

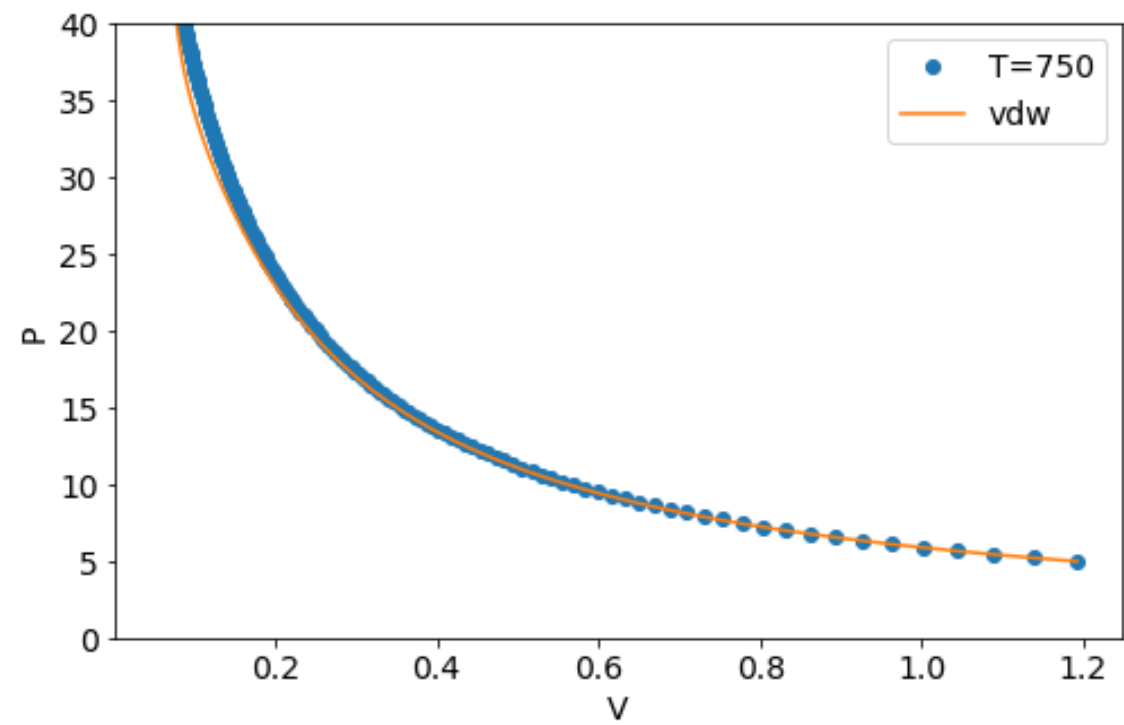
$$[a] = [P] \frac{[V]^2}{[n]^2}$$

\uparrow attrazione \uparrow repulsione

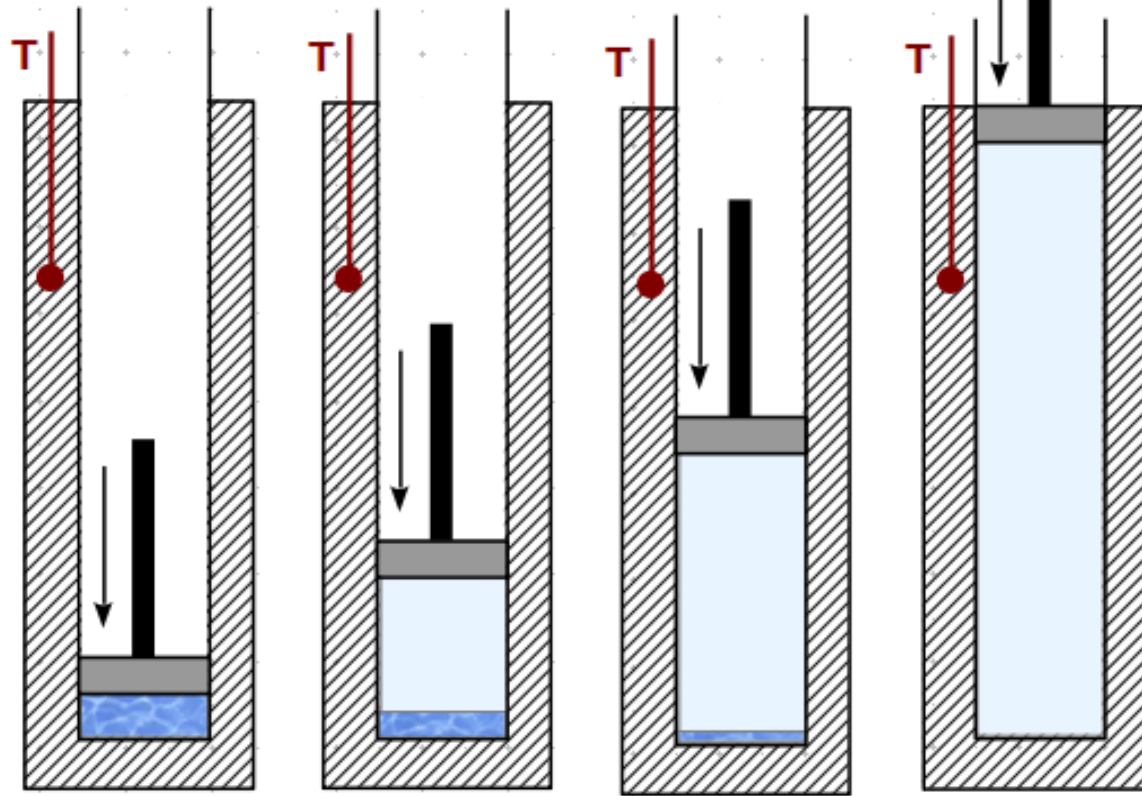
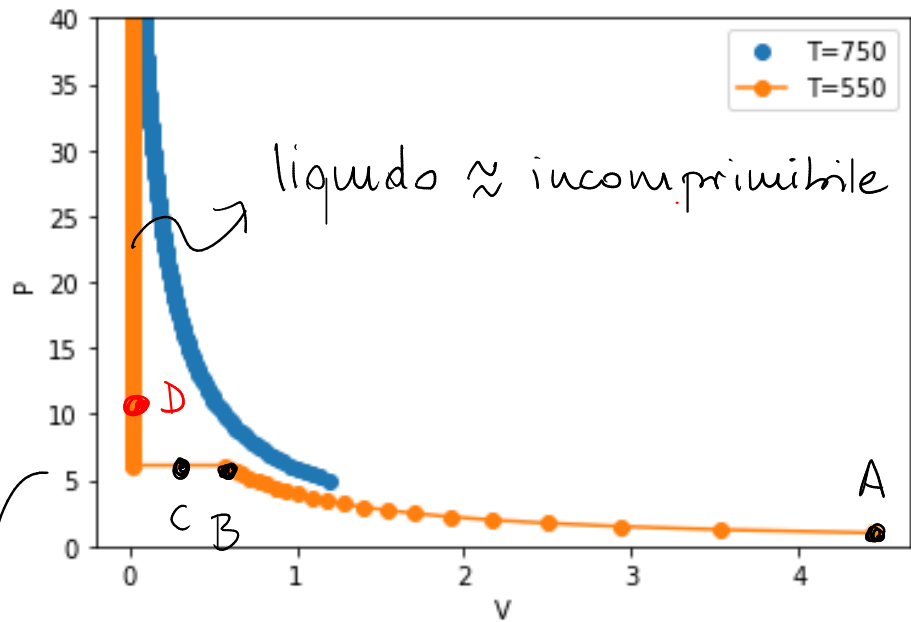
Fattori di conversione:

$$\left\{ \frac{\text{l}^2 \text{ bar}}{\text{mol}^2} = \frac{(10^{-3} \text{ m}^3)^2 \cdot 10^5 \text{ Pa}}{\text{mol}^2} = \frac{10^{-6} \text{ m}^6 \cdot 10^5 \text{ Pa}}{\text{mol}^2} = 10^{-1} \frac{\text{Pa m}^6}{\text{mol}^2} \right.$$

$$\left\{ \frac{\text{l}}{\text{mol}} = 10^{-3} \frac{\text{m}^3}{\text{mol}} \right.$$



Coesistenza di fase



D

C

B

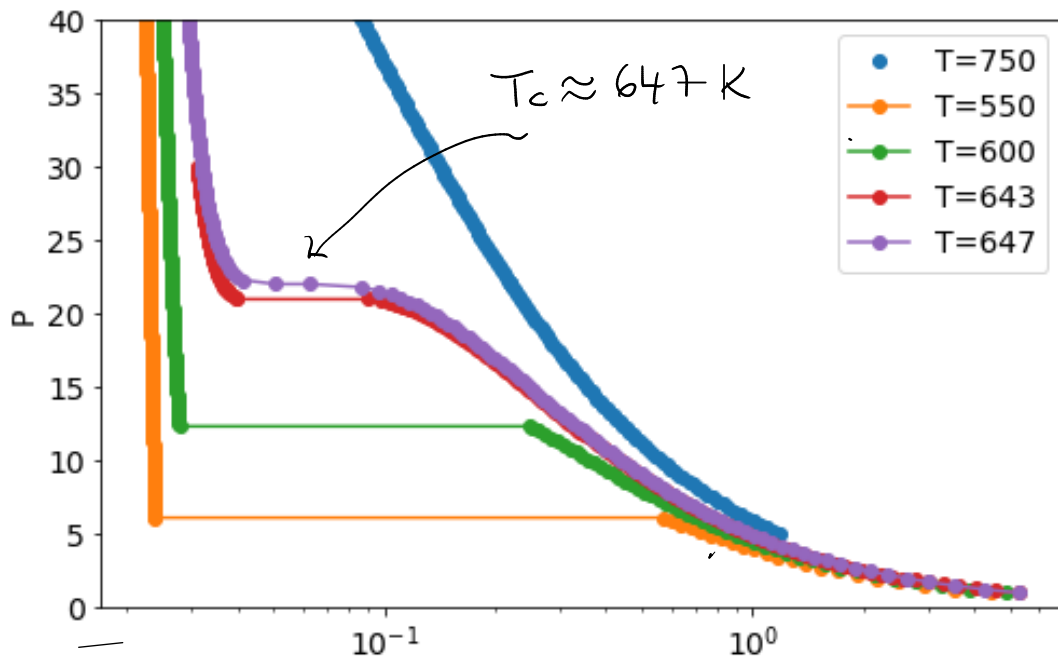
A

~~~~~  
 coesistenza

coesistenza di fase

pressione di coesistenza

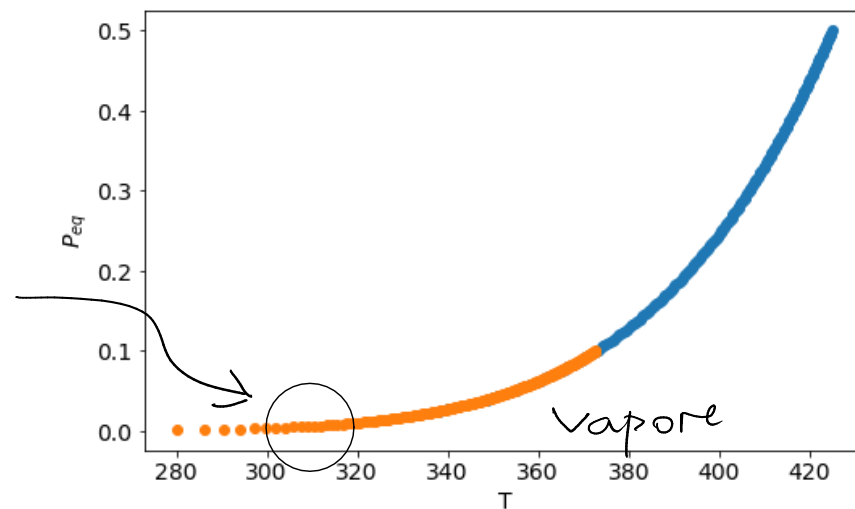
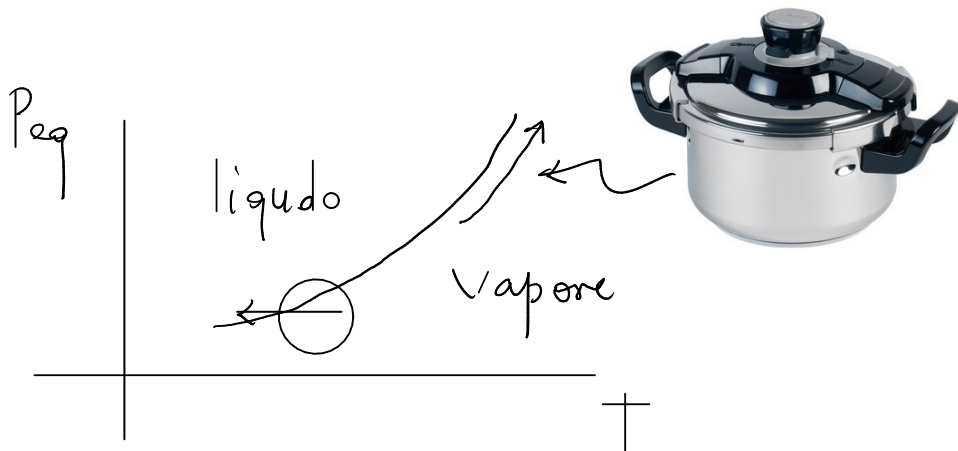
$P_{eq}(T) \equiv$  pressione alla quale le  
 2 fasi "coesistono" a  $T$



$T_c \equiv$  temperatura critica  
 $T < T_c \Rightarrow$  transizione di fase

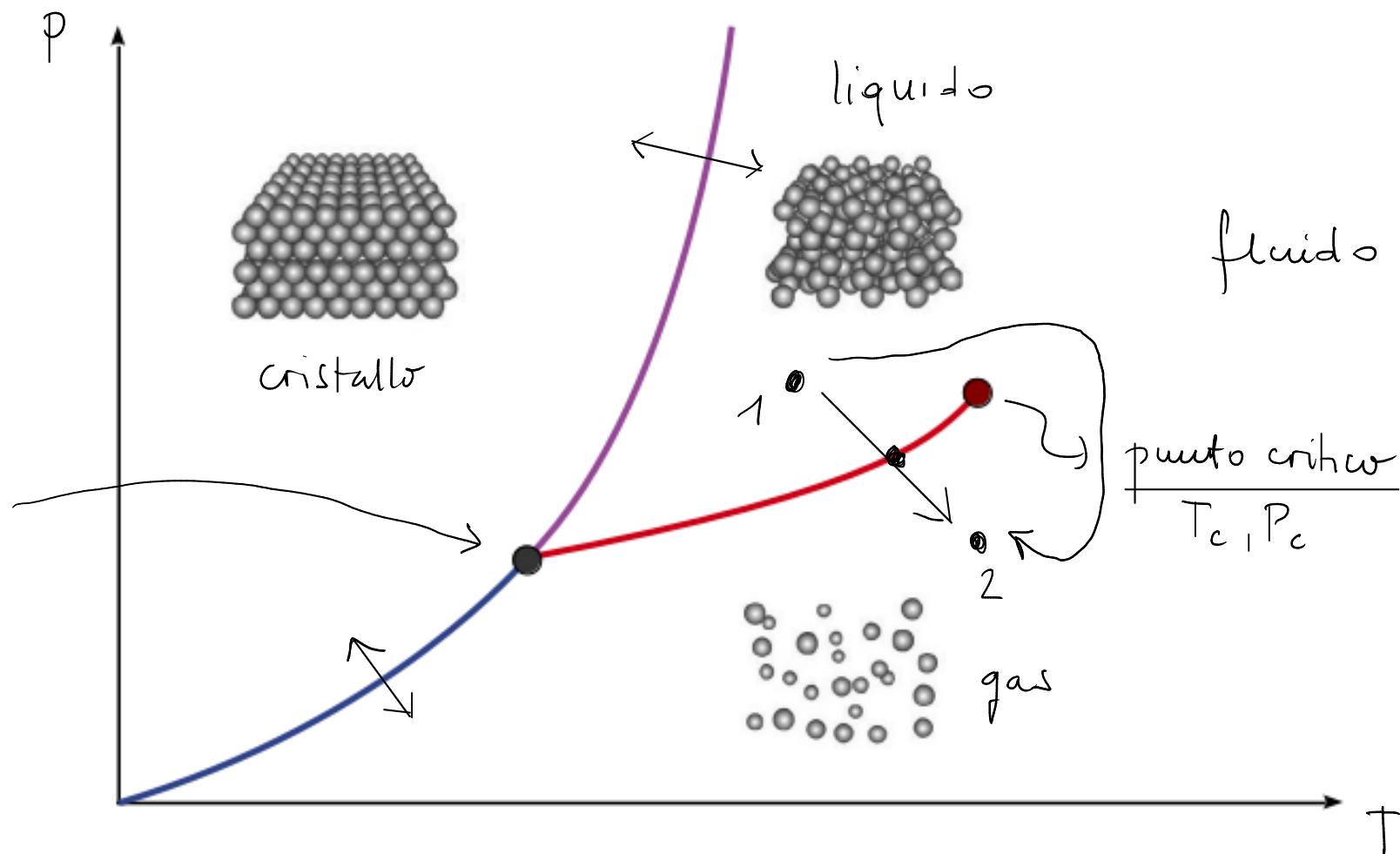
$P_{eq}(T) = ?$

$P_{eq}$  è una funzione  
 crescente di  $T$



# Diagramma di fase di materiali "normali"

punto triplo:  
coesistenza  
delle 3 fasi



# Diagramma di fase dell' $H_2O$

$\rho_{\text{crist}} < \rho_{\text{liquido}}$

