INTRODUZIONE

Sistema disordinato : assenza di ordine a lungo raggio

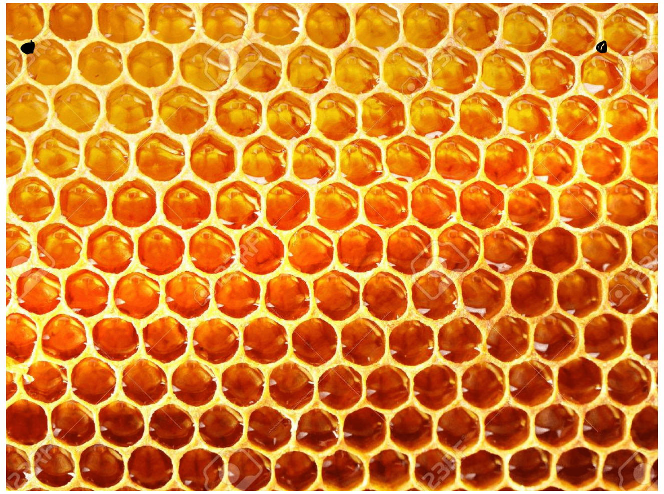
1) Sistemi di particelle

$$H = K(\{\vec{v}_i\}) + U(\{\vec{r}_i\})$$ ← dofs posizionali

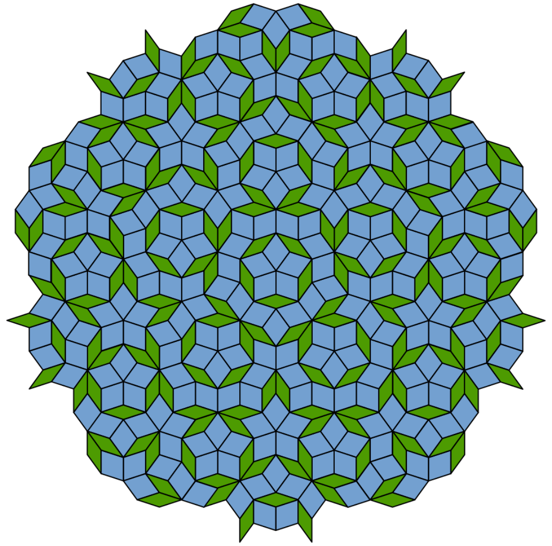
↗ ordine periodico

↘ ordine quasi-cristallo ('80)

cristallino → spettro diffrazione discreto



honeycomb 2d



tassellazione di Penrose

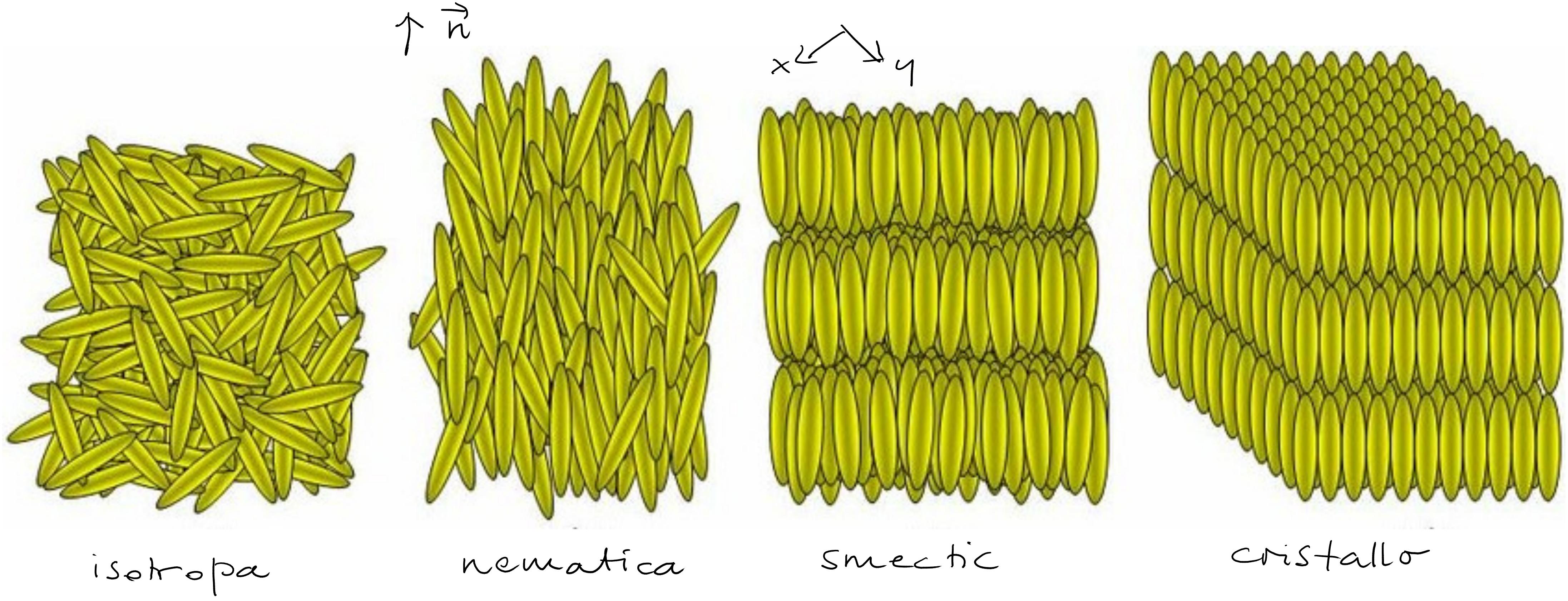
2) Sistemi di spin su reticolo (es. magnetismo)

$$H = H(\{\vec{\sigma}_i\})$$ ← dofs orientazionali

$\uparrow \uparrow \; \cdots\cdots \; \uparrow \uparrow \; \cdots\cdots$

3) Ibridi $\{\vec{r}_i\} + \{\vec{\sigma}_i\}$

- cristalli liquidi
- particelle in 2d



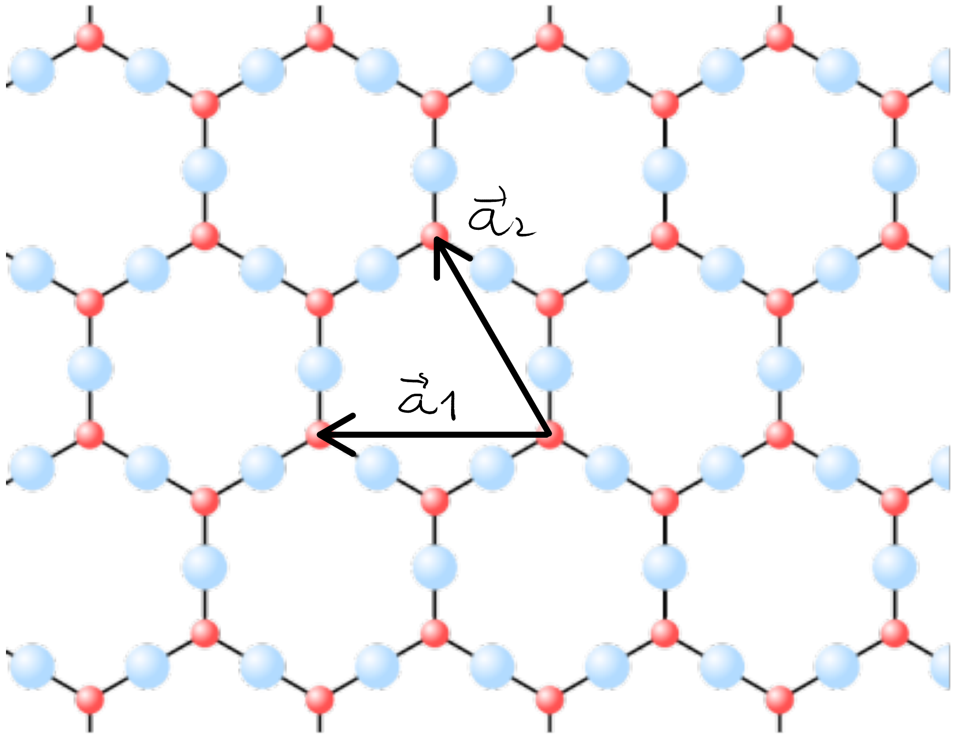
Copyright Pekka Tallavaara

SIMMETRIE E FASI DELLA MATERIA

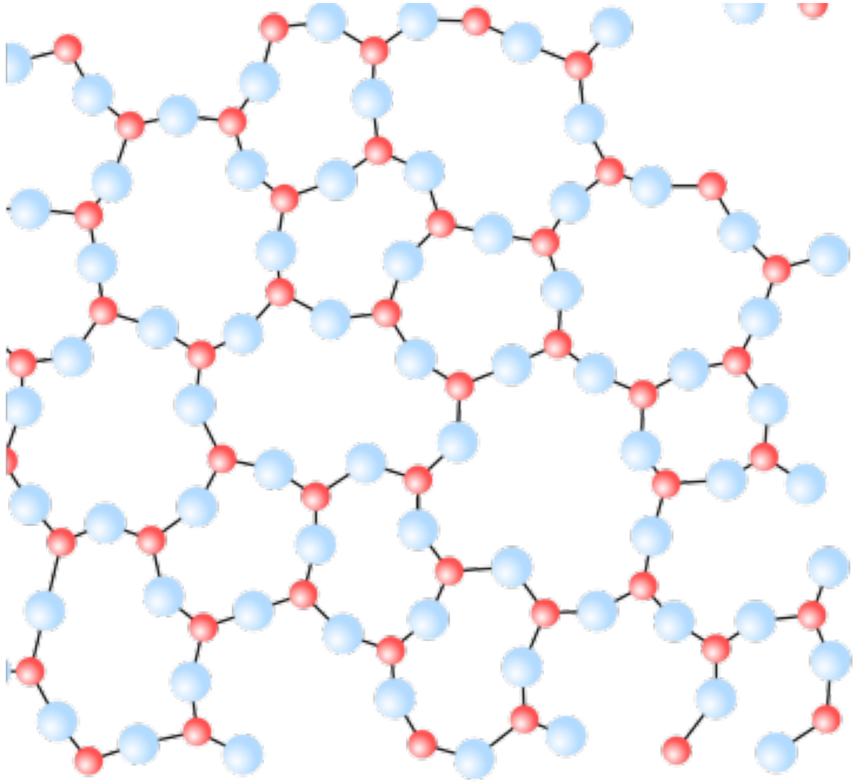
1) Configurazione (sistema di particelle)

Simmetria per traslazione discreta

$$T: \vec{r} \longrightarrow \vec{r} + l_1 \vec{a}_1 + l_2 \vec{a}_2 \qquad l_1, l_2 \in \mathbb{Z}$$



reticolo periodico



amorfo

2) Funzioni $F(\{\vec{r}_i\})$

simmetrica rispetto a $\mathcal{T}$ se $F(\{\vec{r}_i\}) = F(\mathcal{T}(\{\vec{r}_i\}))$

Hamiltoniana possiede simmetria $\mathcal{T}$ se $H(\{\vec{r}_i\}) = H(\mathcal{T}(\{\vec{r}_i\}))$

Es: modello possiede simmetria per traslazione continua

$$\mathcal{T}: \vec{r} \to \vec{r} + \vec{R} \qquad \vec{R} \in \mathbb{R}^3 \qquad \forall\, \vec{r}_i$$

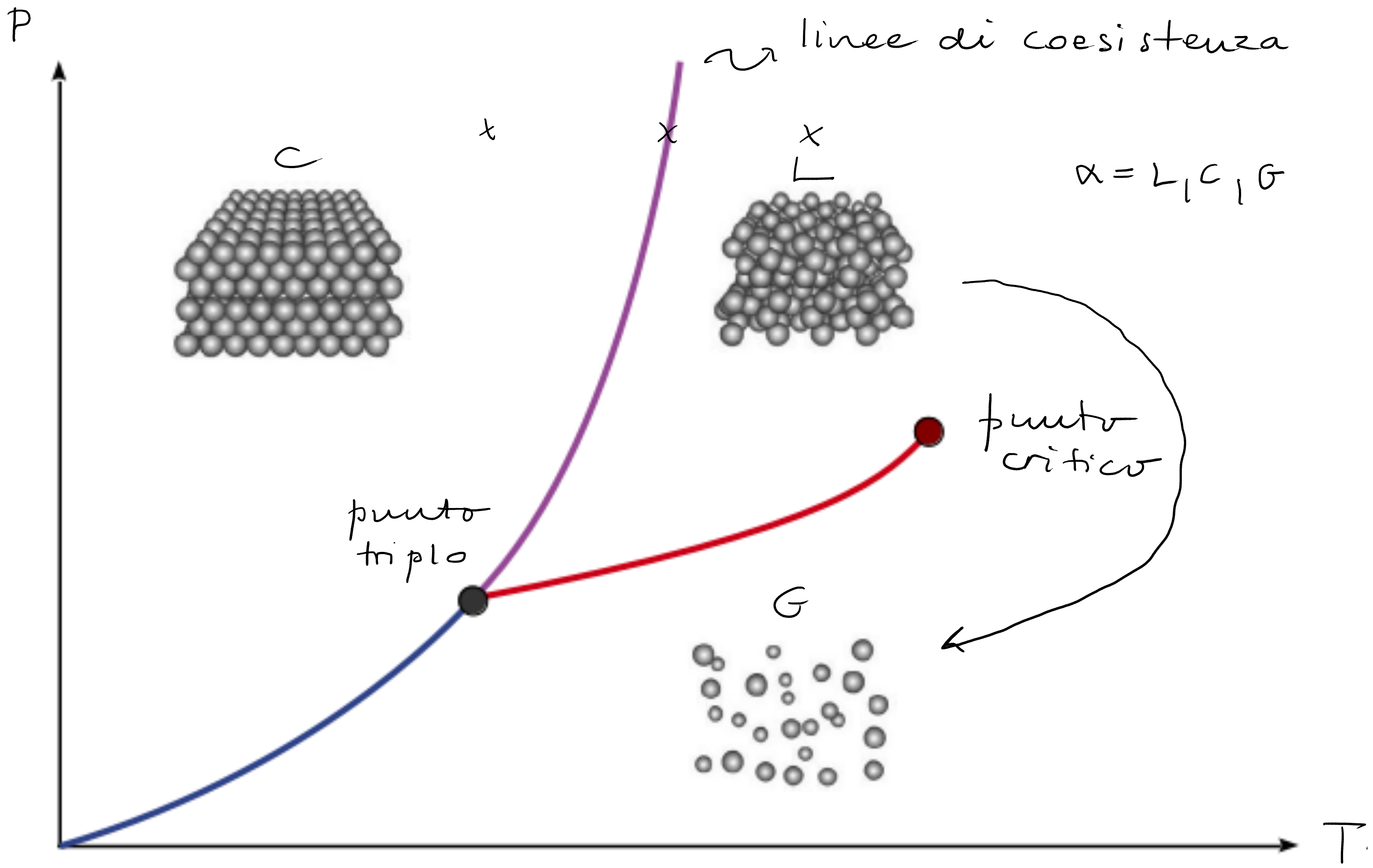
$$H(\mathcal{T}(\{\vec{r}_i\})) = H(\{\vec{r}_i\})$$

Simmetrie globali

3) Fase (stato)

Sottoinsieme di microstati compatibili con i vincoli esterni (es, V, N, T)
proprietà macro omogenee

Diagramma di fase : gas rari (Ar, Ne, Kr, ...)



Media termica : $F(\vec{r})$

$$\langle F(\vec{r}) \rangle_\alpha = \frac{\mathrm{Tr}_\alpha\left[e^{-\beta H} \hat{F}(\vec{r}) \right]}{\mathrm{Tr}_\alpha\left[e^{-\beta H} \right]}$$

Es.: densità locale

$$\langle \rho(\vec{r}) \rangle_\alpha \rightarrow \hat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)$$

↑ densità microscopica

$$H = K + U(\{\vec{r}_i\}) = K + \sum_{i=1}^{N} \sum_{j>i} u(\vec{r}_i - \vec{r}_j)$$ → invariante per traslazione continua

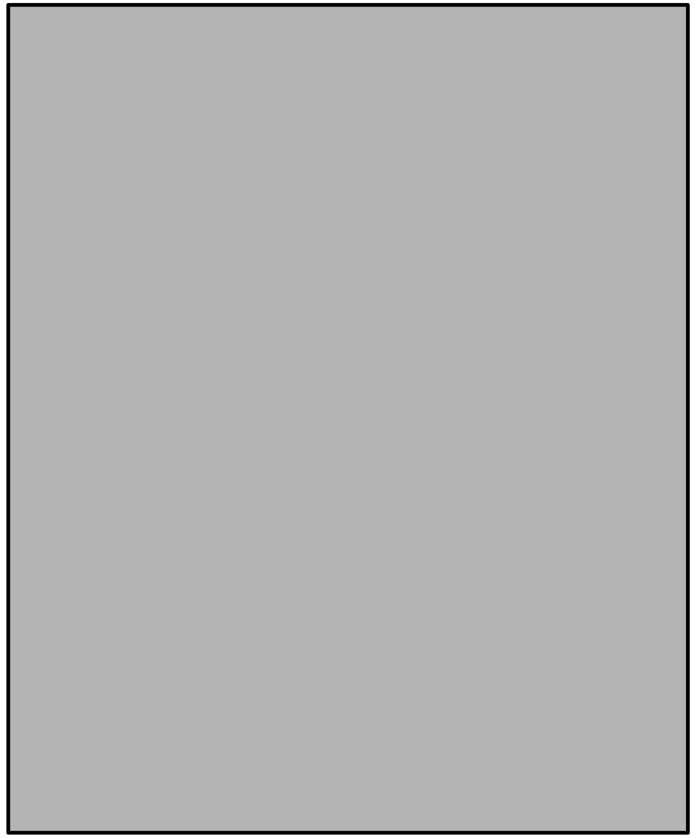
Densità locale $\langle \rho(\vec{r}) \rangle_\alpha$

$T : \vec{r} \to \vec{r} + \vec{R}$ traslazione continua

$T_\ell : \vec{r} \to \vec{r} + \vec{R}_\ell$ traslazione discreta

$\langle \rho(T(\vec{r})) \rangle_\alpha = \langle \rho(\vec{r}) \rangle_\alpha$

$\langle \rho(T_\ell(\vec{r})) \rangle_\alpha = \langle \rho(\vec{r}) \rangle_\alpha$



LIQUIDO

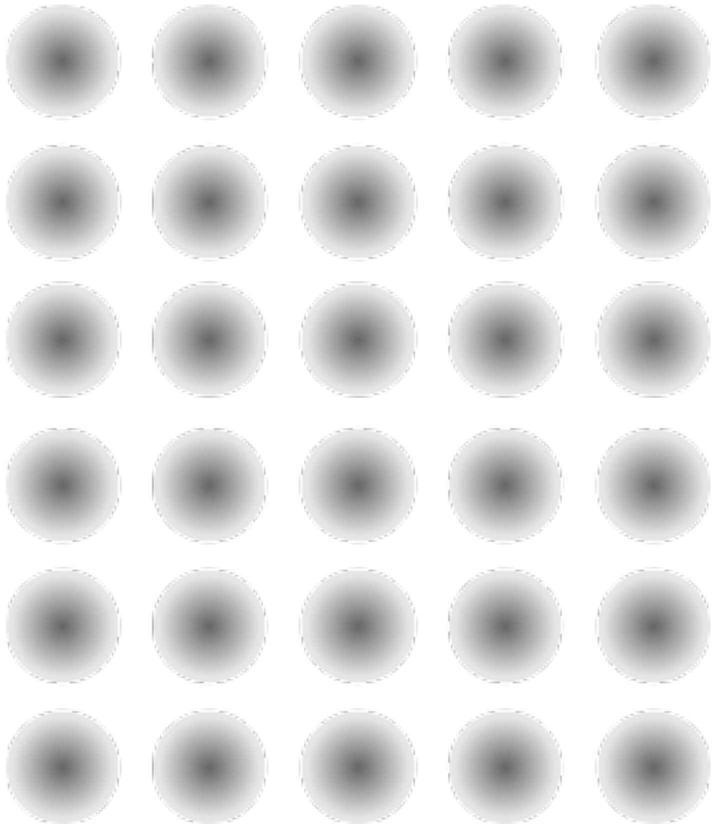
GAS

$\longrightarrow$

rottura spontanea di simmetria

$\Downarrow$

ORDINE A LUNGO RAGGIO

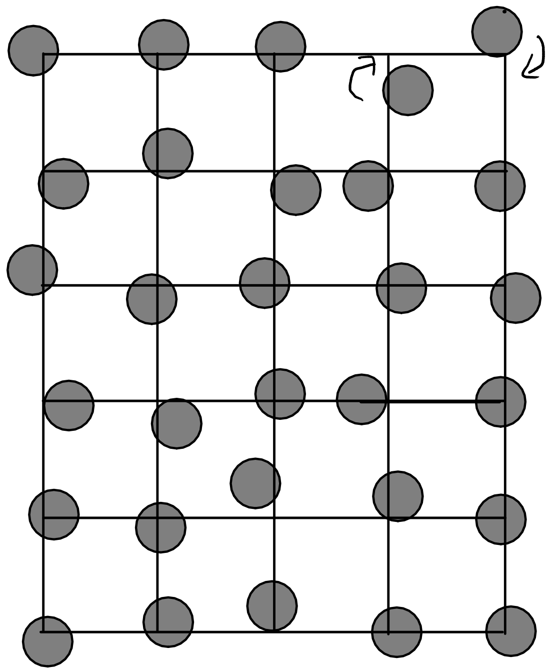


CRISTALLO

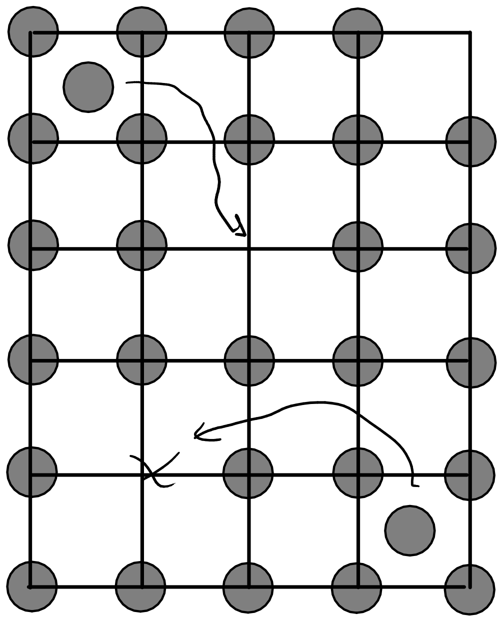
TIPOLOGIE DI DISORDINE

Casuale / aleatorio : n. defs $\gg 1$, effetti termici → entropia ⚠

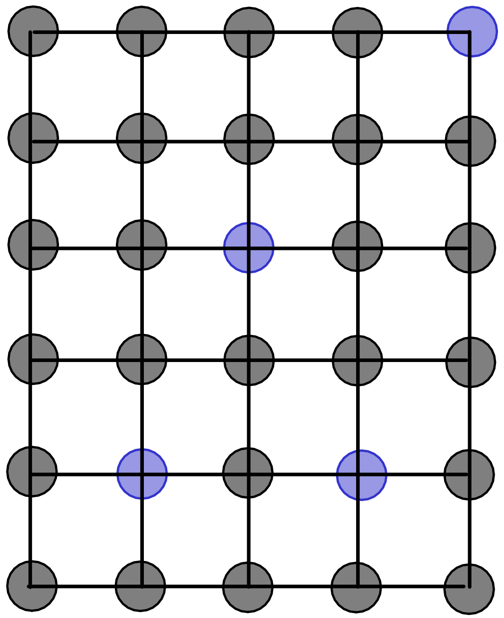
Disordine sostituzionale



vibrazioni

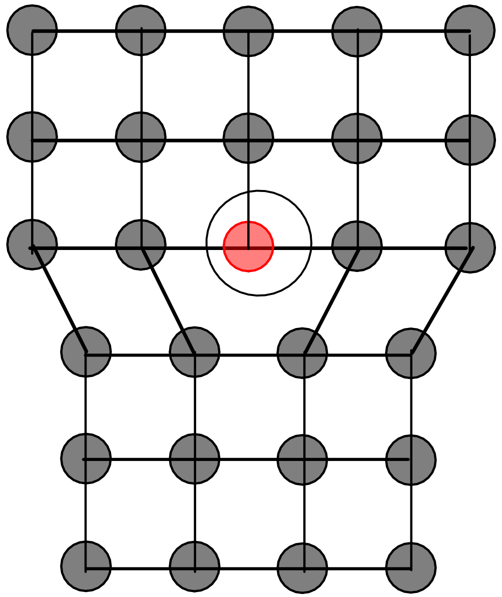


difetti
vacanze
interstiziali

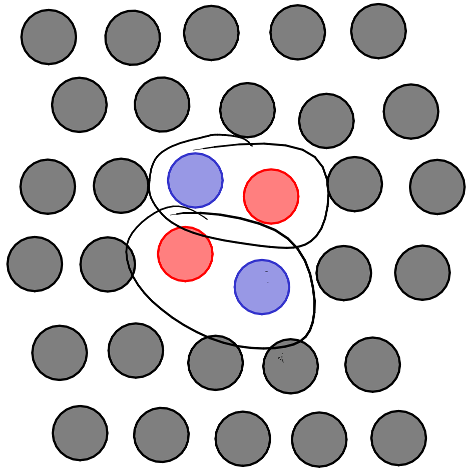


leghe metalliche

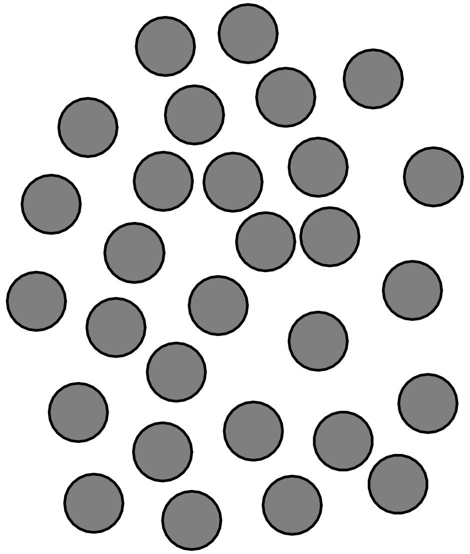
Disordine topologico



dislocazione



coppia di dislocazioni



sistema amorfo

Disordine gelato

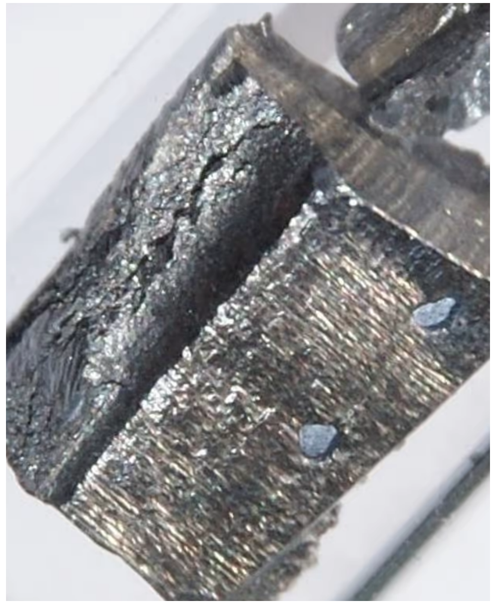
sistemi porosi

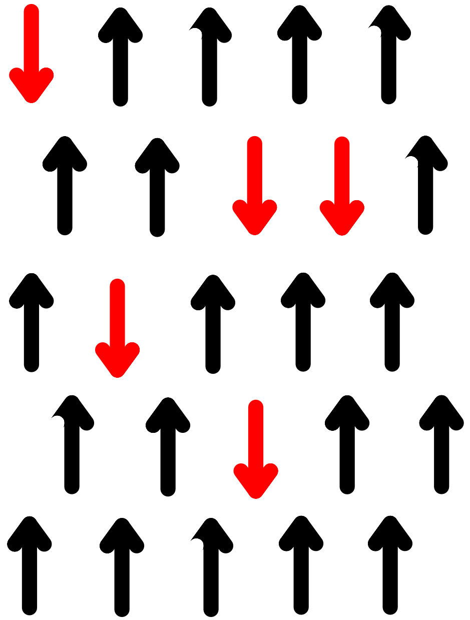
$$H = H_f(\{\vec r_i\}) + H_{fm}(\{\vec r_i\}; \{\vec r_i^{(m)}\})$$

$\overline{\qquad\quad}$ ← sul disordine

$\langle \dots \rangle$ ← termica

vetri di spin $\quad \sigma_i = \pm 1$



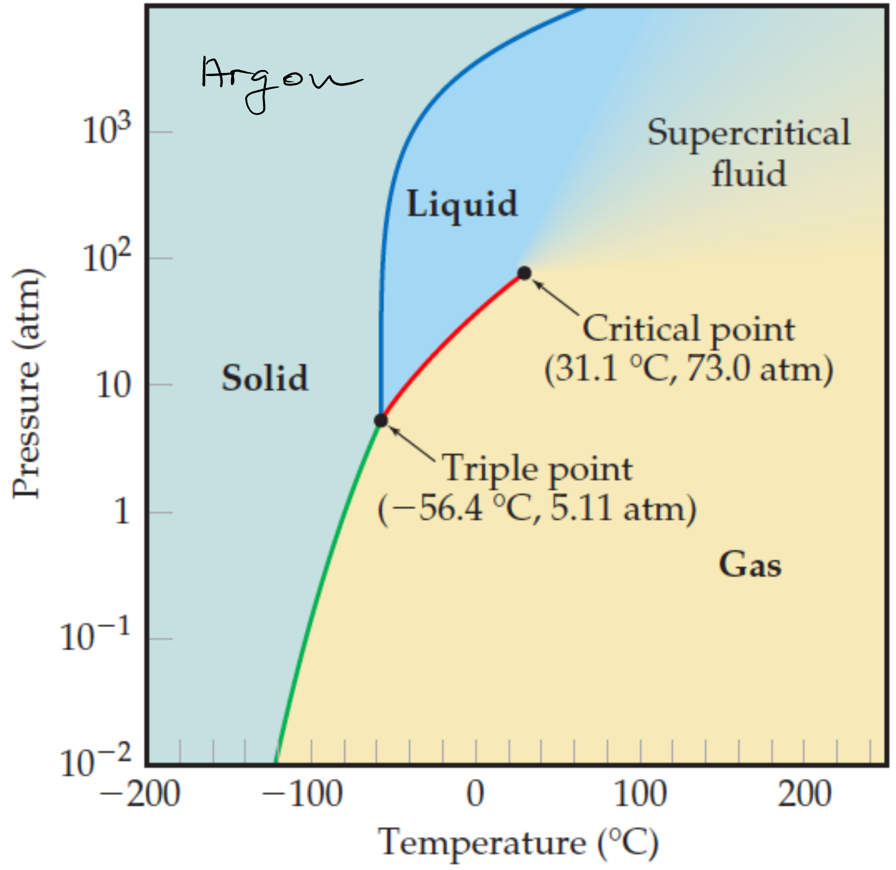


Ising : $H = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j$

↑ primi vicini

Edwards Anderson : $H = -\sum_{\langle ij \rangle} J_{ij} \sigma_i \sigma_j$

$p(J_{ij})$ gaussiana $\quad$ spin glass



THE JOURNAL OF CHEMICAL PHYSICS **131**, 104502 (2009)

Evidence for a liquid-solid critical point in a simple monatomic system

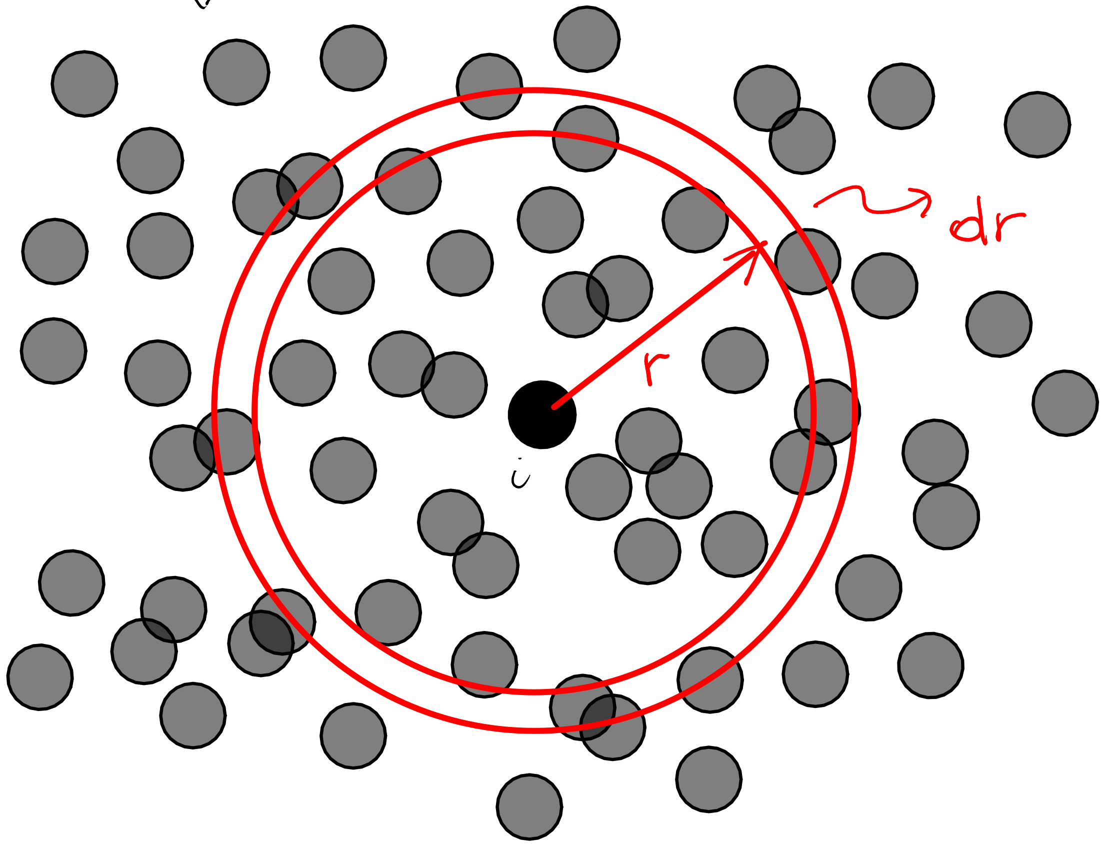
Måns Elenius[1,a)] and Mikhail Dzugutov[2]
[1]*Department of Numerical Analysis, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*
[2]*Department of Materials Science and Engineering, Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

(Received 5 June 2009; accepted 10 August 2009; published online 8 September 2009)

It is commonly believed that the transition line separating a liquid and a solid cannot be interrupted by a critical point. This opinion is based on the traditional symmetry argument that an isotropic liquid cannot be continuously transformed into a crystal with a discrete rotational and translational symmetry. We present here a molecular-dynamics simulation of a simple monatomic system suggesting the existence of a liquid-solid spinodal terminating at a critical point. We show that, in the critical region, the isotropic liquid continuously transforms into a phase with a mesoscopic order similar to that of the smectic liquid crystals. We argue that the existence of both the spinodal and the critical point can be explained by the close structural proximity between the mesophase and the crystal. This indicates a possibility of finding a similar thermodynamic behavior in gelating colloids, liquid crystals, and polymers. © *2009 American Institute of Physics*. [doi:10.1063/1.3213616]

ORDINE E CORRELAZIONI

$\rho = \frac{N}{V}$

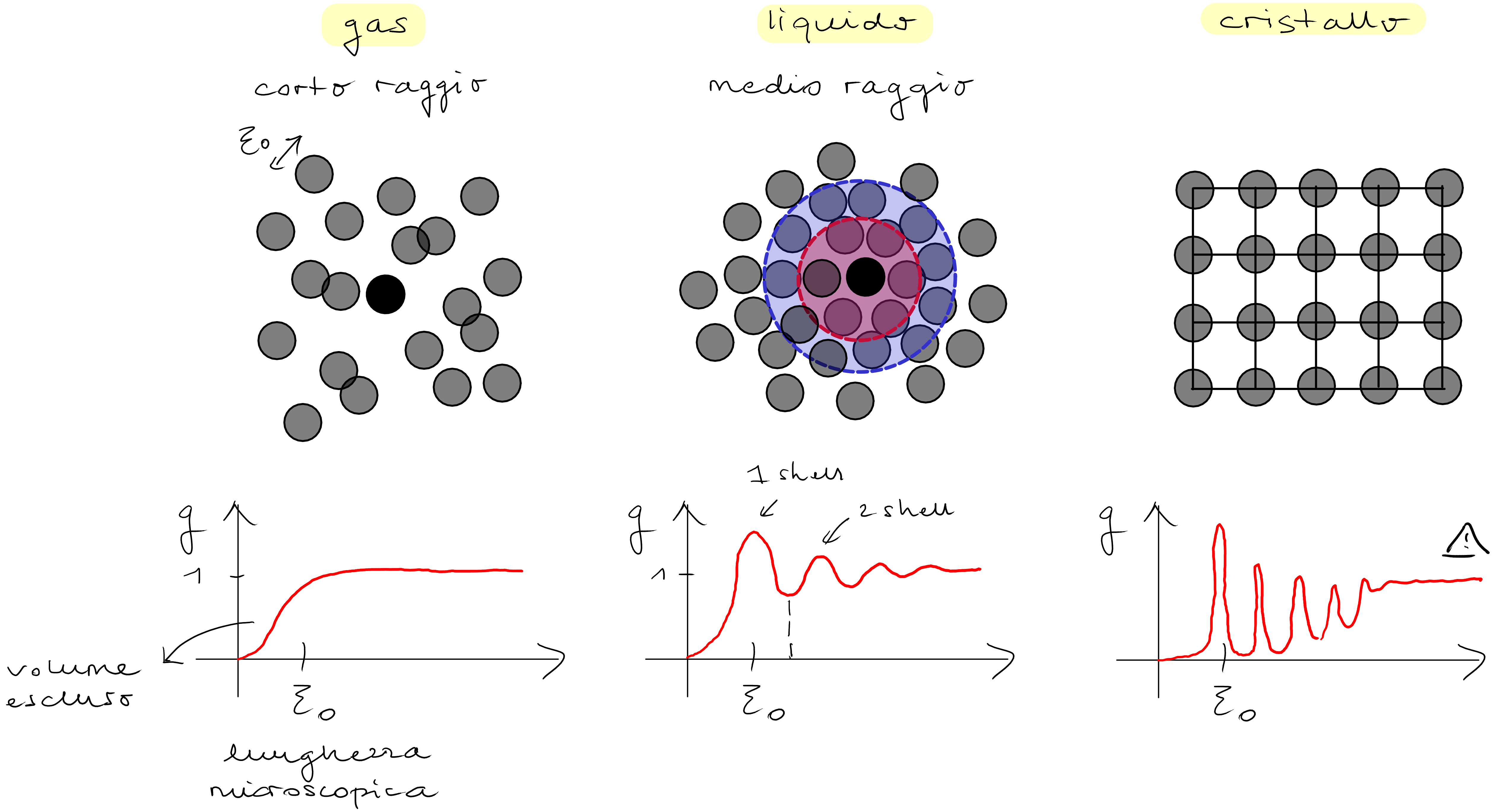


Funzione di distribuzione radiale $g(r)$

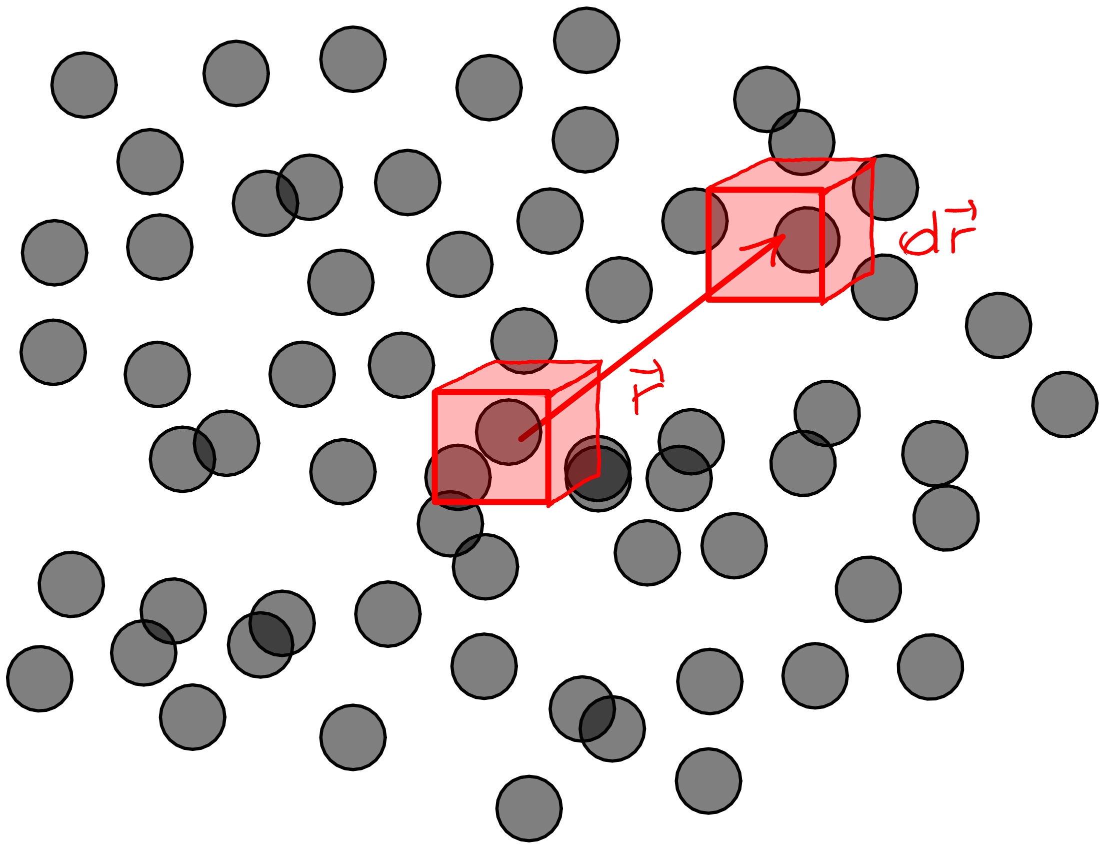
$$g(r) = \frac{\left\langle \frac{1}{N} \sum_{i=1}^{N} n_i(r) \right\rangle}{4\pi r^2 dr \cdot \rho}$$

← n. particelle a distanza compresa tra r e r+dr da i

g.p. : $g(r) = 1$



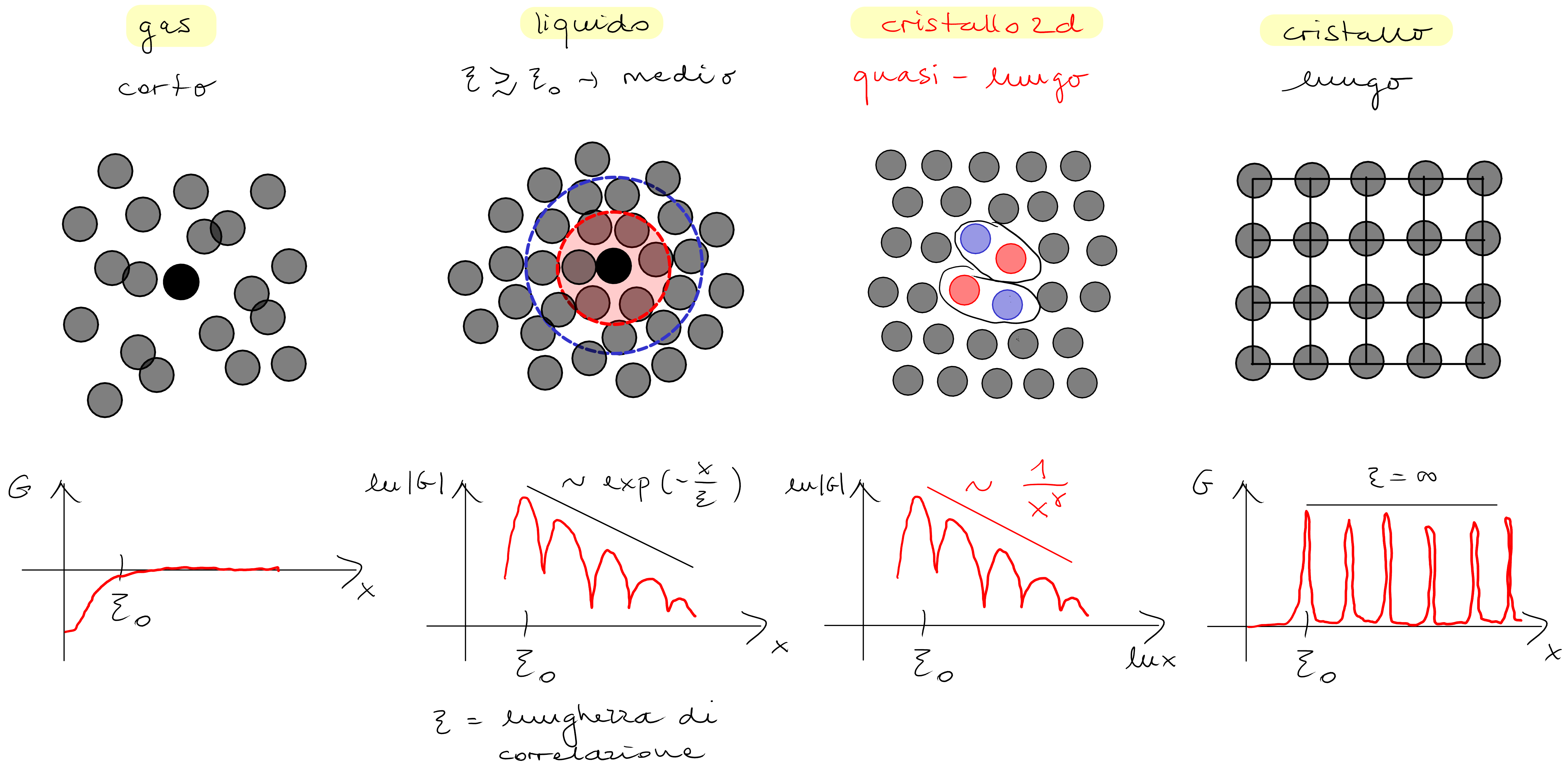
gas
corto raggio
ξ_0
liquido
medio raggio
cristallo
g
1
volume escluso
ξ_0
lunghezza microscopica
1 shell
2 shell
g
1
ξ_0
g
ξ_0



Funzione di correlazione della densità microscopica $\hat{\rho}$

$$\hat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i)$$

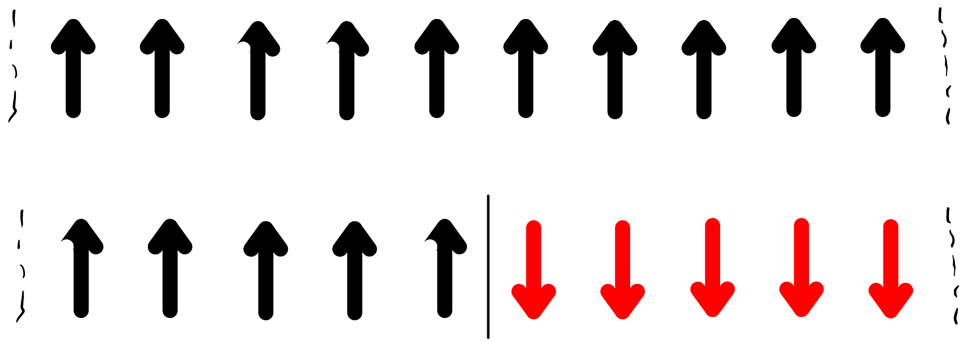
$$\Rightarrow \quad G(\vec{r}) \to G(x)$$


gas
corto
liquido
ξ ≳ ξ0 → medio
cristallo 2d
quasi - lungo
cristallo
lungo
G
x
ξ0
ln|G|
~ exp(-x/ξ)
x
ξ0
ξ = lunghezza di correlazione
ln|G|
~ 1/x^γ
ξ0
ln x
G
ξ = ∞
ξ0
x

ORDINE E DIMENSIONALITÀ

'30 – '40 Peierls, Landau: in 1d non c'è ordine a lungo raggio
dipende se simmetria **discreta** o **continua**

1) **Spins 1d**, no campo esterno, N spins, PBC ⇒ Ising $\sigma_i = \pm 1$



interfaccia

$$H = -\sum_{\langle ij \rangle} J \sigma_i \sigma_j \qquad J > 0 \text{ ferromagnetica}$$

$$F = -NJ$$

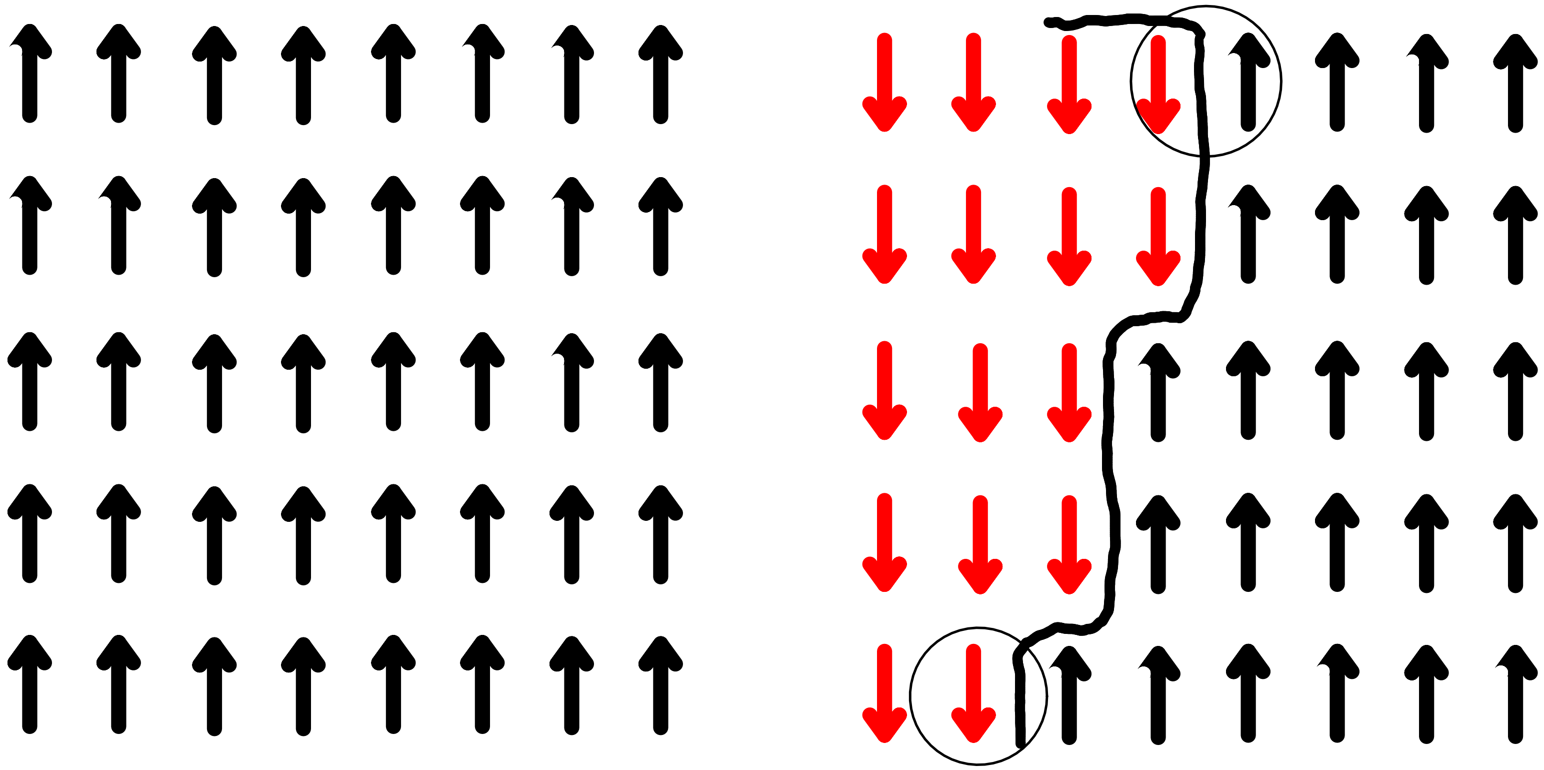
$$\left.\begin{aligned} \Delta E &= 2J > 0 \\ \Delta S &= k_B \ln N \end{aligned}\right\} \quad \Delta F = 2J - k_B T \ln N$$

$\forall T \; \exists N$ t.c. $\Delta F < 0$

⇒ fase ferromagnetica non è stabile

⇒ NO ORDINE A LUNGO RAGGIO

2) Spins 2d , no campo esterno , N spins , PBC $\Rightarrow$ Ising $\sigma_i = \pm 1$



$$H = - \sum_{\langle ij \rangle} J \sigma_i \sigma_j \qquad J > 0$$

n coppie di spins sull'interfaccia

z numero di coordinazione

$$\Delta E = 2 J n$$

$$\Delta S = k_B \ln \left[(z-1)^n \right]$$

$$\Delta F = \left[2J - k_B T \ln (z-1) \right] \cdot n$$

$$T_c = \frac{2J}{k_B \ln (z-1)} \approx 1.82 \frac{J}{k_B}$$

$T > T_c$: se $n \to \infty$, $\Delta F \to -\infty$ fase paramagnetica

$T < T_c$: fase ferromagnetica $\Rightarrow$ ORDINE A LUNGO RAGGIO POSSIBILE IN 2D

1941: Kramers-Wannier duality $\quad T_c = 2{,}269\ J/k_B$

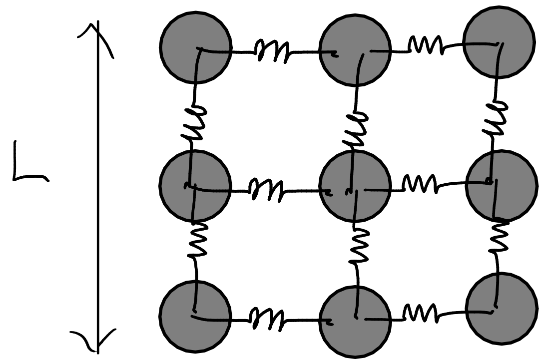
1943: Onsager prima soluzione esatta del modello di Ising 2d

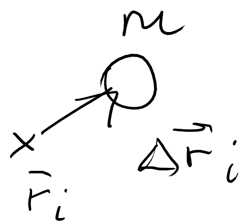
1953: Kac & Ward metodo combinatorio

Lower critical dimension : $d = 1$ (simmetria discreta)

3) Sistema di N particelle, simmetria continua, PBC

Vibrazioni armoniche





Spostamento quadratico medio

$$\langle |\Delta\vec{r}|^2 \rangle = \left\langle \frac{1}{N} \sum_{i=1}^{N} |\Delta\vec{r}_i|^2 \right\rangle$$

Modi normali : $D(\omega)$

$$g(\omega) \sim \omega^{d-1} \qquad \sim \omega^2 \quad d=3$$

$$\langle |\Delta\vec{r}|^2 \rangle = \frac{d \cdot k_B T}{m} \int_{\omega_{min}}^{\infty} d\omega \, \frac{g(\omega)}{\omega^2}$$

$$k_{min} = \frac{2\pi}{L} \qquad \omega_{min} \simeq \frac{k}{L} \qquad \underline{\omega \text{ piccoli}}$$

$$\sim \int_{k/L}^{\infty} d\omega \, \omega^{d-3}$$

- $d \geq 3$: $\langle |\Delta\vec{r}|^2 \rangle \to$ cost
- $d = 2$: $\langle |\Delta\vec{r}|^2 \rangle \sim \ln L$
- $d = 1$: $\langle |\Delta\vec{r}|^2 \rangle \sim \frac{1}{L}$

($d=1,2$) $\to \infty$ se $L \to \infty$

$\Rightarrow$ NO ORDINE LUNGO RAGGIO in $d = 1, 2$

'60. Hohenberg, Mermin, Wagner

Sotto ipotesi abbastanza generali sulla natura delle interazioni e dei costituenti elementari, sistemi con simmetria continua non possiedono ordine a lungo raggio in 1d e 2d

Lower critical dimension : 2 (simmetria continua)

In 2d: ordine quasi-lungo raggio

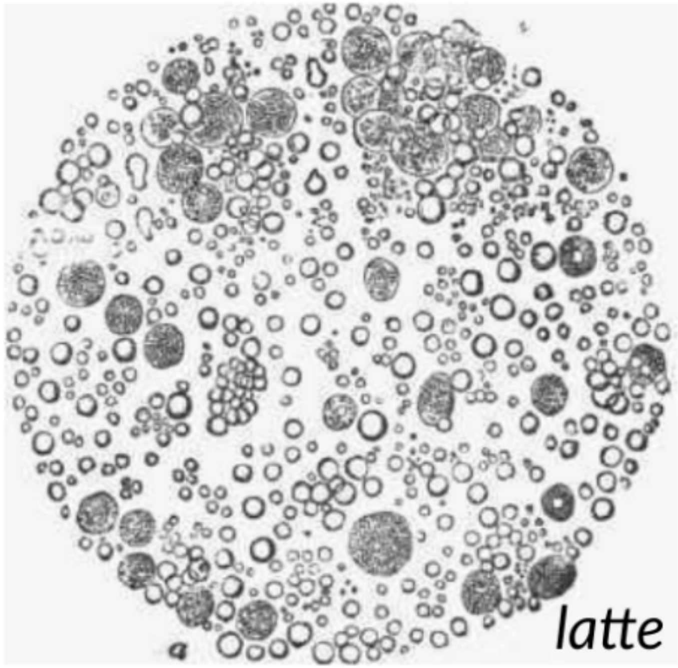
MATERIA CONDENSATA DURA E SOFFICE

Scala atomica $10^{-10} - 10^{-9}$

Scala mesoscopica $10^{-7} - 10^{-5}$

Scala macroscopica $10^{-2} - 10^{0}$

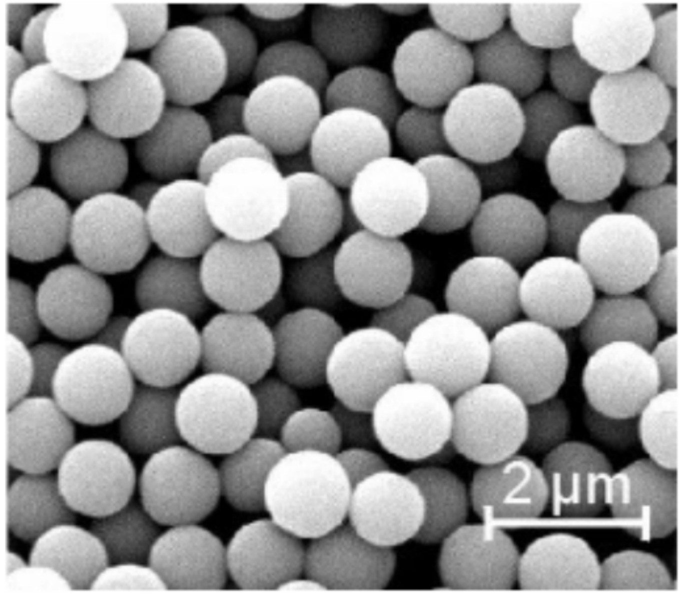
Lunghezza [m]



DURA

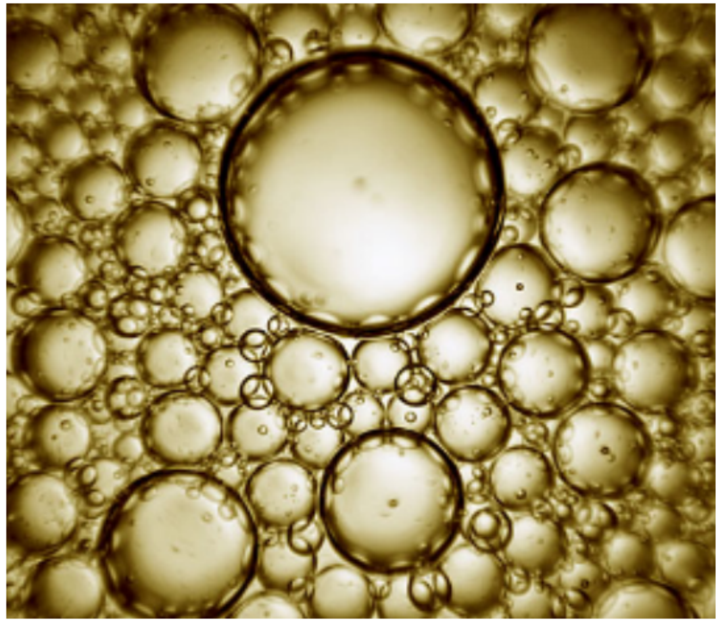
SOFFICE

PMMA



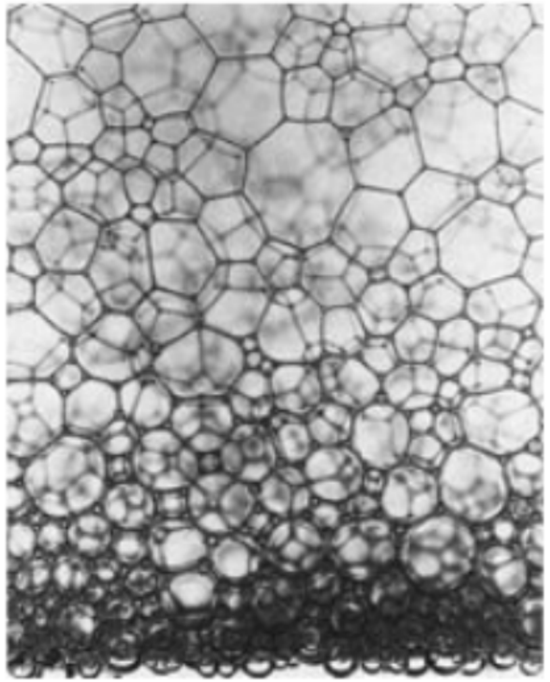
SOSPENSIONE COLLOIDALE

es.: inchiostro
pittura



EMULSIONE

es.: maionese
latte



SCHIUMA

es: estintore

SOLIDO

elasticità

FLUIDO

viscosità

visco - elasticità

LIQUIDI

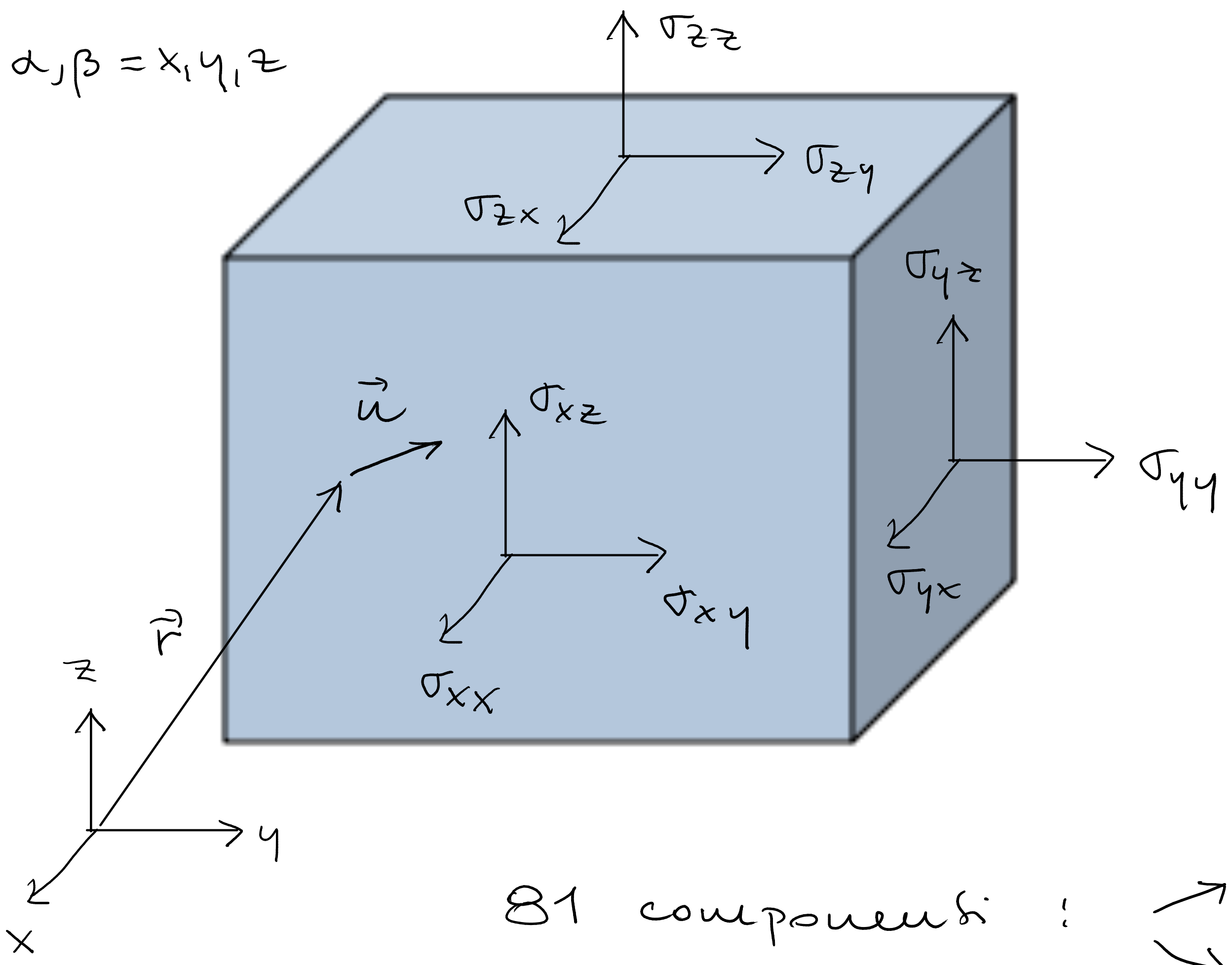
MATERIA SOFFICE

ELASTICITÀ

Sforzo = modulo x deformazione ⇒ solido Hookiano $F = k \Delta x$

F/A SI: Pa adimensionale

$\alpha, \beta = x, y, z$



Sforzo: $\sigma_{\alpha\beta}$ simmetrico $\alpha \leftrightarrow \beta$

Deformazione: $\gamma_{\alpha\beta} = \dfrac{\partial u_\alpha}{\partial r_\beta}$

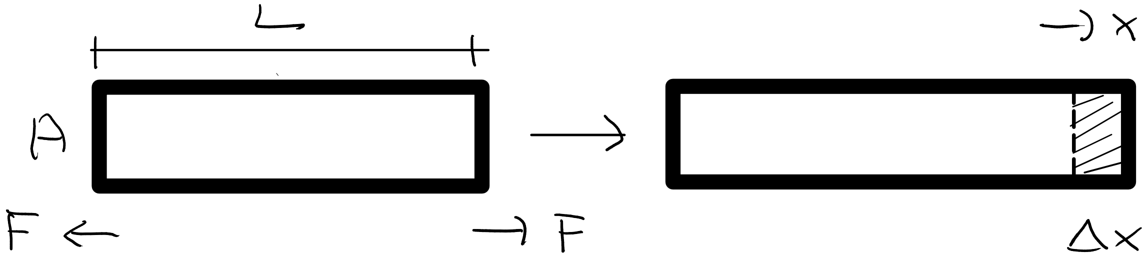
$$\rightarrow \frac{1}{2}\left(\frac{\partial u_\alpha}{\partial r_\beta} + \frac{\partial u_\beta}{\partial r_\alpha}\right)$$

Modulo elastico: $C_{\alpha\beta\theta\delta}$ (costanti elastiche)

$$\sigma_{\alpha\beta} = \sum_{\theta\delta} C_{\alpha\beta\theta\delta}\, \gamma_{\theta\delta}$$

81 componenti:
- 2 : Y, G omogeneo, isotropo
- 3 : cristallo cubico

1) Sforzo di trazione



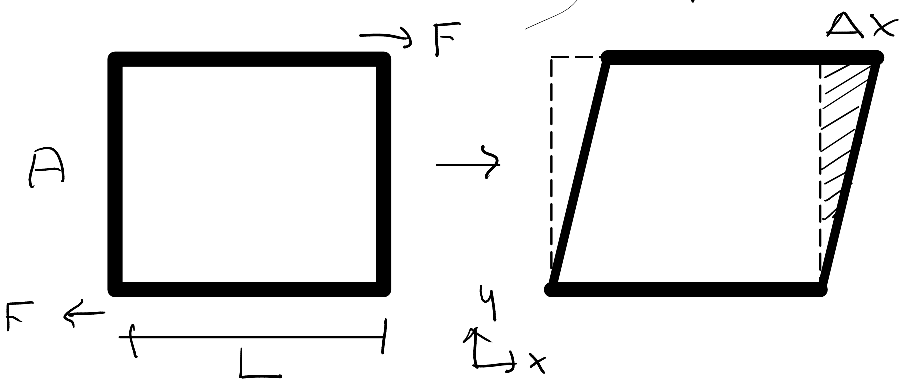
sforzo : $\frac{F}{A} = \sigma_{xx} = \sigma$

deformazione : $\gamma_{xx} = \frac{\Delta x}{L} = \gamma$

$\sigma = Y \gamma$ ← modulo di Young

Es: gomma $Y \sim 0.1 - 0.01$ GPa , diamante $Y \sim 10^3$ GPa

2) Sforzo di taglio

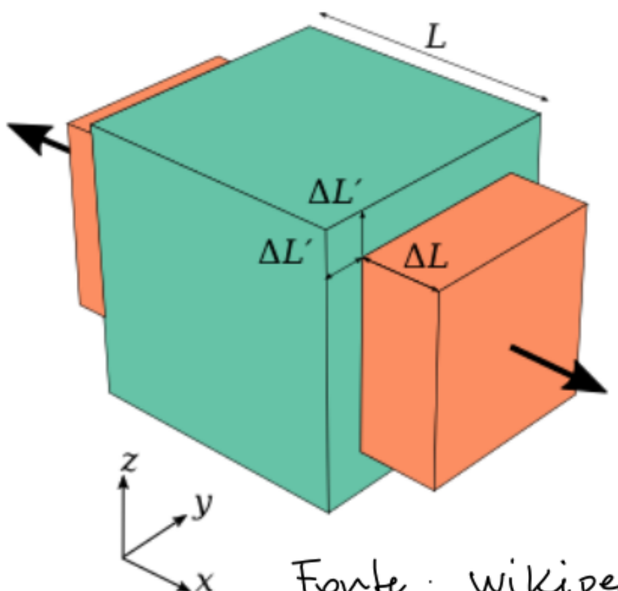


sforzo : $\sigma_{xy} = \frac{F}{A} = \sigma$

def. : $\gamma_{xy} = \frac{\Delta x}{L} = \gamma$

$\sigma = G \gamma$ ← modulo di taglio

Es. : gomma 6×10^{-4} GPa diamante 500 GPa



Fonte : wikipedia "Poisson's ratio"

Coefficiente di Poisson : $\nu = - \frac{\Delta L'}{\Delta L}$ → trasversale / → longitudinale

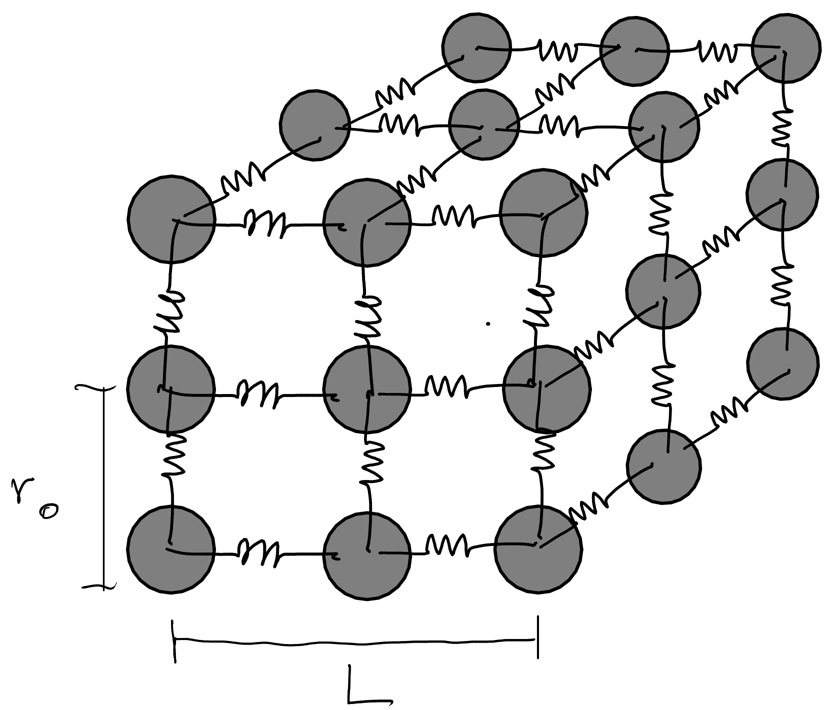
isotropi e omogenei : $Y = 2G(1+\nu)$

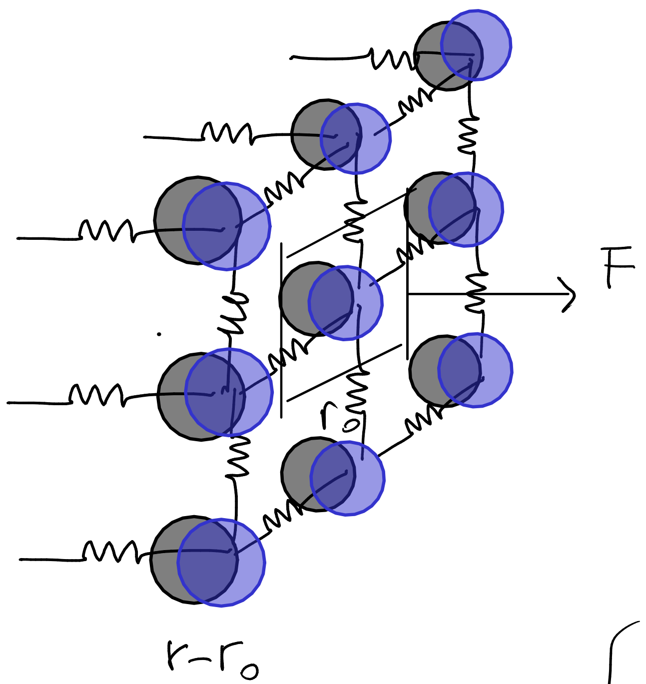
$0 \lesssim \nu < 0.5$

(0 ↑ es. sughero; 0.5 ↑ incomprimibile es. gomma)

Modello micro

Cf. "Effective interactions in condensed matter physics" C.N. Likos 2001 p. 274



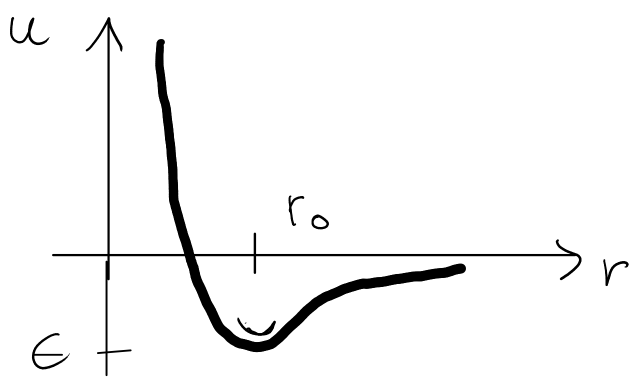


- interazioni
- scala di lunghezza

Sforzo di trazione:

$$\sigma = Y \gamma$$

$$\begin{cases} \sigma = \dfrac{F}{A} = \dfrac{k(r-r_0)}{r_0^2} \\ \gamma = \dfrac{\Delta x}{L} = \dfrac{r-r_0}{r_0} \end{cases}$$



$$\frac{k\,\cancel{(r-r_0)}}{r_0^{\cancel{2}}} = Y \frac{\cancel{(r-r_0)}}{\cancel{r_0}}$$

$$Y = \frac{k}{r_0} \sim \frac{\epsilon}{r_0^3}$$

$$[Y] = \frac{E}{V}$$

$$u(r) = \epsilon\, f\left(\frac{r}{r_0}\right)$$

$$u(r) \approx u(r_0) + \frac{1}{2} \left.\frac{d^2u}{dr^2}\right|_{r_0} (r-r_0)^2$$

$$k = \frac{\epsilon}{r_0^2} f''(1) \sim \frac{\epsilon}{r_0^2}$$

$$Y \sim \frac{\epsilon}{r_0^3}$$

$$\frac{Y_{soffice}}{Y_{duro}} \sim \left(\frac{\epsilon_{soffice}}{\epsilon_{duro}}\right)\left(\frac{r_{0,duro}}{r_{0,soffice}}\right)^3$$

materia dura:

$r_0 \sim 10^{-10}$ m

$\epsilon \sim 100\, k_B T$

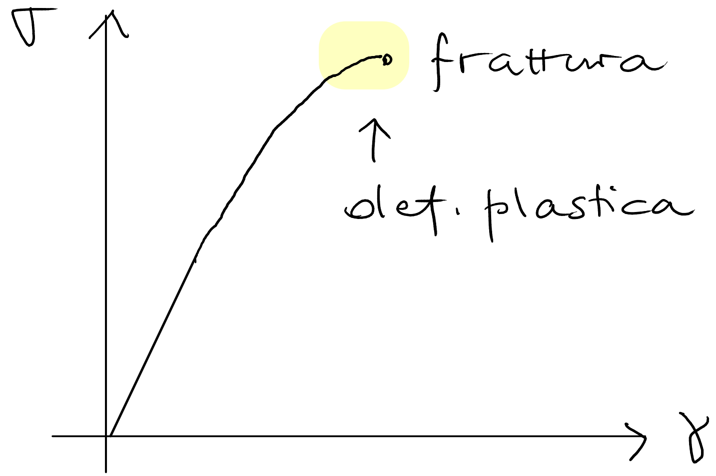
materia soffice:

$r_0 \sim 10^{-6}$ m

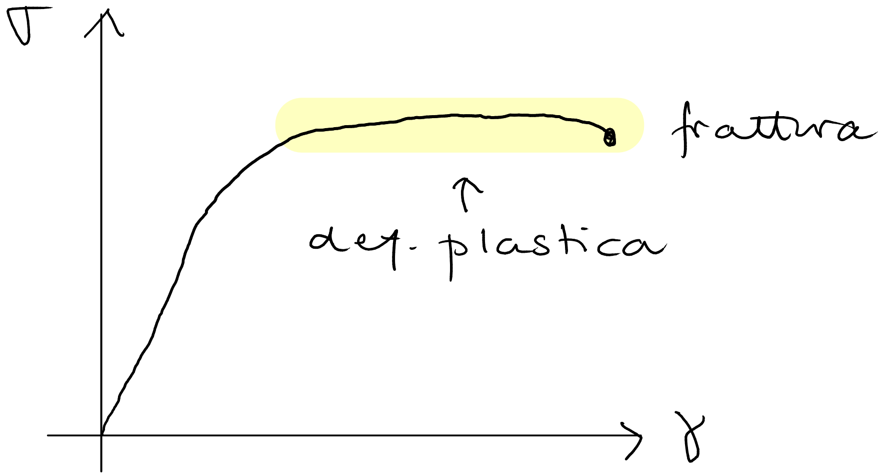
$\epsilon \sim 10\, k_B T$

$$\frac{Y_{soffice}}{Y_{duro}} \sim 10^{-1} \times 10^{-12} \sim 10^{-13} \;!!$$

fragili



duttili



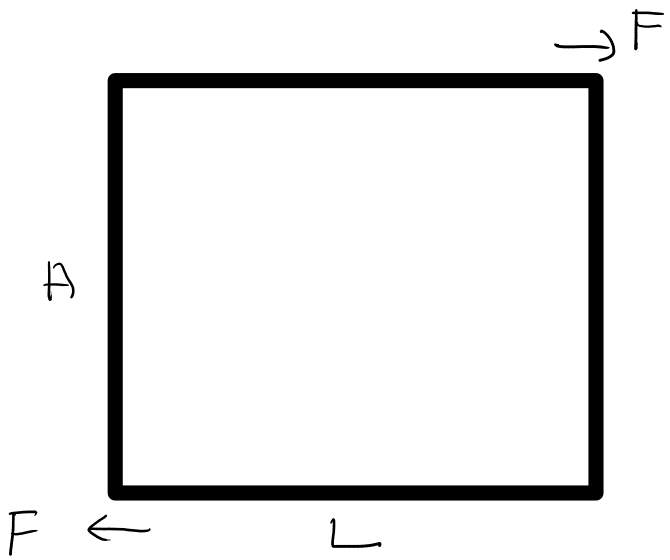
Brittle Fracture

Ductile Fracture

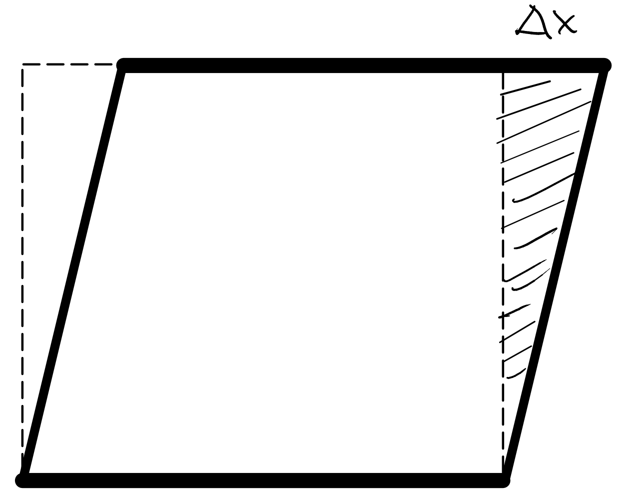
VISCOSITÀ

Hooke : sforzo ~ deformazione
equilibrio

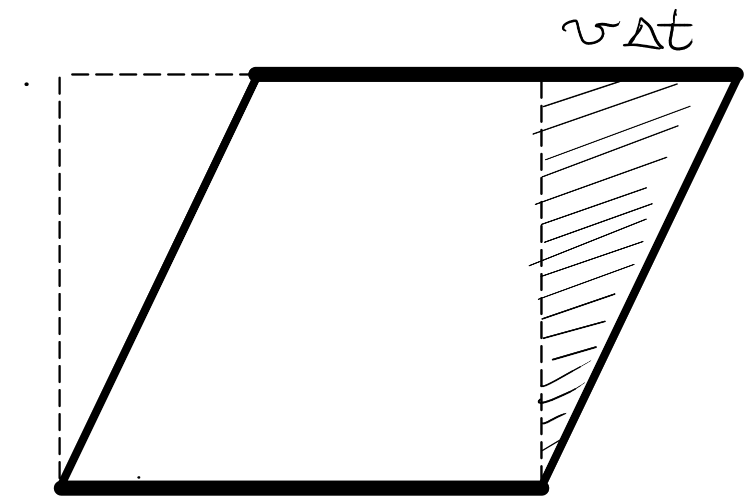
sforzo ~ tasso di deformazione
stazionario



$\sigma = \frac{F}{A}$



$\gamma = \frac{v \Delta t}{L}$



$\dot{\gamma} = \frac{\gamma}{\Delta t} = \frac{v}{L}$

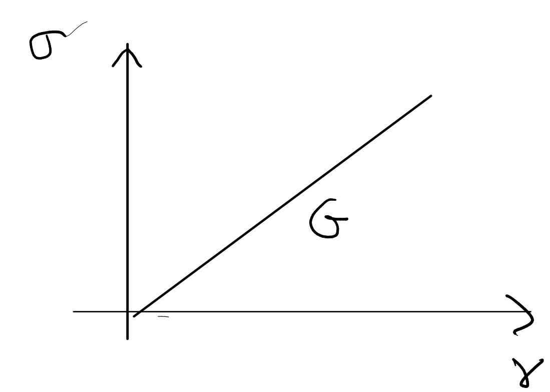
Fluido Newtoniano : $\sigma = \eta \dot{\gamma}$ η = viscosità SI : Pa·s

ES. : H_2O @ T_{amb} $T \simeq 90°C$

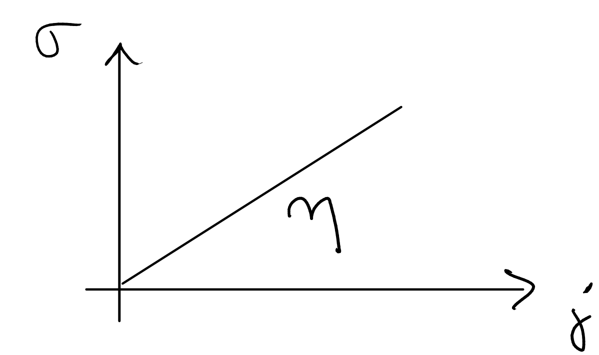
$\eta \sim 10^{-3}$ Pa·s $\eta \sim 10^{-4}$ Pa·s

Miele Liquido @ T_g

$\eta \sim 1$ Pa·s $\eta \sim 10^{12}$ Pa·s

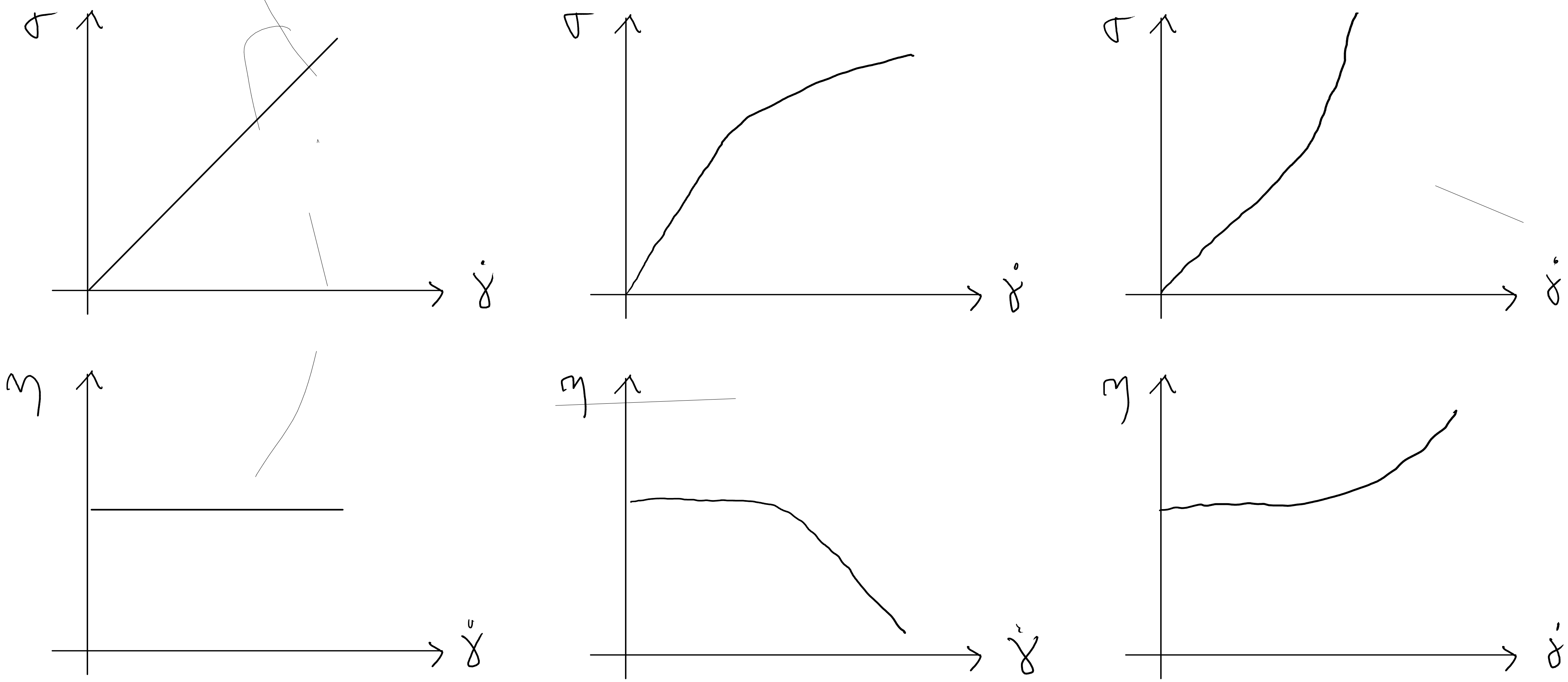


Hooke



Newton

$$\sigma = \eta(\dot{\gamma})\,\dot{\gamma}$$



fluido Newtoniano

assottigliamento al taglio

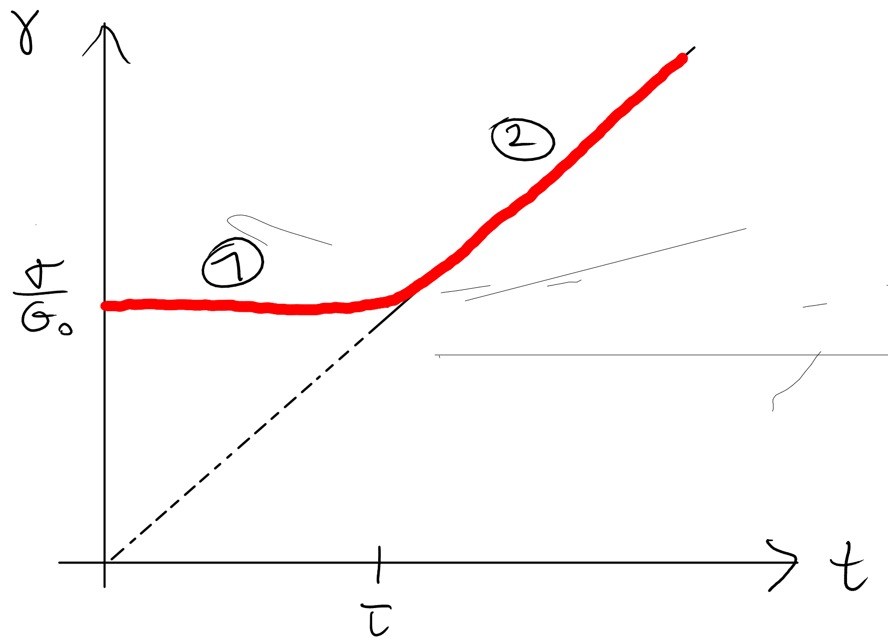
shear thinning

ispessimento al taglio

shear thickening

fluido non-Newtoniano

VISCO - ELASTICITÀ



Applico sforzo a $t = 0$

$$\begin{cases} \sigma = G_0 \gamma & ① \\ \sigma = \eta \dot{\gamma} & ② \end{cases}$$

G_0 = modulo istantaneo di taglio

τ = tempo di rilassamento

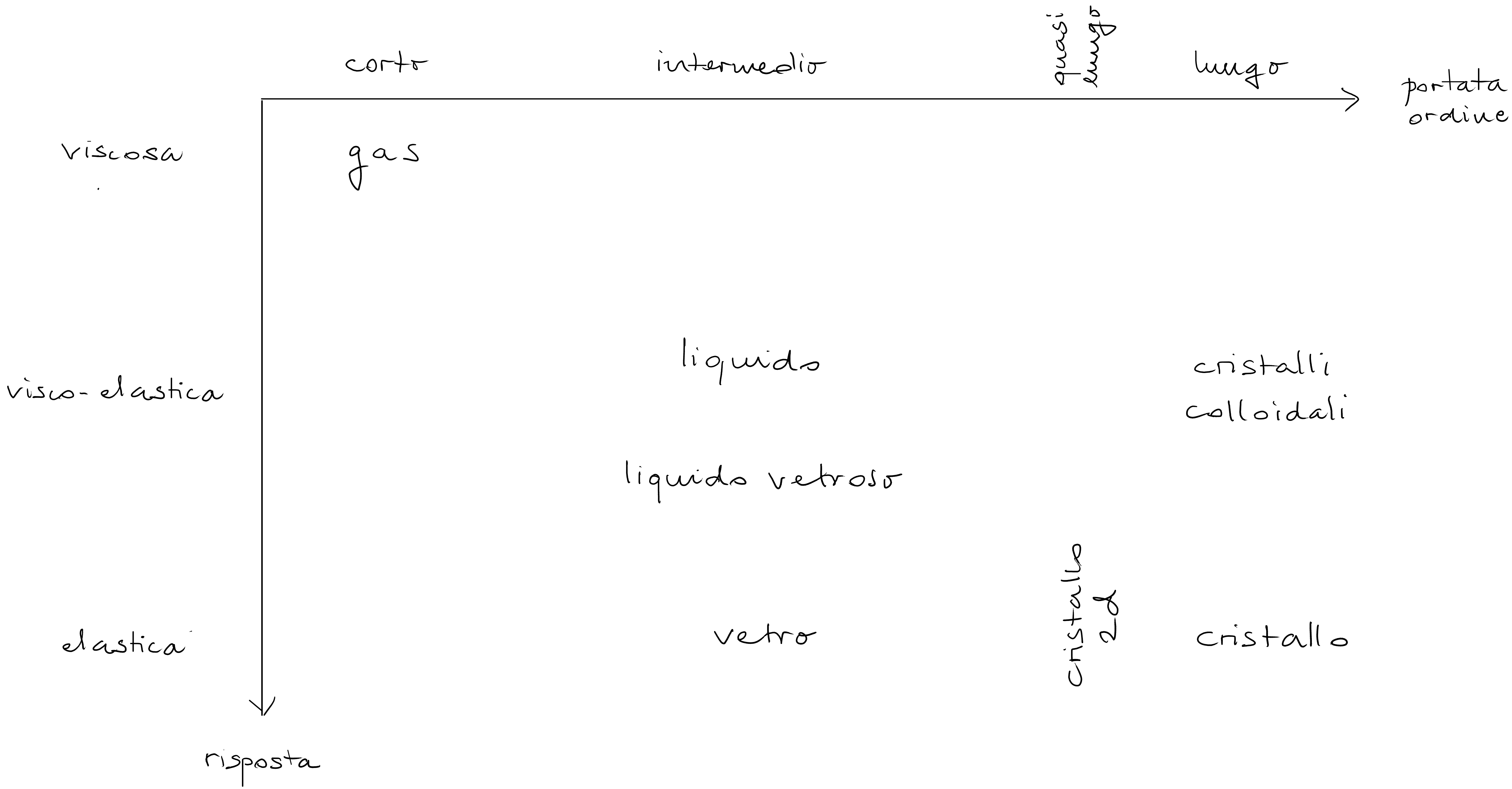
Modello di Maxwell:

$$\dot{\gamma} \cdot \tau = \frac{\sigma}{G_0} \rightarrow \frac{\sigma}{\eta} \tau = \frac{\sigma}{G_0} \Rightarrow \eta = G_0 \tau$$

Es.: $G_0 \sim 10^9$ Pa

$\tau \sim 10^{-12}$ s

$\eta \approx 10^9 \text{ Pa} \times 10^{-12} \text{ s} \approx 10^{-3} \text{ Pa} \cdot \text{s}$


corto
intermedio
quasi lungo
lungo
portata ordine
viscosa
gas
visco-elastica
liquido
cristalli colloidali
liquido vetroso
elastica
vetro
cristallo 2d
cristallo
risposta