Fluides complexes et interfaces

Introduction

① Solide et liquide

solide : matériau qui résiste à la déformation

= modules élastiques

= ∃ forme d'équilibre

liquide = résiste à l'écoulement

= viscosité

= dissipation d'énergie

② Les matériaux complexes

comportement macroscopique
- → liquides et solides viscoélastiques
- → comportements qui dependent du temps
- → liquides non newtoniens

origine microscopique
- → melanges de φ
- → polymères
- → cristaux liquides
- → suspensions

Chapitre 1
Des solides élastiques vers des solides complexes

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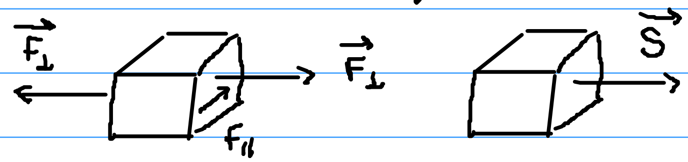
1 – Solides élastiques – régime linéaire

__contrainte__ $\dfrac{\text{Force}}{\text{Surface}}$



Force de compression / traction

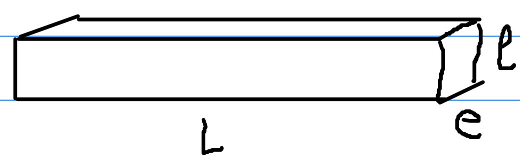
$$\sigma = \frac{F_\perp}{S}$$

Force de cisaillement

$$\sigma = \frac{F_\parallel}{S}$$

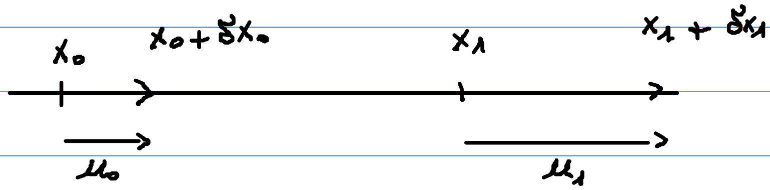
$$[\sigma] = \text{Pascal}$$

__Déformation__



$$\varepsilon_L = \frac{\Delta L}{L} \qquad \varepsilon_e = \frac{\Delta e}{e} \qquad \varepsilon_\ell = \frac{\Delta \ell}{\ell}$$

__Déplacement__ $u(x)$

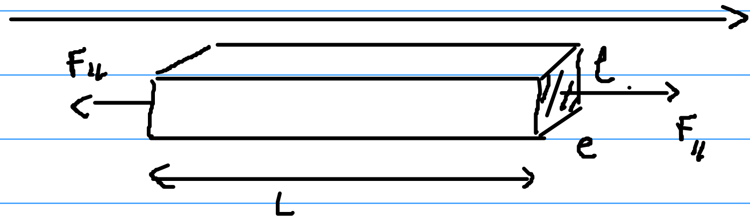


$$\varepsilon = \frac{\cancel{x_1} + \delta x_1 - (\cancel{x_0} + \delta x_0) - (\cancel{x_1} - \cancel{x_0})}{x_1 - x_0}$$

$$= \frac{\delta x_1 - \delta x_0}{x_1 - x_0} = \frac{u(x_1) - u(x_0)}{x_1 - x_0}$$

$$\xrightarrow[x_1 \to x_0]{} \boxed{\frac{\partial u}{\partial x} = \varepsilon}$$

* lien contrainte – déformation Loi de Hook



$\sigma = \dfrac{F_\parallel}{e\ell}$ $\qquad \varepsilon_\parallel = \dfrac{\Delta L}{L} = \dfrac{\sigma}{E}$

E = module d'Young

métaux, verre $E \simeq 10^9$ Pa

polymères, caoutchouc $E \simeq 10^6$ Pa

gels $E \simeq 10^3$ Pa

$$\varepsilon_\perp = \frac{\Delta e}{e} = \frac{\Delta \ell}{\ell} = -\nu\, \varepsilon_\parallel = -\frac{\nu}{E}\sigma$$

coefficient de poisson

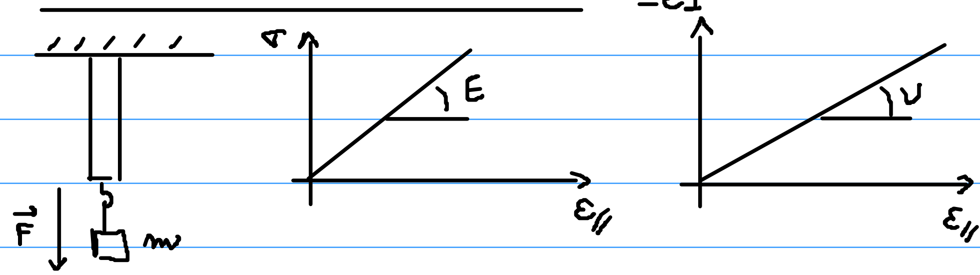
$$0 \leq \nu \leq 0,5$$

liège

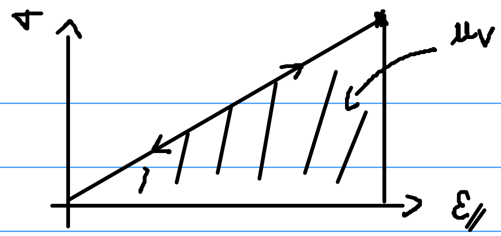
matériau incompressible caoutchouc

$\nu \leq 0$ matériaux auxétiques

Test de traction uniaxial



* energie stockée



travail $\delta W = F_{\parallel} \times dL$

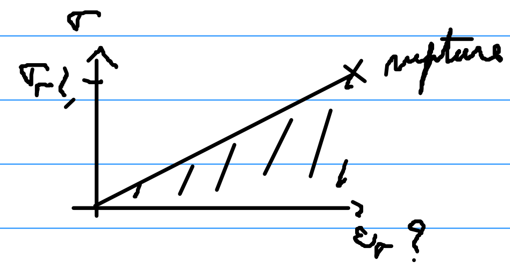
$$du_v = \frac{\delta W}{L e \ell} = \sigma \, d\varepsilon = E \varepsilon \, d\varepsilon$$

$$u_v = \int_0^{\varepsilon_{max}} E \varepsilon \, d\varepsilon = \frac{1}{2} E \varepsilon_{max}^2$$

matériau élastique = reversible

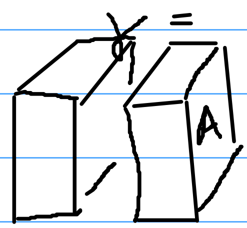
= u_v energie stockée pendant la charge
restituée pendant la décharge

2 - Rupture des matériaux



a) la tension de surface

γ = energie necessaire à créer de la surface



Coût energétique $2\gamma A$

$$[\gamma] = J/m^2$$

ex métal $u \simeq 10 k_B T /$ liaison
$a \simeq 10^{-20} \, m^2 \; (1 \, Å^2)$

$$2\gamma = \frac{u}{a} = \frac{\cancel{10} \times 1{,}38 \cdot 10^{\cancel{-23}} \times 3\cancel{00}}{\cancel{10^{-20}}} \simeq 4{,}2 \, J/m^2$$

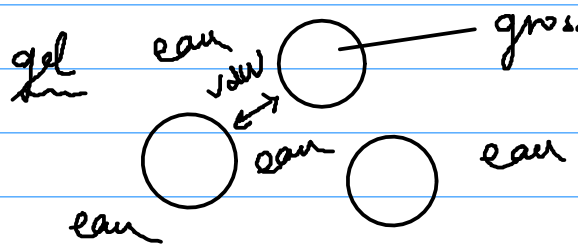
$\gamma \simeq 2{,}1 \, J/m^2$ Rq mercure $\gamma = 436 \, mJ/m^2$

Bon ordre de grandeur

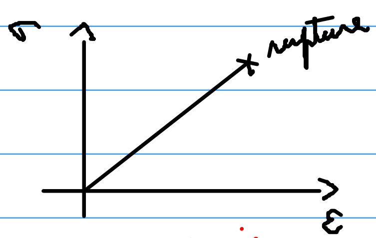
liaison VdW	liaison electrostatiq	liaison metallique	liaison covalente
$k_B T$	$10 k_B T$	$10 k_B T$	$100 k_B T$

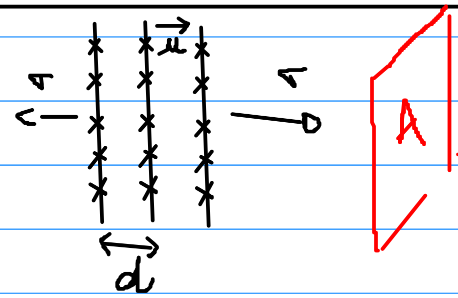
$\underbrace{k_B T}_{\text{matière molle}}$

matière molle ⟶ deformation et rupture facile
⟶ sensible à la temperature ambiante



b) contrainte à la rupture d'un materiau fragile





$$\overbrace{A \times 2\gamma}^{\text{énergie surfacique}} = \overbrace{\int_0^{u_{max}} \sigma \, d\varepsilon \times A d}^{\text{energie volumique}} \qquad \sigma = E\varepsilon = E\frac{u}{d}$$

$$2\gamma = \int_0^{u_{max}} d \, E \frac{u}{d^2} du = \frac{1}{2} E \frac{u_{max}^2}{d^2}$$

$$u_{max} = \frac{\sigma_r d}{E}$$

$$2\gamma = \frac{1}{2}\frac{1}{E}\sigma_r^2 \times d$$

$$\sigma_r = \sqrt{\frac{4\gamma E}{d}}$$

metal (acier) $\quad \gamma = 200\ mN/m$

$d = 1\ nm$

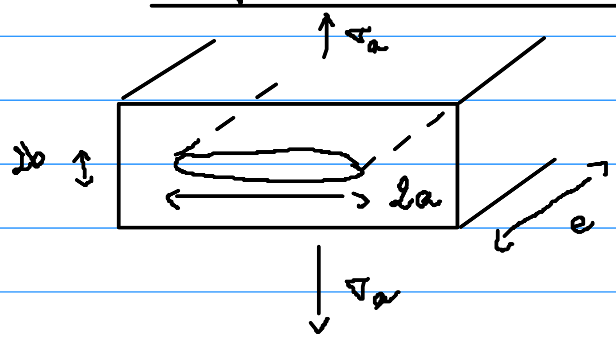
$E = 210\ GPa$

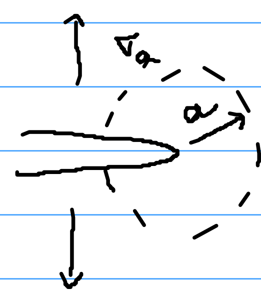
$$\sigma_r = 2\sqrt{\frac{0{,}2 \times 2{,}1 \cdot 10^{11}}{10^{-9}}} = 12\ GPa$$

$$\sigma_r^{exp} = 0{,}36\ GPa \quad (30 \text{ fois moins})$$

$\rightsquigarrow \exists$ défauts

c) Rupture d'un matériau fragile - le critère de Griffith





$a \to a + da \qquad dU = \underbrace{dU_s}_{\text{énergie de surface}} - \underbrace{dU_e}_{\text{relaxation des contraintes élastiques}}$

$$dU_s = 4\gamma\, e\, da \qquad dU_{el} = \frac{\sigma_a^2}{2E} \times 2\pi a\, da \times e$$

A l'équilibre $\quad dU = 0$

$$4\gamma = \frac{\sigma_{ar}^2}{E}\pi a$$

$$\sigma_r = \sqrt{\frac{4\gamma E}{\pi a}} \qquad a \sim 0{,}3\,\mu m$$

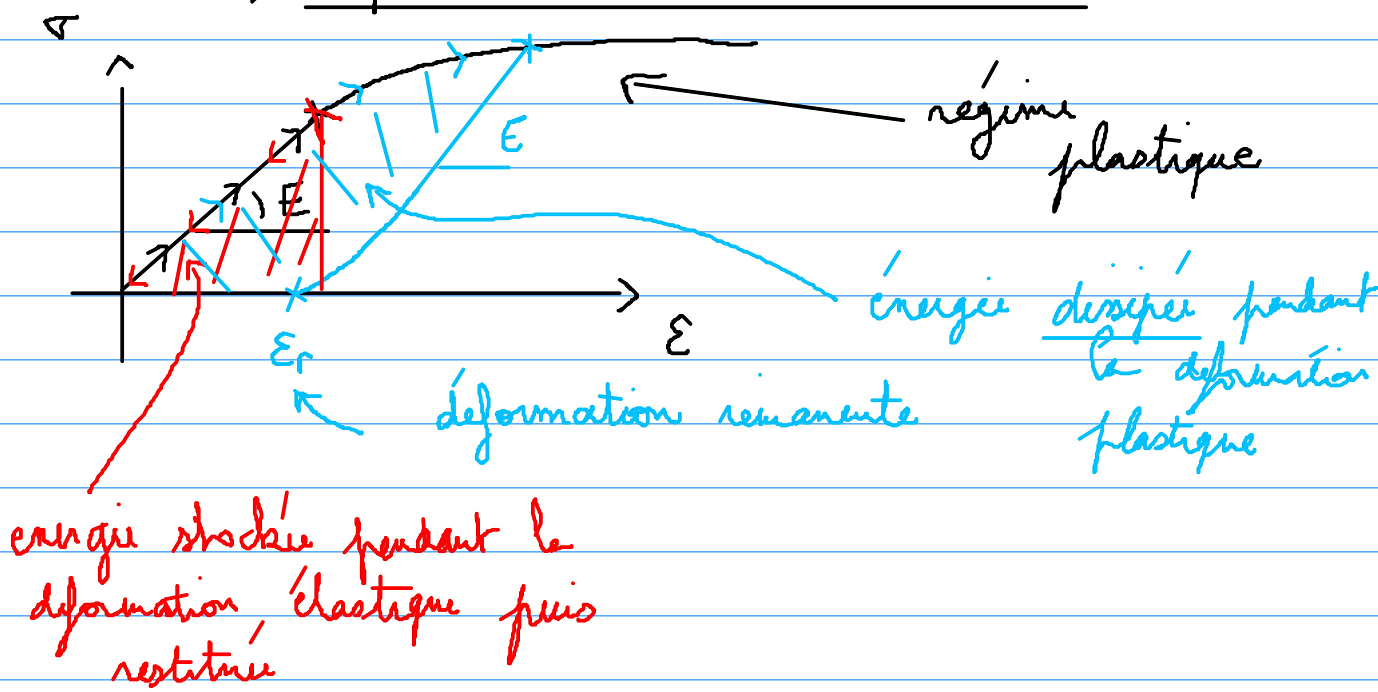
$$= \sqrt{\frac{4 \times 2 \cdot 10^{-1} \times 2 \cdot 10^{11}}{\pi \times 3 \cdot 10^{-7}}}$$

$$= 0{,}4 \text{ GPa}$$

OK pour l'ordre de grandeur

$\Rightarrow$ défauts importants

d) rupture des matériaux ductiles



$\Rightarrow$ dans le regime plastique, on a un écoulement

$\to$ σ cst avec $\varepsilon \nearrow$

$\to$ dissipation d'energie

$\Rightarrow$ fluage.

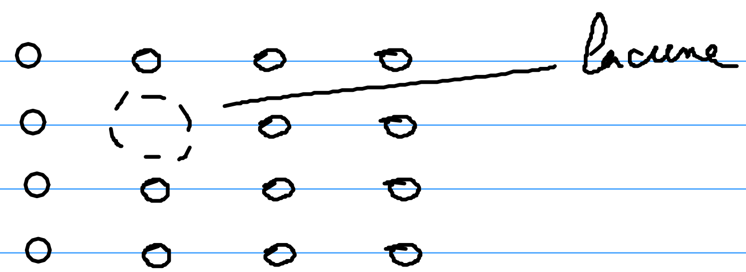
En résumé γ = énergie nécessaire pour générer de la surface

rupture fragile	rupture ductile
énergie $\ll 2\gamma$	énergie $\gg 2\gamma$
microfissure	présence de dissipation

$\rightsquigarrow$ importance des défauts

e) Les défauts dans les cristaux

les lacunes

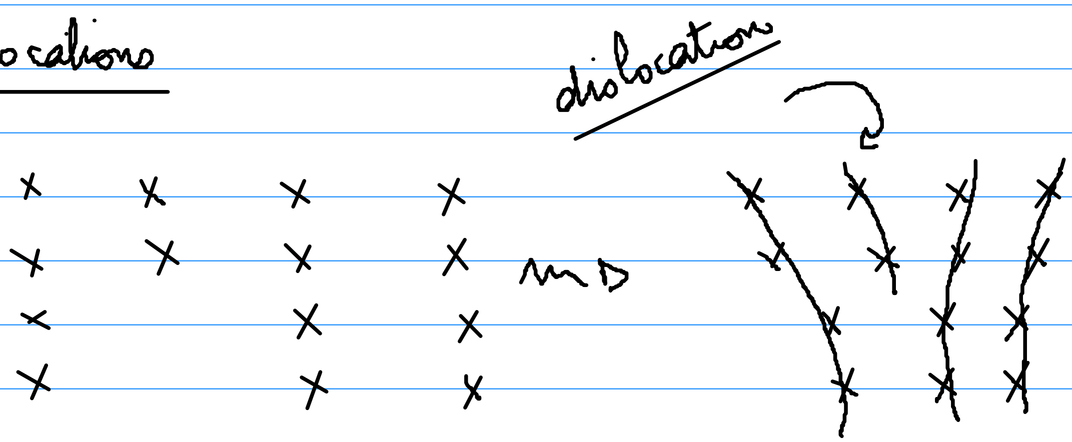


* énergie associée aux lacunes $\sim 1\ eV$
* faible concentration

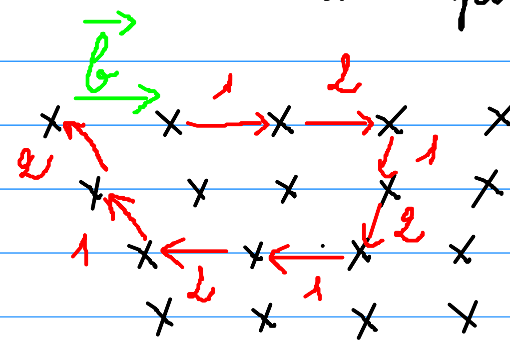
ex Cuivre $T < T_f$

$c \simeq 5.10^{-5}$ lacune/atome

les dislocations



dislocation = caractérisé par un vecteur de Bürger



$\vec{b}$ = vecteur manquant pour fermer la boucle.

3) Les solides viscoélastiques

<u>1D</u>

solide élastique $\sigma = E\varepsilon$

fluide visqueux $\sigma = \eta\dot{\varepsilon}$

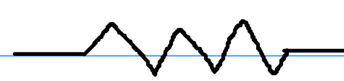
ε = déformation = gradient de déplacement

$= \dfrac{\partial u}{\partial x}$

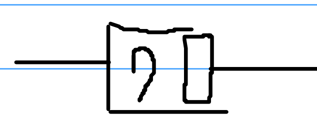
$$\dot{\varepsilon} = \frac{\partial}{\partial x}\left(\frac{\partial u}{\partial t}\right) = \frac{\partial v}{\partial x} = \text{cisaillement}$$

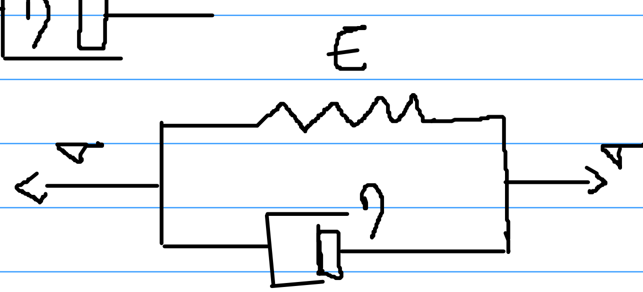
solide viscoélastique $\sigma = E\varepsilon + \eta\dot{\varepsilon}$

$\sigma = E\varepsilon$



$\sigma = \eta\dot{\varepsilon}$





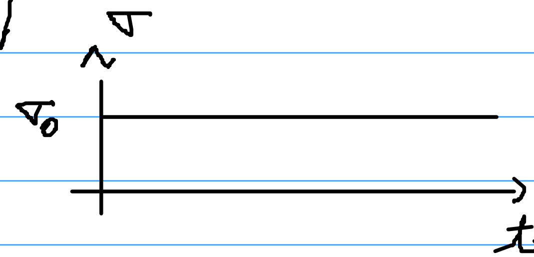
a) Le modèle de Kelvin–Voigt

$$\sigma = E\varepsilon + \eta\dot{\varepsilon}$$

exemple

$t < 0 \quad \sigma = 0$

$t \geq 0 \quad \sigma_0 = 0$

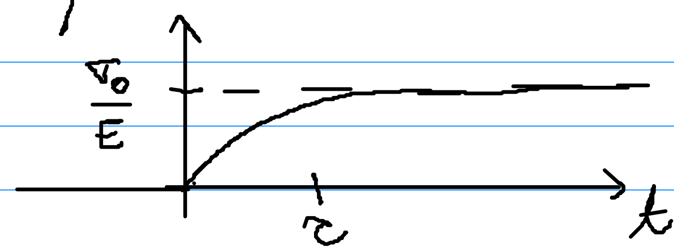


$$\dot{\varepsilon} + \frac{E}{\eta}\varepsilon = \frac{\sigma_0}{\eta} \qquad \tau = \frac{\eta}{E}$$

$t \ll \tau$ réponse visqueuse

$t \gg \tau$ réponse élastique

$$\varepsilon = \frac{\sigma_0}{E}\left(1 - e^{-t/\tau}\right)$$



contrainte oscillante $\quad \sigma = \sigma_0 \cos \omega t$

$$\sigma^* = \sigma_0\, e^{i\omega t}$$

$$\varepsilon^* = \varepsilon_0\, e^{i\omega t}$$

$$\dot{\varepsilon}^* + \frac{E}{\eta}\varepsilon^* = \frac{\sigma^*}{\eta}$$

$$\left(i\omega + \frac{E}{\eta}\right)\varepsilon_0 = \frac{\sigma_0}{\eta}$$

$$\boxed{\varepsilon_0 = \frac{\sigma_0}{E + i\omega\eta}}$$

$$\tilde{\sigma}^* = \underbrace{(E + i\omega\eta)}_{G \,=\, E + i\omega\eta} \, \tilde{\varepsilon}^*$$

$$G' = \mathrm{Re}(G) = \text{module élastique} = \text{module de stockage}$$

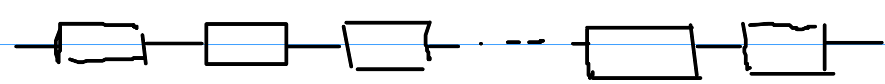
$$G'' = \mathrm{Im}(G) = \omega\eta = \text{module visqueux} = \text{module de perte}$$

$\varepsilon = \varepsilon_0 \cos \omega t$

$$\hookrightarrow \sigma = \mathrm{Re}(\sigma^*) = \underbrace{E\varepsilon_0 \cos\omega t}_{\text{réponse en phase}} - \underbrace{\omega\eta\,\varepsilon_0 \sin\omega t}_{\text{réponse en opposition de phase}}$$

b) L'exemple des polymères et l'élasticité entropique

polymère



$\times N$

ex latex

$\times N$

Comportement en traction

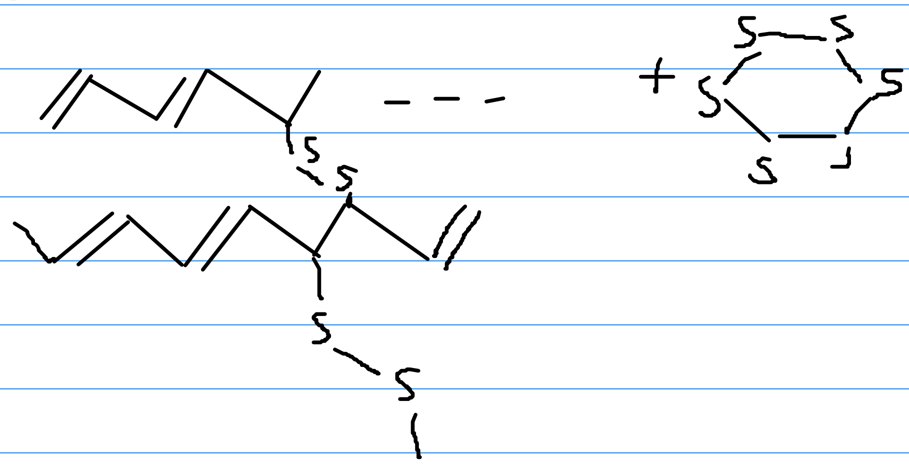
* faible traction = résistance élastique d'origine entropique

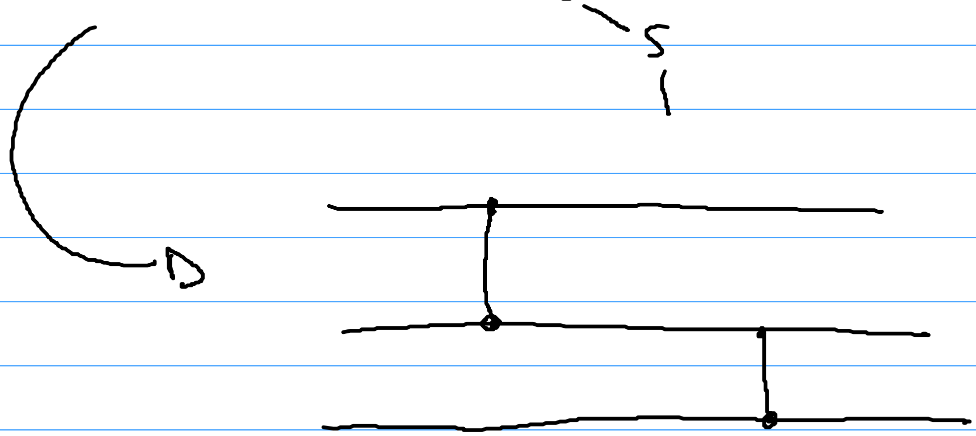
* + forte traction => écoulement des chaîne

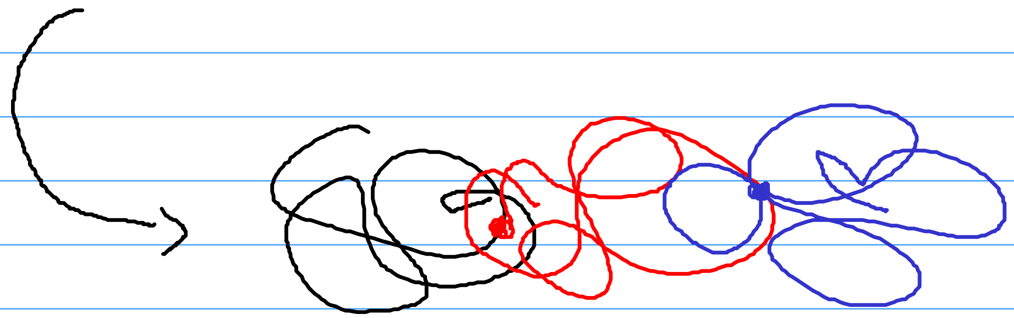
=> liquide viscoélasticité
=> pour avoir un solide
= réticulation

Réticulation

ex







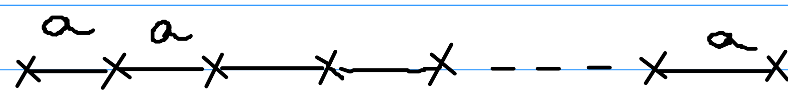
* faible traction = résistance élastique d'origine entropique $\Rightarrow E_e$

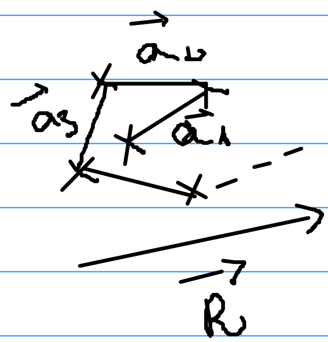
* + forte traction $\Rightarrow$ écoulement des chaîne

* très forte traction $\Rightarrow$ résistance des nœuds (liaisons chimiques) $\Rightarrow E_r$

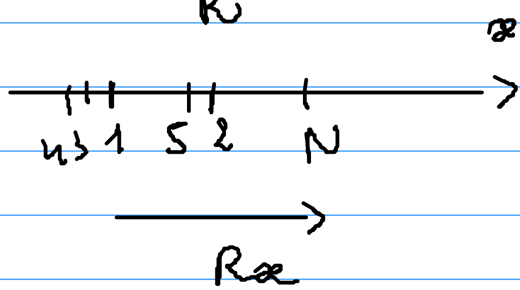
$$E_r \gg E_e$$

Elasticité entropique

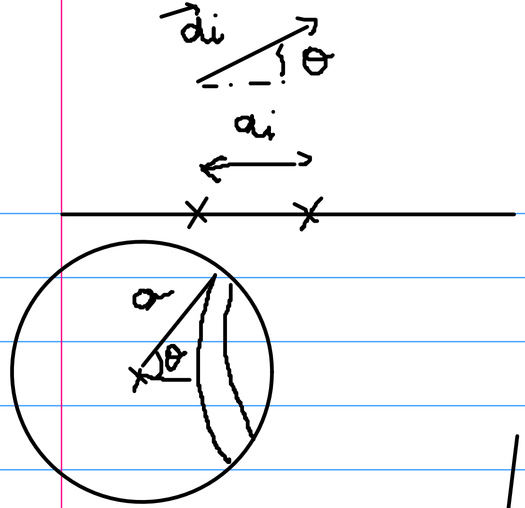




marche aléatoire
$\vec{R}\,(a, N)$



$$\vec{R} = \sum \vec{a_i} \Rightarrow \langle \vec{R} \rangle = \vec{0}$$
$$\langle \vec{R}^2 \rangle \neq 0$$



$$a_i = a\cos\theta$$

probabilité

$$\langle a_x \rangle = \int_0^\pi a\cos\theta \; p(\theta)$$

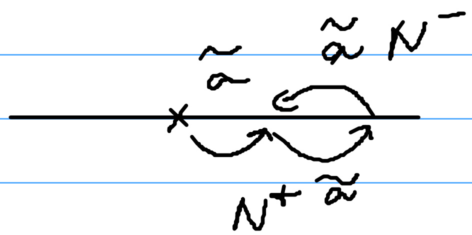
$$= \int_0^\pi a\cos\theta \, \frac{2\pi a^2 \sin\theta}{4\pi a^2} \, d\theta = 0$$

$$\langle a_x^2 \rangle = \int_0^\pi \frac{1}{2} a^2 \cos^2\theta \sin\theta \, d\theta = \frac{a^2}{2}\left[-\frac{\cos^3\theta}{3}\right]_0^\pi$$

$$= \frac{a^2}{3}$$

pas moyen

$$\tilde{a} = \frac{a}{\sqrt{3}}$$



N^+ pas vers la droite

N^- pas vers la gauche

$N = N^+ + N^-$

$$P(N^+, N^-) = \frac{1}{2^N} \frac{N!}{N^+! \, N^-!}$$

$$n! = \underbrace{\left(\frac{n}{e}\right)^n \sqrt{2\pi n}} \left(1 + \frac{1}{12n} + \frac{1}{288 n^2} + \cdots\right)$$

$$\begin{aligned}
\ln P = & -N \ln 2 \\
& + N \ln N - \cancel{N} + \ln\sqrt{\cancel{2\pi} N} \\
& - N^+ \ln N^+ + \cancel{N^+} - \ln\sqrt{\cancel{2\pi} N^+} \\
& - N^- \ln N^- + \cancel{N^-} - \ln\sqrt{2\pi N^-}
\end{aligned}$$

$$N^+ = \frac{N}{2}\left(1+\frac{2m}{N}\right) \qquad N^- = \frac{N}{2}\left(1-\frac{2m}{N}\right)$$

$$\ln P(N^+,N^-) = -N\ln 2 - \frac{1}{2}\ln 2\pi + N\ln N + \frac{1}{2}\ln N$$

$$-\frac{N}{2}\left(1+\frac{2m}{N}\right)\ln\frac{N}{2} - \frac{N}{2}\left(1+\frac{2m}{N}\right)\ln\left(1+\frac{2m}{N}\right)$$

$$-\frac{1}{2}\ln\frac{N}{2} - \frac{1}{2}\ln\left(1+\frac{2m}{N}\right)$$

$$-\frac{N}{2}\left(1-\frac{2m}{N}\right)\ln\frac{N}{2} - \frac{N}{2}\left(1-\frac{2m}{N}\right)\ln\left(1-\frac{2m}{N}\right)$$

$$-\frac{1}{2}\ln\frac{N}{2} - \frac{1}{2}\ln\left(1-\frac{2m}{N}\right)$$

$$= -\frac{1}{2}\ln 2\pi - \cancel{N\ln 2} + \frac{N}{2}\left(\cancel{1}+\cancel{\frac{2m}{N}}\right)\ln 2 + \frac{1}{2}\ln 2$$

$$+\frac{N}{2}\left(\cancel{1}-\cancel{\frac{2m}{N}}\right)\ln 2 + \frac{1}{2}\ln 2$$

$$+\left(\cancel{N} + \cancel{\frac{1}{2}} - \frac{N}{2}\left(\cancel{1}+\cancel{\frac{2m}{N}}\right) - \frac{N}{2}\left(\cancel{1}-\cancel{\frac{2m}{N}}\right) - \cancel{\frac{1}{2}} - \frac{1}{2}\right)\ln N$$

$$+\left(-\frac{N}{2}\left(1+\frac{2m}{N}\right) - \frac{1}{2}\right)\ln\left(1+\frac{2m}{N}\right)$$

$$+\left(-N/2\,(1-2m/N) - 1/2\right)\ln(1-2m/N)$$

$$= -\frac{1}{2}\ln 2\pi + \ln 2 - \frac{1}{2}\ln N$$

$$-\left(\frac{N}{2}\left(1+\frac{2m}{N}\right)+\frac{1}{2}\right)\ln\left(1+\frac{2m}{N}\right)$$

$$-\left(\frac{N}{2}\left(1-\frac{2m}{N}\right)+\frac{1}{2}\ln\left(1-\frac{2m}{N}\right)\right.$$

$$= \ln\sqrt{\frac{2}{\pi N}}$$

$$-\left(\frac{N}{2}\left(1+\frac{2m}{N}\right)+\frac{1}{2}\right)\left(\frac{2m}{N}-\frac{4m^2}{2N^2}\right)$$

$$-\left(\frac{N}{2}\left(1-\frac{2m}{N}\right)+\frac{1}{2}\right)\left(-\frac{2m}{N}-\frac{4m^2}{2N^2}\right)$$

$$=\ln\sqrt{\frac{2}{\pi N}}-\left(\frac{N}{2}+1\right)\left(-\frac{2m^2}{N^2}\times 2\right)-\frac{2m^2}{N}\times 2$$

$$=\ln\sqrt{\frac{2}{\pi N}}+\frac{2m^2}{N}+\underbrace{\frac{4m^2}{N^2}}_{\ll}-\frac{4m^2}{N}$$

$$\ln P(N^+,N^-)=\ln\sqrt{\frac{2}{\pi N}}-\frac{2m^2}{N}$$

$$P(N^+,N^-)=\sqrt{\frac{2}{\pi N}}\exp\left(-\frac{2m^2}{N}\right)$$

Gaussienne $\frac{1}{\sqrt{2\pi}\,\sigma}e^{-\frac{x^2}{2\sigma^2}}$

$$\sigma=\sqrt{\frac{N}{4}}$$

$P(R_x)$?

$$m=\frac{N^+-N^-}{2}$$

$$R_x=(N^+-N^-)\frac{a}{\sqrt{3}}=2ma/\sqrt{3}$$

$$P(R_x,N)=P_0\,e^{-\frac{3R_x^2}{2a^2N}}$$

$$P_0=\frac{\sqrt{3}}{\sqrt{2\pi}\sqrt{N}a}\qquad \sigma^2=\frac{Na^2}{3}$$

$$\boxed{P(R_x, N) = \sqrt{\frac{3}{2\pi N a^2}}\; e^{-\frac{3R_x^2}{2Na^2}}}$$

$$P(N, \vec{R}) = P(R_x, N)\, P(R_y, N)\, P(R_z, N)$$

$$= \left(\frac{3}{2\pi N a^2}\right)^{3/2} e^{-\frac{3\vec{R}^2}{2Na^2}}$$

$$\langle \vec{R}^2 \rangle = \int_0^{\infty} R^2\, P(N, \vec{R})\, 4\pi R^2\, dR$$

$$= \int_0^{+\infty} \left(\frac{3}{2\pi N a^2}\right)^{3/2} e^{-\frac{3R^2}{2Na^2}}\; 4\pi R^4\, dR$$

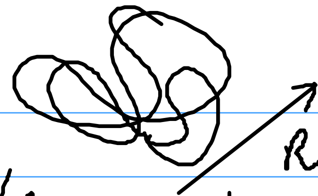
$$x = \sqrt{\frac{3R^2}{2Na^2}} \qquad dx = \sqrt{\frac{3}{2Na^2}}\, dR$$

$$= 4\cancel{\pi} \left(\frac{3}{2\cancel{\pi} N a^2}\right)^{3/2} \left(\frac{2Na^2}{3}\right)^2 \sqrt{\frac{2Na^2}{3}}\; \underbrace{\int_0^{+\infty} e^{-x^2} x^4\, dx}_{\frac{3}{8}\cancel{\sqrt{\pi}}}$$

$$= \frac{1}{2} \left(\frac{2Na^2}{3}\right)^{2+\frac{1}{2}-\frac{3}{2}} \times 3 = Na^2$$

$$\boxed{R^2 = Na^2} \qquad \boxed{R = \sqrt{N}\, a}$$

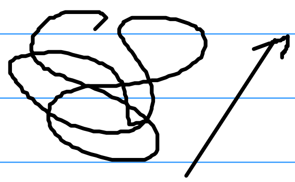
$$R = \sqrt{N}\, a$$



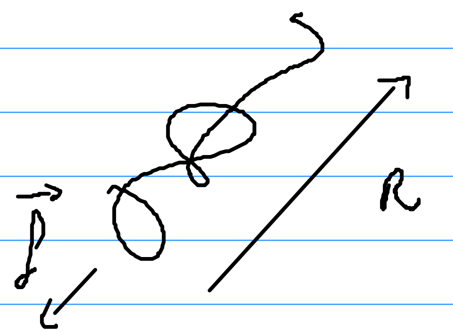
$$P(N,R) = \left(\frac{3}{2\pi N a^2}\right)^{3/2} \exp\left(-\frac{3R^2}{2Na^2}\right)$$

élasticité des polymères

énergie libre $F = \cancel{U} - \underbrace{TS}_{\sim N}$



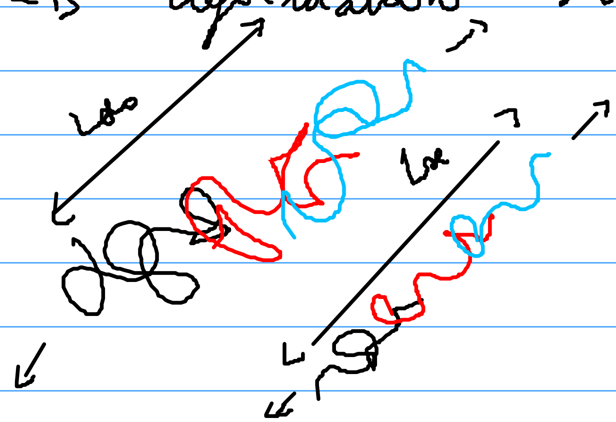
$$R_0 = \sqrt{N}\, a$$



$$\vec{R} = x\vec{i} + y\vec{j} + z\vec{k}$$

$$\vec{R_0} = x_0\vec{i} + y_0\vec{j} + z_0\vec{k}$$

$\rightsquigarrow$ déformation $\lambda_x = \dfrac{x}{x_0}$ $\lambda_y = \dfrac{y}{y_0}$ $\lambda_z = \dfrac{z}{z_0}$

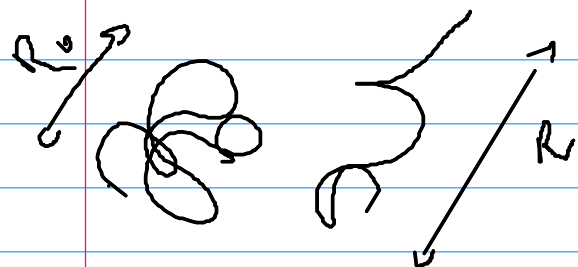


$$\lambda_x = \frac{x}{x_0} = \frac{L_x}{L_{x_0}}$$

$$S = k_B \ln \Omega = k_B \ln P$$

$$P(\vec{R},N) \simeq \overbrace{\left(\frac{3}{2\pi N a^2}\right)^{3/2}}^{\phi_0} e^{-\frac{3R^2}{2Na^2}}$$

$$S = k_B \ln \phi_0 - \frac{3}{2} k_B \frac{R^2}{Na^2}$$



$$\Delta S = -\frac{3}{2} k_B \frac{R^2 - R_0^2}{\langle R_0^2 \rangle} < 0$$

$$\frac{R^2 - R_0^2}{R_0^2} = \frac{x^2 + y^2 + z^2 - (x_0^2 + y_0^2 + z_0^2)}{\langle R_0^2 \rangle}$$

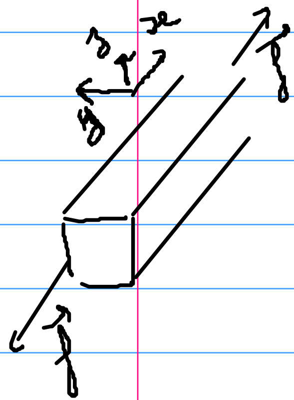
$$= \frac{(\lambda_x^2 - 1)\, x_0^2 + (\lambda_y^2 - 1)\, y_0^2 + (\lambda_z^2 - 1)\, z_0^2}{\langle R_0^2 \rangle}$$

$$\frac{\Sigma (R^2 - R_0^2)}{\langle R_0^2 \rangle} = \frac{(\lambda_x^2 - 1)\Sigma x_0^2 + (\lambda_y^2 - 1)\Sigma y_0^2 + (\lambda_z^2 - 1)\Sigma z_0^2}{\langle R_0^2 \rangle}$$

$$\Big\{ \langle x_0^2 \rangle = \frac{\langle R_0^2 \rangle}{3} = \frac{\Sigma x_0^2}{N}$$

$$\frac{\Sigma (R^2 - R_0^2)}{\langle R_0^2 \rangle} = \frac{N}{3}\left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)$$

$$\Delta F = -T\Delta S = \frac{1}{2} N k_B T \left(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3\right)$$



Traction uniaxiale + matériau incompressible

Volume = cst

$$L_{x_0} L_{y_0} L_{z_0} = L_x L_y L_z \qquad \lambda_y = \lambda_z$$
$$\lambda_x = \lambda$$

$$\lambda_x \lambda_y \lambda_z = 1$$

$$\lambda_y = \lambda_z = \frac{1}{\sqrt{\lambda}}$$

$$\Delta F = \frac{N}{2} k_B T \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)$$

force de traction

$$f = \frac{\partial \Delta F}{\partial L_x} = \frac{1}{L_{x_0}} \frac{\partial \Delta F}{\partial \lambda}$$

$$= \frac{N}{\cancel{2}} k_B T \frac{1}{L_{x_0}} \left(\cancel{2}\lambda - \frac{\cancel{2}}{\lambda^2} \right)$$

contrainte vraie

$$\sigma_V = \frac{f}{L_z L_y}$$

contrainte ingénieur

$$\sigma_I = \frac{f}{L_{z_0} L_{y_0}}$$

$$\lambda = L_x / L_{x_0}$$

$$\sigma_V = N k_B T \frac{1}{L_x L_y L_z} \left(\lambda^2 - \frac{1}{\lambda} \right) = \frac{N}{V} k_B T \left(\lambda^2 - \frac{1}{\lambda} \right)$$

$$\sigma_I = \frac{N k_B T}{V} \left(\lambda - \frac{1}{\lambda^2} \right)$$

→ à grande déformation $\sigma_I = \frac{N}{V} k_B T \lambda$

$$\sigma_I = E_e \lambda \qquad \boxed{E_e = \frac{N}{V} k_B T}$$

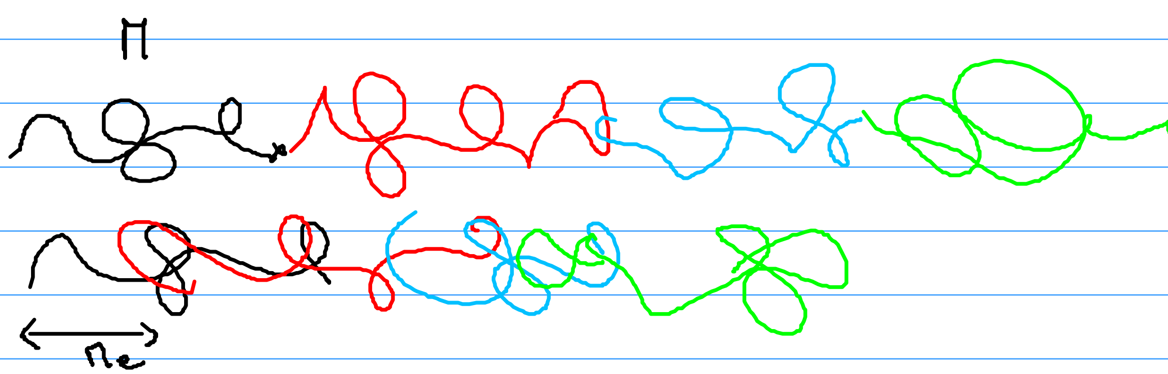
$E_e \propto T$ $\Rightarrow$ quand un elastique chauffe, son elasticité $\nearrow$

$\Rightarrow$ elasticité entropique

$$PV = N k_B T = \frac{N}{\mathcal{N}_a} RT \Rightarrow P = \frac{N}{V} \frac{RT}{\mathcal{N}_A}$$

$$P = \frac{N}{V} k_B T = E_e \qquad = RT \frac{\rho}{M_e}$$

$$\boxed{E_e = \frac{RT}{M_e} \rho}$$



M_e = masse molaire entre enchevêtrement
N_e = nb de monomères entre enchevêtrements
$R_e = N_e \sqrt{a}$
= taille d'une sous pelote non enchevêtrée