Elastomers & Gels

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Outline of lectures :

I What are elastomers ? gels ?

- examples from nature & technology

Microscopic picture ?

- compare/contrast with other 'solid' phases
- thermodynamics ; enthalpy, entropy & elasticity
- Simple models of chain elasticity & dynamics

Macroscopic picture ?

- elasticity (linear/nonlinear), visco/poro-elasticity
- fracture/failure, flow, ageing
- bulk vs. low-dimensional behaviors

II Formalism & Phenomenology (Statics) of elastomers

- Extension, compression, dilatation, shear, lubrication
- Bending, twisting, buckling
- 'Free'-surface phenomena ; contact, adhesion, fracture

~~Dynamical phenomena~~

- ~~wave propagation in bulk, along interfaces~~
- ~~damping, inelasticity, shocks, ...~~

Instabilities

- geometric, material, ~~thermodynamic~~ nonlinearities
- examples & (simple) analysis

III. Formalism & Phenomenology (Dynamics) of gels

- role of fluid movements in clays, colloids, sponges, cells, tissues, ...
- swelling & diffusion

Poroelasticity

- passive
- active, i.e. with phase transitions, electrokinetics ....

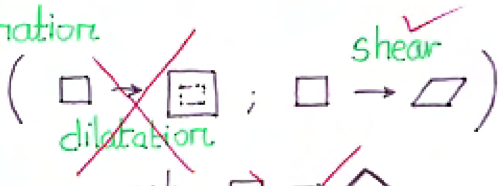
References :

- Polymer physics ; M. Rubinstein & R. Colby (Oxford, 2003)
- Physics of rubber elasticity ; L. Treloar (Oxford, 1972)
- Mathematical treatise on elasticity ; A.E.H. Love (Dover, 1944)
- Poroelasticity in geomechanics ; C. Wang (Princeton, 1999)

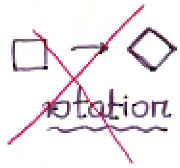
What is a solid ?

- condensed phase which resists <u>change in shape</u>,

i.e. deformation



not



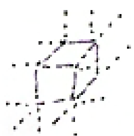
i.e. it has finite shear rigidity
(resists changes in material angles !)

[cf. Rheology definition : $\underset{\text{complex modulus}}{G^*(\omega)} = \underset{\text{storage modulus}}{G'(\omega)} + i\,\underset{\text{loss modulus}}{G''(\omega)}$

$$\lim_{\omega \to 0} G^*(\omega) = G_{eq} \neq 0 \; !$$]

types of solids : crystalline

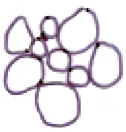
- underlying reference state (periodic 'Bravais' lattice)



e.g. 'pure', 'clean' Si, ...

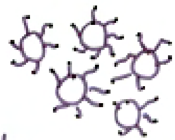
amorphous

- disordered 'reference' state



grains

polymer networks
(& entanglements ?)

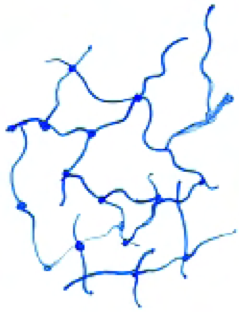


colloids

'glasses'

- heterogeneous
- scale-dependent properties ?

- out-of-equilibrium
- nonlinear



Many polymer chains in solvent

gelation ↓ crosslinked (chemically, physically)

A large (∞) branched cluster — covalent ? pH, temp.

∞ branched polymer - Gel (via a sol-gel transition) (in solvent)

∞ branched polymer - Elastomer (e.g. via vulcanization) (no solvent)

although the distinction is more often than not subtle

(fluid permeation ?)

Elastomers . e.g. (latex) rubber , elastin, collagen , resilin , spider silk

vertebrates — insects

\+ many artificial long-chain polymers that are chemically crosslinked.

- capable of large, reversible deformations
- high toughness (energy absorption)
- often composites, large mol. wt polymers + crosslinkers / fillers

Gels . e.g. yogurt, jello, tofu, ...

clays & colloids (some types)

\+ artificial analogs (polyacrilamide based...)

- very soft (low stiffness)
- fluid-filled (large volume fraction)

Microscopic view

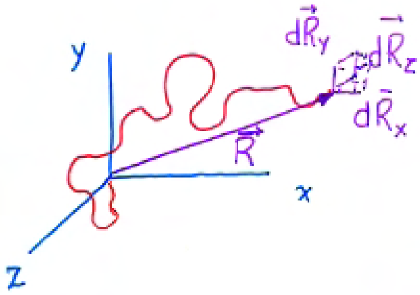
- connecting configuration to (mechanical) properties

(focus here on polymers ; contrast with colloids ?)

single polymer chain

$\sim$ random walk in 3-d

- ignore steric/self-avoidance effects & interactions
- infinitely flexible at joints between monomers
- large # of monomers N of size b



$\therefore$

$$P_{3d}(N,\vec{R}) = \left(\frac{3}{2\pi N b^2}\right)^{3/2} e^{-3\vec{R}^2/2Nb^2}$$

product of 3 Gaussians ! independent

where $\langle \vec{R} \rangle = 0$ - mean end-end distance

$\langle \vec{R}^2 \rangle = Nb^2 = R_G^2$ - radius of gyration

& $dP(N,R) = P_{3d}(N,\vec{R}) . 4\pi R^2 dR$ - end-to-end probability distribution

(Note : Not valid when $|\vec{R}| > Nb$! Why ?)

Thermodynamics : $\underset{\text{entropy}}{S} = k_B \ln P_{3d} + \text{const.}$

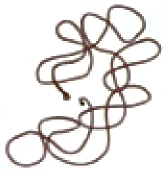
$$= -\frac{3}{2} k_B \, \vec{R}^2/Nb^2 + \text{const.}$$

$$dF = dU - TdS \qquad (\text{const. } T)$$

Helmholtz free energy

$$= -TdS \qquad (\text{if } dU = 0 \text{ as here !})$$

i.e. $\;dF/d\vec{R} = +\frac{1}{2}\,\frac{3k_BT}{Nb^2}\cdot\vec{R} = \underset{\sim}{f}$ (force required to keep the ends a distance $\vec{R}$ apart)

P_{3d} () $\gg$ P_{3d} ()

more configurations — higher S fewer configurations — lower S

i.e. external work done by $\underset{\sim}{f}$ reduces S (not does increase U !)

compare with spring (Hookean): $\mathcal{U} = \frac{1}{2}k(x-x_0)^2$

stiffness $k = \dfrac{3k_BT}{Nb^2}$, $\nearrow$ with T, $\searrow$ with N

natural length $x_0 = 0$! (e.g. slinky)

valid when $\vec{R} \ll Nb$, i.e. fails when $|\underset{\sim}{f}| \approx k_BT/Nb^2 \cdot Nb$ $\sim k_BT/b$

e.g. for b (Kuhn length) $\sim 1\,nm$, (polyethylene) $T \sim 300^\circ K$

$|\underset{\sim}{f}| \sim 4.10^{-12}\,N \approx \underset{\sim}{4\,pN}$.

(e.g. DNA, $b \sim 100\,nm$, $|\underset{\sim}{f}| \sim 10^{-14}\,N \ll$ forces applied by motors etc. $\Rightarrow$ need a better description !)

2 important effects left out:

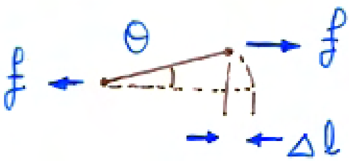
(i) finite chain length $\Rightarrow$ nonlinearity

(ii) finite short-range 'bending' interaction

Scaling concepts :

(i) 'Kuhn' links of length b → freely jointed chain

$f \approx 0$ $\qquad$ f 'large' $\qquad$ $R \sim R_{max}$



$$R \sim R_{max} - \underbrace{\frac{R_{max}}{b}}_{\#\text{ of segments (blobs)}} \cdot \underbrace{\Delta l}_{\text{red'n in length per 'blob'}}$$

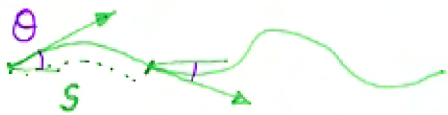
equipartition ⇒ $k_B T \sim f\, b \langle 1 - \cos\theta \rangle$

i.e. $k_B T \sim f\, b \langle \theta^2 \rangle$ $\qquad$ ⇒ $\Delta l \sim b\langle \theta^2 \rangle \sim k_B T / f$

$$\therefore \quad R \sim R_{max} - \frac{R_{max}}{b} \cdot \frac{k_B T}{f} \quad \Rightarrow \quad f \sim \frac{k_B T}{b} \cdot \frac{1}{(1 - R/R_{max})}$$

'strain' stiffening !

(ii) Persistence of tangent ?



$$\langle \cos\theta(s) \rangle = e^{-s/2l_p}$$

energetics : $k_B T \sim B \underbrace{\int K^2 \, ds}_{\text{bending energy}} \sim B \cdot 1/l_p^2 \cdot l_p$

K - curvature

B - bending stiffness ($N.m^2$)

$l_p \sim B/k_B T$ - persistence length $\qquad$ (~ 50 nm, DNA)

Macroscopic view (Continuum / coarse-grained)

T - temp.
V - volume
l - extension

elasticity from entropy $\Rightarrow$ at const. extension,

$$\partial f / \partial T \big|_{l,V} > 0$$

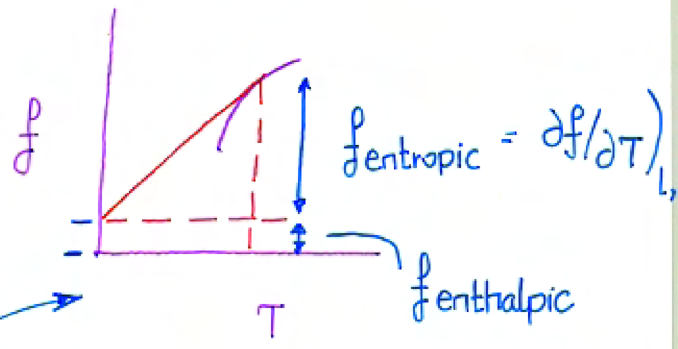
(unlike for a crystal !)

$\Rightarrow$ at const. temperature $\partial S / \partial l \big|_{T,V} < 0$ (i.e. heat is released !)

indeed $\partial S / \partial l \big|_{T,V} = - \partial f / \partial T \big|_{l,V}$ Maxwell relation

energetic (enthalpic) contribution ?

$$f_{enthalpic} / f_{entropic} \sim 0{\cdot}1$$



experiment

Scaling up from single chain ?

(i) Gaussian chain !

(ii) Affine deformations (i.e. μ-scopic def. $\equiv$ macro def.) for cross-links

(iii) Isochoric (no volume changes)

chain def.

Affine $\Rightarrow$ $R_x = \lambda_1 R_{x_0}$

$R_y = \lambda_2 R_{y_0}$

$R_z = \lambda_3 R_{z_0}$

$$\Delta F = -T \Delta S = +\frac{3}{2} \frac{k_B T}{N b^2} \cdot \left[(\lambda_1^2 - 1) \sum_{i=0}^{\rho} (R_{x_0}^2)_i + (\lambda_2^2 - 1) \sum_{i=0}^{\rho} (R_{y_0}^2)_i + (\lambda_3^2 - 1) \sum_{i=0}^{\rho} (R_{z_0}\right.$$

Random orientations (ideal state!) $\Rightarrow$ $\sum (R_{x_0})_i^2 = \sum (R_{y_0})_i^2$

$$= \sum (R_{z_0})_i^2 = \frac{1}{3} \sum_{i=1}^{\rho} R^2$$

$$= \rho N b^2/3$$

$$\therefore \quad \Delta F' = - T \Delta S = \frac{1}{2} \rho k_B T \left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right)$$

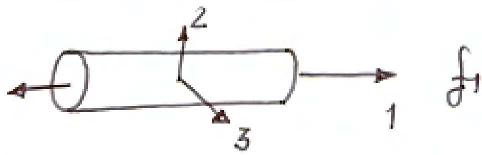
$\rho k_B T \equiv G' =$ shear modulus · 1 constant elasticity!

$\lambda_i \equiv$ stretches (principal)

⊕ Incompressibility (nonlinear constraint) $\lambda_1 \lambda_2 \lambda_3 = 1.$

Neo-Hookean model : $\mu \in [10^3 \sim 10^7]$ Pa

e.g. Uni-axial extension



$$\lambda_1 = \lambda, \quad \lambda_2 = \lambda_3 = 1/\sqrt{\lambda}$$

$$\therefore \quad \Delta F' = \frac{1}{2} \rho k_B T \left(\lambda^2 + \frac{2}{\lambda} - 3 \right)$$

& the force $f_1 = \dfrac{\partial (\Delta F)}{\partial l_1} = \dfrac{\partial (\Delta F)}{\partial (\lambda l_1^0)} = \dfrac{1}{l_1^0} \dfrac{\partial (\Delta F)}{\partial \lambda}$

$$= \frac{\rho k_B T}{l_1^0} \left(\lambda - \frac{1}{\lambda^2} \right) \cdot l_1^0 \cdot l_2^0 \, l_3^0$$

true stress $= f_1 / l_2 l_3 = \dfrac{\rho k_B T}{\cancel{l_1^0 l_2^0 l_3^0}} \cdot \left(\lambda^2 - \dfrac{1}{\lambda} \right) \cancel{l_1^0 l_2^0 l_3^0}$

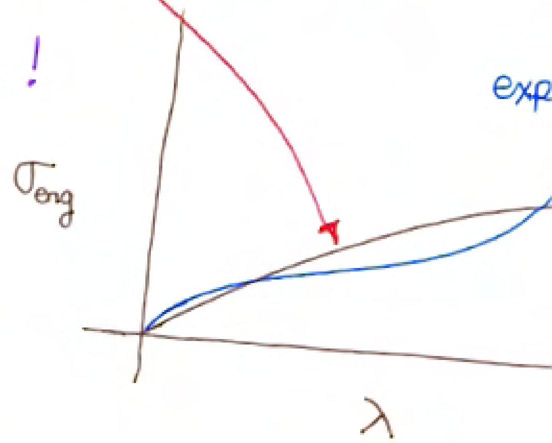
per unit current area.

engineering stress $= \rho k_B T \left(\lambda - \frac{1}{\lambda^2} \right)$ - per unit reference a

Note : Many definitions of stress !

Cauchy stress :-

relative to current configuration



Non-affine models :

- difficult to calculate
- need extra assumptions
- phenomenological

$\oplus$

Simulations $\rightarrow$??

Simple fix - $\Delta F = -J_c \log \left(1 - J_1/J_c \right) \times \cdot \frac{\rho k_B T}{2}$ (Gent,

new const.

$J_1 = \sum_{i=1}^{3} \lambda_i^2 - 3$

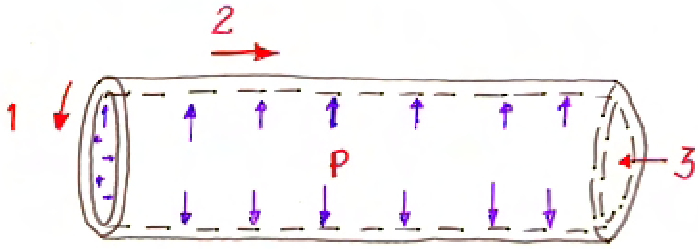
$J_1 \ll J_c \Rightarrow \Delta F \rightarrow$ neo - Hookean model

$J_1 \rightarrow J_c \Rightarrow \frac{\partial(\Delta F)}{\partial J_1} \rightarrow \infty \left[\frac{1}{1 - J_1/J_c} \right]$ ✓

- no μ-scopic derivation !

Consequences ? Inflation instabilities ....

Shock waves .....



R_0 - undeformed radius

t_0 - " thickness

$t_0/R_0 \ll 1$

$\lambda_1 \lambda_2 \lambda_3 = 1$

$\Rightarrow \lambda_3 = 1/\lambda_1\lambda_2$ = 'thickness' stretch.

$R = R_0 \lambda_1$, $t = t_0/\lambda_1\lambda_2$

$\sigma_3 \approx p$, $\sigma_2 = pR/2t$ $\quad \left[\because \sigma_2 . 2t . \pi R = p . \pi R^2\right]$

$\ll \sigma_1, \sigma_2$

$\sigma_1 = pR/t = 2\sigma_2$ $\quad \left[\because \sigma_1 2tL = p\, 2R . L\right]$

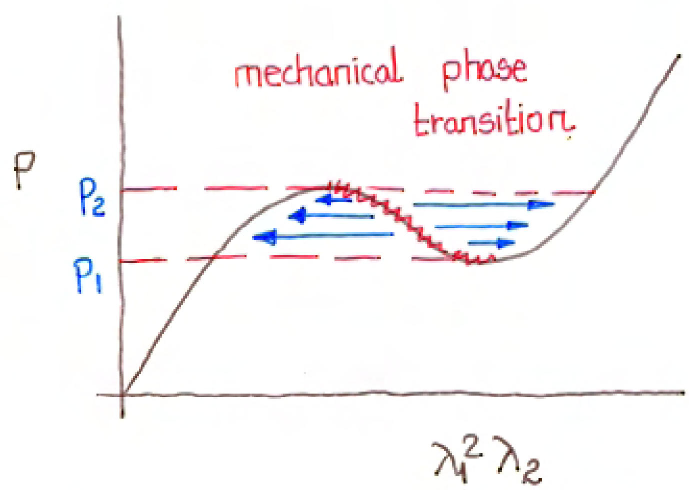
But $\Delta F = -J_c \cdot \rho \dfrac{k_B T}{2} \ln\left[1 - J_1/J_c\right]$, $J_1 = \left(\lambda_1^2 + \lambda_2^2 + \dfrac{1}{\lambda_1^2\lambda_2^2} - 3\right)$

$\sigma_1 = \lambda_1 \dfrac{\partial(\Delta F)}{\partial \lambda_1}$ etc.

$\sim \left(\lambda_1^2 - \dfrac{1}{\lambda_1^2\lambda_2^2}\right) \Big/ \left(1 - J_1/J_c\right)$

$\rightarrow$ find $p(\lambda_1^2\lambda_2)$

local volume expansion ratio



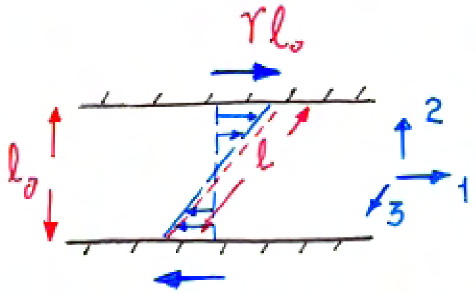
As $p \uparrow$,

multiple states for $p \in [p_1, p_2]$

i.e. aneurysms / bubbles !

'physical' explanation ??

Shear ?



γ - shear strain

= $\angle$ of rotation of material element

If l_0 = const. , $l = l_0(1+4\gamma^2)^{1/2}$

$\sim l_0(1+2\gamma^2)$

i.e. shear $\Rightarrow$ extension (nonlinear effect !)

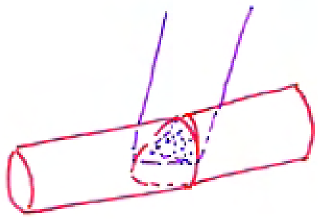
i.e. shear $\Rightarrow$ normal stress (tensile !) i.e. $\sigma_{22} \neq 0$

Also, $\because$ of incompressibility $\Rightarrow$ $\sigma_{33} \neq 0$

if confined in out-of-plane direction !

σ_{22} , σ_{33} $\sim G' \underbrace{\gamma^2}$

$\hookrightarrow$ jamming !



while cutting / sawing .

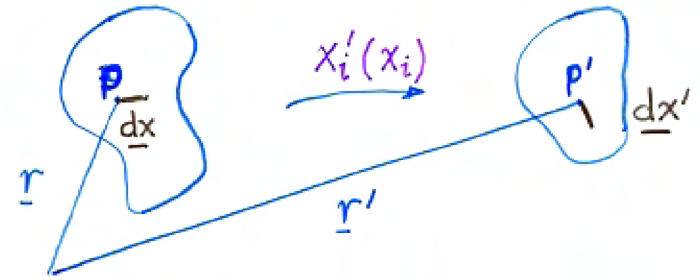
"Poynting - Weissenberg" effect

So far ; simple homogeneous deformations .

Inhomogeneous deformations ??

$\hookrightarrow$ tensorial formalism for elasticity / continuum mechanics

Geometry of deformation



displacement

$$\underline{u} = \underline{r}' - \underline{r}$$

✓ $\underline{u}(P)$ - Lagrangian description ✓

$\underline{u}(P')$ - Eulerian –"–

$$u_i = x_i'(x_i) - x_i \quad ; \quad i = 1,2,3$$

$$dl = |d\underline{x}| = \sqrt{dx_1^2 + dx_2^2 + dx_3^2} \quad \ldots\ldots$$

$$dl' = |d\underline{x}'| = \sqrt{(du_1 + dx_1)^2 + \ldots}$$

i.e. $\quad dl'^2 = dl^2 + 2\epsilon_{ik}\, dx_i\, dx_k$ — change in shape locally

$$\epsilon_{ik} = \frac{1}{2}\left(\partial u_i/\partial x_k + \partial u_k/\partial x_i\right) + \frac{1}{2}\,\partial u_l/\partial x_i\,\partial u_l/\partial x_k$$

Strain tensor (symmetric) nonlinear (geometry)

Eigenvalues of $(\delta_{ik} + \epsilon_{ik}) = \lambda_j \ , \ j = 1,2,3$

↳ principal stretches

$\lambda_j - 1$ - principal strains

Strain invariants : $\operatorname{tr}\underline{\epsilon}\ ,\ \det\underline{\epsilon}\ ,\ \operatorname{tr}\underline{\epsilon}^2 - (\operatorname{tr}\underline{\epsilon})^2$

Energy/volume $\mathcal{U} = \mathcal{U}(\ldots, \ldots, \ldots)$

or F

Stress (tensor) $\sigma_{ik} = f(\epsilon_{ik})$

possibly nonlinear !

$$F = \int \frac{1}{2} \cdot \sigma_{ik} \epsilon_{ik} \, dv$$

(linear) isotropic

Hookean elasticity : $\epsilon_{ik} = \frac{1}{2}\left(\partial u_i/\partial x_k + \partial u_k/\partial x_i\right)$

$$dF = \frac{1}{2} K \epsilon_{ii}^2 + \mu \left(\epsilon_{ik} - \frac{1}{3}\epsilon_{ii}\delta_{ik}\right)^2$$

dilatation ($\nabla \cdot \underline{u}$)

shear (deviatoric) strain

K = dilatational (bulk) modulus

$\mu \equiv G \equiv G'$ = shear modulus

2 const.

(non-central forces)

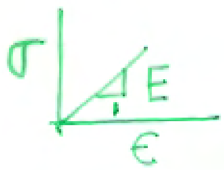
- $K > 0$, $\mu > 0$!

Neo-Hookean model : $\epsilon_{ii} = 0$; nonlinear strain

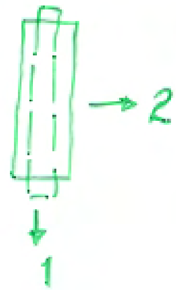
$dF = \mu \epsilon_{ik}^2$; pressure unknown !

Equivalent moduli :

Young's modulus E



uni-axial extension



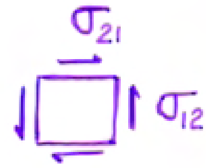
Poisson ratio $\nu = -\epsilon_{22}/\epsilon_{11}$

lateral contraction

$\nu \in [-1, 1/2]$

auxetic   incompressible

Force + torque balance $\quad \sigma_{ij} = \sigma_{ji}$



$\oplus \quad \partial \sigma_{ij} / \partial x_j = 0$

Eqns. of static equilibrium

$$\sigma_{ij} = K \epsilon_{kk} \delta_{ij} + 2\mu \left(\epsilon_{ij} - \tfrac{1}{3} \delta_{ij} \epsilon_{kk} \right)$$

$$\epsilon_{ij} = \tfrac{1}{2} \left(\partial u_i / \partial x_j + \partial u_j / \partial x_i \right)$$

$$\partial \sigma_{ij} / \partial x_j + f_i = 0$$

volumetric force

i.e. $\quad \Delta \underline{u} + \dfrac{1}{1-2\nu} \nabla (\nabla \cdot \underline{u}) = 0 \quad [\text{if } \underline{f} = 0]$

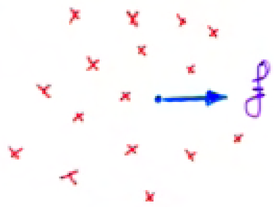
Stokes-Rayleigh analogy:

u (displ.)	$\longrightarrow$	v (velocity)
$\underline{\epsilon}$ (strain)	$\longrightarrow$	$\underline{\dot{\epsilon}}$ (strain rate)
$K \to \infty$ $(\nu \to 1/2)$		no 'bulk' viscosity normally
μ (shear modulus)		η (shear viscosity)

$\Rightarrow \eta \Delta \underline{v} - \nabla p = 0 \quad \leftarrow$ Stokes flow

$+ \quad \nabla \cdot \underline{v} = 0 \qquad$ + Bound. condns. (where dragons lie!)

Point forces, line forces, dipoles etc.



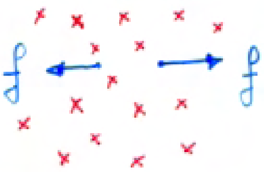
2-d . $\underset{\sim}{u} \sim \frac{f}{G} \ln |r-r'|$

$\epsilon \sim \nabla u \sim \frac{f}{G|r-r'|}$, $\sigma \sim G.\nabla u$

& $\int \sigma \, ds = f = \text{const.}$

3-d $\quad u \sim \frac{f}{G|r-r'|}$ since $\int \sigma \, ds = f$ in 3-d $\Rightarrow \sigma \sim f/r^2$

& //ly for dipoles etc.



2-d : $u \sim f/G|r-r'|$

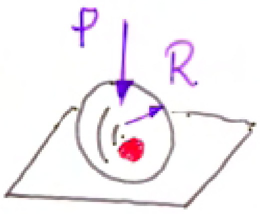
3-d : $u \sim f/G(r-r')^2$

Why ? care

Role of confinement - layers, filaments, plates, membranes etc.

Bulk → surfaces (soft ∵ of geometric freedom !)

Contact & adhesion -:



contact patch size : a $\quad$ sphere radius : R

force : P

small deformation limit $\quad \delta \sim a^2/R$ (parabolic !)

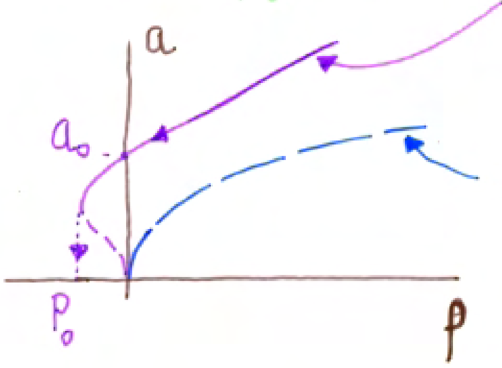
$$U \sim -P\delta + G.(\delta/a)^2.a^3$$

$\Delta U / \Delta \delta = 0$ $\Rightarrow$ $P \sim G\, \underbrace{\delta^{3/2}}_{\text{geometric nonlinearity.}} R^{1/2}$; $a \sim (PR/G)^{1/3}$

Hertz

(cf. deformation of a drop/bubble : $\underset{\text{why ?}}{P \sim \gamma . R}$)

elastomers/gels ? Adhesive contact (γ - energy/area)



a_0 ? contact without ext. force

P_0 ? jump-off force (pull)

· $P_0 \sim \gamma . a$ - dimensional analysis

· $\gamma . a_0^2 \sim G . (\delta / a_0)^2 . a_0^3$ energy balance

$\Rightarrow a_0 \sim (\gamma R^2 / G)^{1/3}$; Colloids $G \sim 10^3$ Pa , $R \sim 10\ \mu m$
$\gamma \sim 10^{-2}\ J/m^2$

$\Rightarrow$ $a_0 \sim 1\ \mu m$, $P_0 \sim 10^{-8}$ N

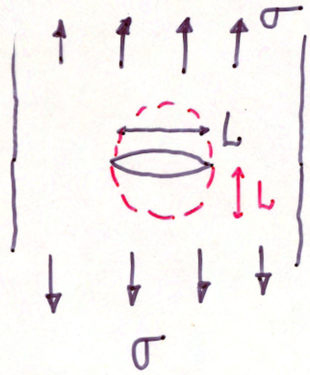
dynamics of soft contacts ? Ageing in gels ?

Fracture/failure ? often spontaneous - why ?

- externally loaded (gravity) + delicate (fragile)

- thermally activated ?

Griffith theory



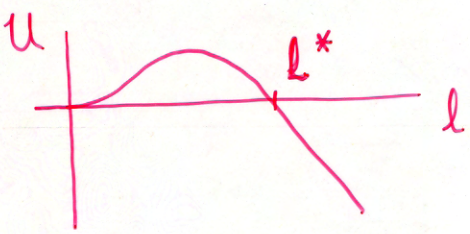
$$U \sim -\sigma^2/G \cdot L^3 + \gamma L^2$$

benefit

cost

$$\partial U/\partial L = 0 \Rightarrow L^* \sim G\gamma/\sigma^2$$

critical crack size for growth



$$U^* \sim G^2\gamma^3/\sigma^4 \quad (3\text{-d})$$

$$\sim G\gamma^2/\sigma^2 \quad (2\text{-d})$$

prob. of failure $\sim e^{-U^*/k_B T}$

& waiting time for failure $\tau \sim e^{U^*/k_B T} \sim e^{G\gamma^2/\sigma^2 k_B T}$ (2-d)

expt. on Langmuir layers (crystalline)

J. Meunier et al.

fracture mechanics

- well developed for brittle materials
- much remains in understanding soft materials

kinetic process (even in the presence of a force!)

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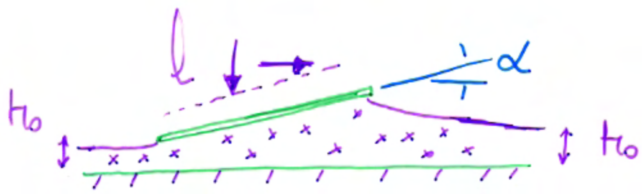
Layers, films and filaments

e.g.

jamming your teeth in place !

or how to increase friction using geometry



Incompressible elastomer.

$$\nabla\cdot\underline{u} = 0 \qquad \underline{u} = (u,v)$$

$$\mu\nabla^2\underline{u} = \nabla p$$

i.e. $\partial u/\partial x + \partial v/\partial y = 0$ (#)

$$\mu\left(\cancel{\partial^2 u/\partial x^2} + \partial^2 u/\partial y^2\right) = \partial p/\partial x$$

$$\mu\left(\cancel{\partial^2 v/\partial x^2} + \partial^2 v/\partial y^2\right) = \partial p/\partial y$$

$\ell \gg h_0$

$\Rightarrow u \gg v$, from (#)

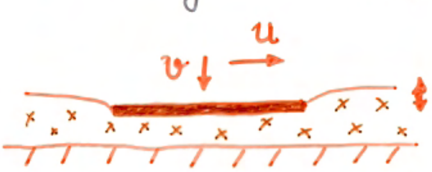
$$p/\ell \sim \mu u/h_0^2 \quad \Rightarrow \quad p \sim \mu u/h_0 \cdot \ell/h_0$$

geometric magnification

Since $v \sim uh/\ell$; $p \sim \mu v/h_0 \cdot (\ell/h_0)^2$

- way to design 'jams' ?? (swelling induced)
- tilt by angle α $\Rightarrow$ normal force $\sim \mu U\alpha . \ell^3/h_0^3$ (WHY?)

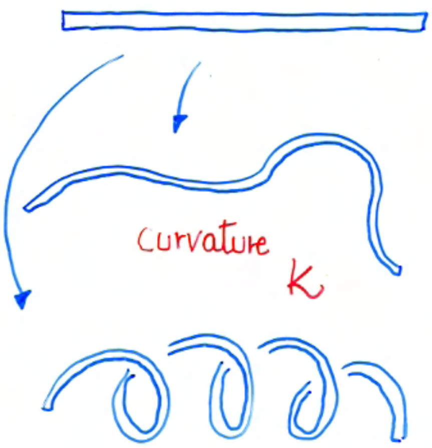
What if the elastomer is compressible ?



(2-d)

force/length $f \sim \mu(v/h_0)\cdot\ell$ ↕

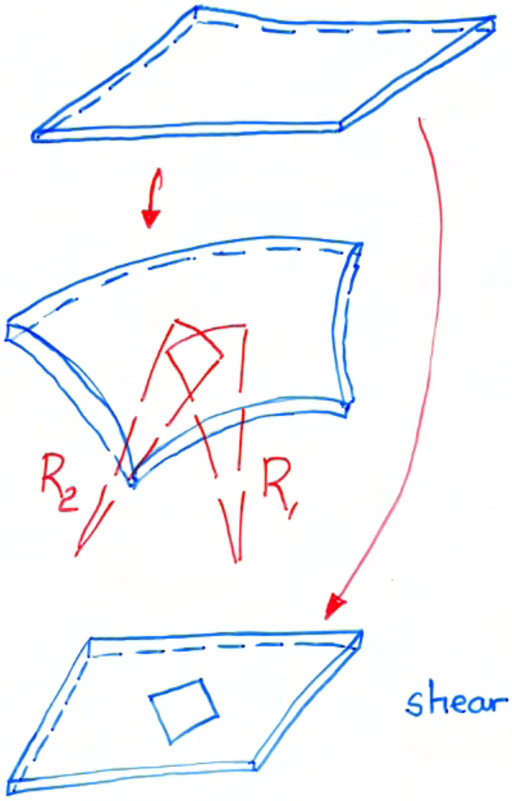
$\sim \mu(u/h_0)\cdot\ell$ ↔



Curvature K

torsion (& twist) τ_e, τ_g

+ stretch/shear



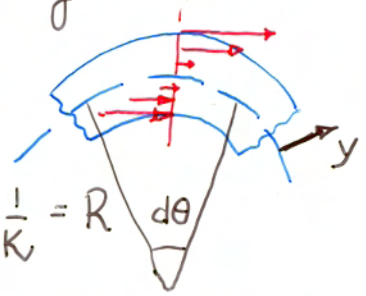
2 curvatures

$K_1 = 1/R_1$

$K_2 = 1/R_2$

shear/extension

bending



strain $\epsilon = yK$

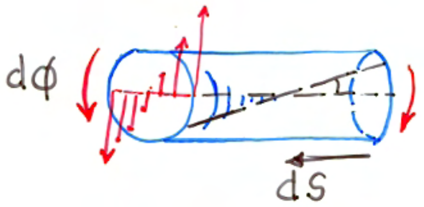
$$\left(\frac{(R+y)d\theta - R d\theta}{R d\theta} \right)$$

stress $\sigma = E y K$

$$\int \sigma \, dA = 0 = \text{force}$$

$$\int \sigma . y \, dA \cong \underbrace{E r^4} K = \text{Moment}$$

twisting



shear strain $\gamma = r \frac{d\phi}{ds}$

stress $\sigma = \mu . r \, d\phi/ds$

Torque (twisting) $T = \int \sigma . r \, dA$

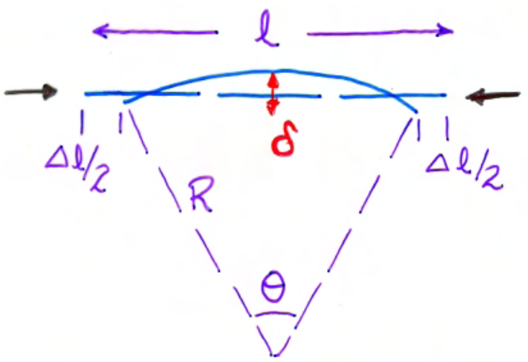
$$\cong \underbrace{\mu . r^4} \tau_e$$

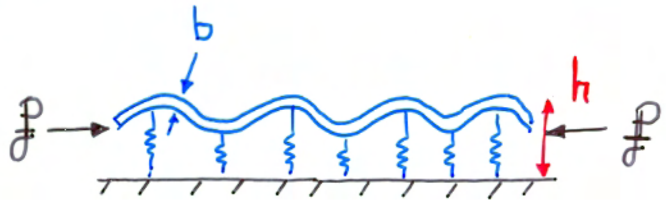
τ_e - engineering twist $= d\phi/ds$

$$U_{Bend} = \frac{1}{2} \int \underbrace{E r^4}_{B} K^2 dA \; ; \; U_{Twist} = \frac{1}{2} \int \mu r^4 \tau_e^2 \, ds$$

Slender filaments/sheets : bending/twisting is easy. (WHY?)

Instabilities involving filaments :





$U_{compr.} \sim \int E\,\epsilon^2\, dA.d\ell \sim E\,(\Delta\ell/\ell)^2.\ell.r^2$

$\sim E\,\Delta\ell^2\, r^2/\ell$

$U_{bend.} \sim \int E r^4\, K^2\, d\ell \quad ; \quad K \sim 1/R \sim \delta/\ell^2$

Pythagoras $\Rightarrow \delta^2 \sim \Delta\ell.\ell$

$\Rightarrow U_{bend.} \sim E r^4\, \Delta\ell/\ell^2$

Exchange of stability : $U_{bend.} \lesssim U_{compr.}$

i.e. $r^2/\ell^2 \lesssim \Delta\ell/\ell$

At onset $f.\delta \sim E r^4\, \delta/\ell^2$

$\Rightarrow f_c \sim E r^4/\ell^2$

Euler, 1742

What if there is a foundation?
e.g. skin (modulus μ)

Wavelength of wrinkles ? λ
Amplitude " — " ? δ

$U_{bend} \sim E b^3\, \delta^2/\lambda^4 . \lambda$
(per unit width)
$U_{fund.} \sim \mu\,(\delta/h)^2.h.\lambda$

Min. $(U_{bend.} + U_{fund.})$

with $\delta^2/\lambda^2 \sim \Delta$ - applied strain
(inextensibility)

min. $\left(Eb^3/\lambda^2 + \mu\lambda^2/h\right)\Delta.\lambda$

$\Rightarrow \lambda \sim (E/\mu)^{1/4}.(b^3 h)^{1/4}$

$\delta \sim \lambda.\Delta^{1/2}$

$h \to \infty$? $\quad \lambda \sim (E/\mu)^{1/3}\, b$
$\to$ skin

? Interfacial engineering ? (with skins)

Tallest tree ? $\rho g.\ell.r^2.\delta \sim E r^4.\delta/\ell^2$

$\Rightarrow \ell_c \sim (E r^2/\rho g)^{1/3}$

Longest horizontal branch ?

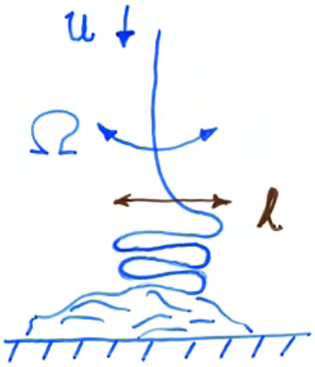
structural designs for life ?

So far ; equilibrium behavior (linear, nonlinear)

Non-equilibrium ? kinetics - irreversible (slow) flow

~~dynamics - inertial~~

Application of Stokes-Rayleigh analogy.



- folding (coiling) of viscous sheets, filaments.

$U \sim \Omega l$ · periodic steady state

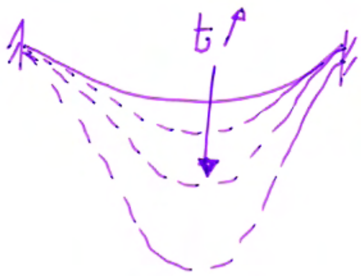
$$\underbrace{\eta \cdot \underbrace{\Omega/l}_{\dot{K}} \cdot r \cdot \underbrace{r}_{\text{Local torque 'arm'}} \cdot \underbrace{r^2}_{\text{area}}} \sim \rho \underbrace{r^2 l}_{\text{vol.}} \cdot g \cdot \underbrace{l}_{\text{torque 'arm'}}$$

- torque balance (NOT energy balance)

$\Rightarrow \left(\frac{\eta\,\Omega\, r^2}{\rho g}\right)^{1/3} \sim l$ (cf. elastic fold length $l \sim \left(Er^2/\rho g\right)^{1/3}$)

(LM et al.) $l \sim \left(\eta U r^2/\rho g\right)^{1/4}$; $\Omega \sim U/l$

$\Omega \left(\gg \sqrt{g/R}\right)$??

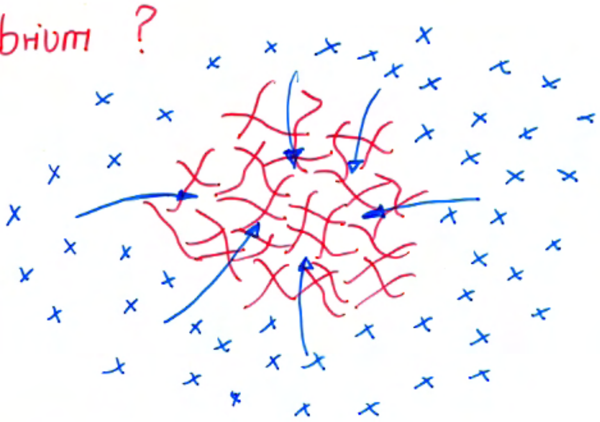


??

Gels : fluid permeation, swelling, shrinking
electro-kinetics, collapse, ...

Swelling equilibrium ?

Φ_0 - conc. without solvent



Elastic stress

$\sim$ Osmotic stress
(of uncrosslinked polymers at same conc. as gel !)

ρ - chain density

$\sim \phi / N b^3$

$$G \sim \rho . k_B T. \frac{(\lambda R_0)^2}{R_*^2}$$

(stress)

reference length
($\sim R_0$, if no interaction with solvent !)

ϕ - polymer vol. fraction

$$\Rightarrow G \sim \phi/_{Nb^3} . k_B T. \lambda^2$$

$$\lambda = \left(\Phi_0/\varphi\right)^{1/3} \quad \Rightarrow \quad G \sim k_B T/_{Nb^3}\, \Phi_0^{2/3} \cdot \underset{\sim}{\varphi^{1/3}}$$

, i.e. swelling $\Downarrow$ G $\searrow$

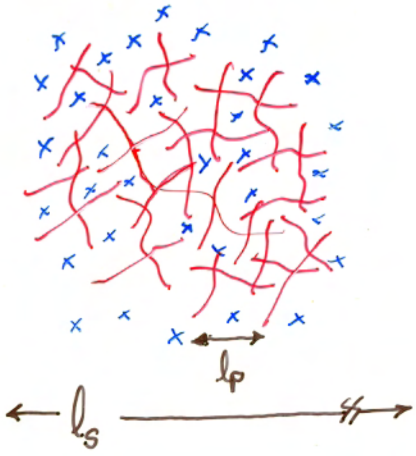
At equil. ; $\Pi_{osmotic} \sim k_B T / l^3_{interaction} \sim k_B T / b^3 \; \varphi^3$

$\sim G \Rightarrow$ equilibrium swelling ratio $\quad \varphi \sim \frac{N^{3/8}}{\Phi_0^{1/4}}$

BUT , What about kinetics ??

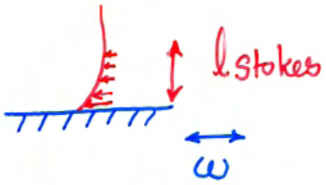
flow through a soft, porous network

pore size ; $l_p << l_s$; system size

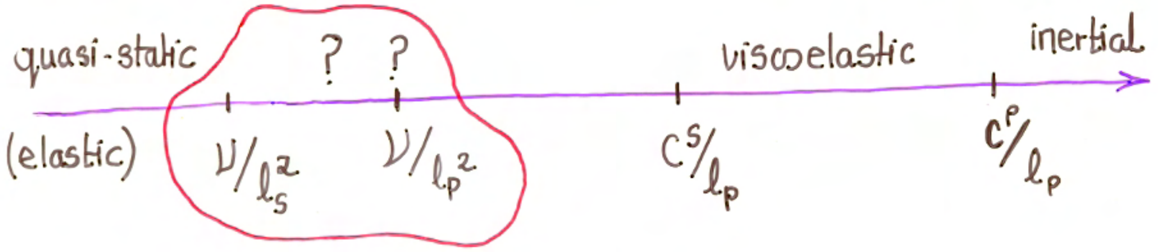


hydrodynamic length scale :

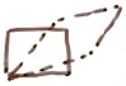
$l_{Stokes} \sim \sqrt{\nu/\omega}$ $\qquad \nu = \eta/\rho$ - kinematic viscosity (momentum diffusion)



- $l_s \gg l_p$ ($\overset{?}{><}$ l_{Stokes}) determines mechanical response !
- driving force / pressure - varies on system scale
- viscous resistance - on pore scale (large gradients !)



c^p, c^s } sound speeds in network

shear ?  - no relative motion between network / fluid !

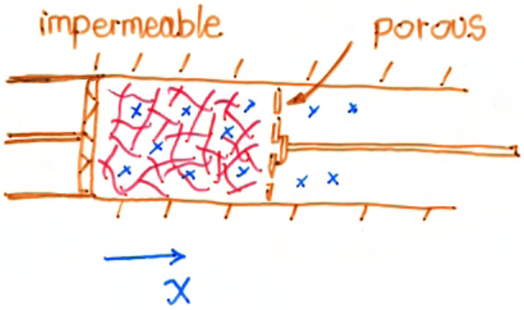
dilatation ?  - squeezing / spongy motion " — " !

not usually probed in rheology - but very important here !

Stokes flow :- $\eta \nabla^2 v \sim \nabla p \Rightarrow \eta\, v/l_p^2 \sim p/l_s$

i.e. $p \sim \eta \cdot v/l_p \cdot \underbrace{l_s/l_p}_{\gg 1} \gg \eta\, v/l_p$ → local viscous stress

⇒ fluid stress tensor $\sigma_{ij} \sim -p\,\delta_{ij}$



$u(x,t)$ - displacement of gel
$v(x,t)$ - velocity of fluid
$\varphi(x,t)$ - polymer volume fraction

total stress $\quad \sigma = K.\, \partial u/\partial x - (1-\varphi)\, p$

[linear mixture theory]

where $K = K(\varphi)$ - network bulk modulus ('drained')

force balance $\Rightarrow \quad \partial\sigma/\partial x = 0 \qquad (\nabla\cdot\underline{\sigma} = 0)$

continuity $\Rightarrow \quad \partial u/\partial t \cdot \varphi = -(1-\varphi)\, v \qquad (\nabla\cdot[\varphi \underline{u}_t + (1-\varphi)\underline{v}] = 0)$

D'arcy law (flow through porous network) $\Rightarrow \quad \underbrace{v - \partial u/\partial t}_{\text{relative velocity of fluid w.r.t. network}} = -\frac{k}{\eta}\cdot \partial p/\partial x \qquad \left(\underline{v} - \underline{u}_t = -\frac{k}{\eta}\nabla p\right)$

where $k(\varphi)$ - hydraulic permeability
$\sim l_p^2$ [from Stokes approx. ; low Re]

$$\therefore \quad K\, \partial^2 u/\partial x^2 \underbrace{=}_{\text{force balance}} \partial p/\partial x \underbrace{=}_{\text{D'arcy's law}} -\eta/k\,(v - \partial u/\partial t) \underbrace{=}_{\text{continuity}} \eta/k(1-\varphi) \cdot \partial u/\partial t$$

i.e. $\quad \partial u/\partial t = \dfrac{Kk}{(1-\varphi)\eta} \cdot \partial^2 u/\partial x^2 \quad \rightarrow$ diffusion equation [for displacement]

B.C.

$x = 0$; $p = P_1$, $u = 0$

$x = 1$; $p = 0$, $\partial u/\partial x = 0$ - free

$p = P_2$, $u = 0$ - clamped

$$\partial p/\partial t = \frac{Kk}{(1-\varphi)\eta} \cdot \partial^2 p/\partial x^2$$

[pressure diffuses !]

Stress diffusion picture

Brot, 1941
reinvented every 20 years ← ceramics, cartilage/tissue, gels, cells, ??

diffusion constant

$$D \cong K k / \eta$$

$$\sim k_B T . \xi . l_p^2 / \eta$$

$K \sim 10^0 - 10^3$ Pa

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

$l_p \sim 10^{-8} - 10^{-9}$ m

$\Rightarrow D_{stress} \sim 10^{-15} - 10^{-10}$ m²/s

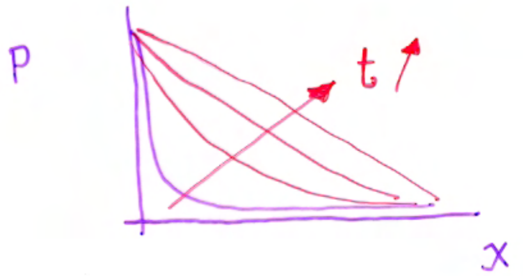
so that equilibration time $\tau \sim L_s^2 / D$ can be very large

→ another 'simple' candidate for slow dynamics in many soft systems.

e.g. Cells - are they mechanically 'compartmentalized' ?

$\tau \sim (10^{-5} m)^2 / 10^{-15} \text{-} 10^{-10} \sim 1 - 10^5$ s !! Yes !!

Settling of gels (foams, soil, ...)



//y for swelling !

→ Most theoretical treatments of these problems are questionable, i.e. great opportunity !!