Structure
Atomic
Molecular
Fibrillar
Cellular
Macroscopic

STRUCTURE AND PROPERTIES OF WOOD-BASED MATERIALS (7)

Wood

Porous, cellular, fibrillar
composite of amorphous polymers

Hygroscopic

Properties

Extensive S_V
Intensive Independent of Extension, valid locally
Specific Material properties

Anisotropy
Homogenity
Isotropy Anisotropy
orthotropy

Periodic Variation

Co-ordinate systems
Rectangular Cartesian
Cylindrical
Spherical

(8)

Properties:

a state equation = characteristic equation
defines relations between properties

example
Specific Volume = function(temperature, moisture)

Parameters of state = Properties

"...a system is in a given state when all its measurable properties have fixed values, ..." (Kestin 1979)

Intensive Properties

Extensive Properties

Specific Properties

$\boxed{\text{Stiffness} \quad \frac{d\sigma}{d\varepsilon}}$

$$Q_{ijkl} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}$$

$\boxed{\text{Stress} \quad \frac{\partial F}{\partial A}}$ $\qquad \sigma_{ij} = \frac{\partial F_i}{\partial A_j}$

$$dF_i = \frac{\partial F_i}{\partial A_j} dA_j = \frac{\partial F_i}{\partial A_1} dA_1 + \frac{\partial F_i}{\partial A_2} dA_2 + \frac{\partial F_i}{\partial A_3} dA_3$$

$$= \sigma_{i1} dA_1 + \sigma_{i2} dA_2 + \sigma_{i3} dA_3$$

$\boxed{\text{Strain} \quad \frac{\partial u}{\partial x}}$ $\qquad du_k = \frac{\partial u_k}{\partial x_l} dx_l$

$$\varepsilon_{kl} = \frac{\partial u_k}{\partial x_l} \qquad = \dots$$

How can we determine σ_{ij} ?

$$d\sigma_{ij} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} d\varepsilon_{kl} = Q_{ijkl}\, d\varepsilon_{kl}$$

$$= Q_{ij11} d\varepsilon_{11} + Q_{ij12} d\varepsilon_{12} + Q_{ij13} d\varepsilon_{13} +$$
$$Q_{ij21} d\varepsilon_{21} + Q_{ij22} d\varepsilon_{22} + Q_{ij23} d\varepsilon_{23} +$$
$$Q_{ij31} d\varepsilon_{31} + Q_{ij32} d\varepsilon_{32} + Q_{ij33} d\varepsilon_{33}$$

STIFFNESS MATRIX

$$[Q] \equiv \begin{bmatrix} Q_{1111} & Q_{1122} & Q_{1133} & Q_{1112} & Q_{1113} & Q_{1121} & Q_{1123} & Q_{1131} & Q_{1132} \\ Q_{2211} & Q_{2222} & Q_{2233} & Q_{2212} & Q_{2213} & Q_{2221} & Q_{2223} & Q_{2231} & Q_{2232} \\ Q_{3311} & Q_{3322} & Q_{3333} & Q_{3312} \dots \\ Q_{1211} & \dots \\ Q_{1311} & \dots \\ Q_{2111} & \dots \\ Q_{2311} & \dots \\ Q_{3111} & \dots \\ Q_{3211} & \dots \end{bmatrix}$$

Total of $9 \times 9 = 81$ components

Stress vector		Stiffness matrix		strain vector
$\bar{\sigma}$	=	$[Q]$	$\cdot$	$\bar{\varepsilon}$

In component form

$$\sigma_{ij} = Q_{ijkl}\, \varepsilon_{kl} \equiv \sum_{k=1}^{3} \sum_{l=1}^{3} Q_{ijkl}\, \varepsilon_{kl}$$

Linear Elasticity

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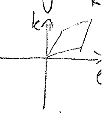
$Q_{ijkl} = Q_{klij}$

Orthotropic symmetry
On-axis crd

$\Rightarrow$

$$\begin{cases} Q_{ijkl} = Q_{jikl} = Q_{ijlk} = Q_{jilk} \\ \sigma_{ij} = \sigma_{ji} \qquad \varepsilon_{kl} = \varepsilon_{lk} \end{cases}$$



$Q_{iikl} = Q_{iikl}\, \delta_{kl}$ (no sum)

$Q_{ijil} = Q_{ijil}\, \delta_{jl}$ (no sum)

9 independent components! $\Leftarrow$

Compliance $\frac{d\varepsilon}{d\sigma}$

$$\begin{cases} C_{ijkl} = \dfrac{\partial \varepsilon_{ij}}{\partial \sigma_{kl}} \\ S_{ijkl} \end{cases}$$

$$[Q]\,[C] = \mathbb{1}$$

Unit matrix

Hooke's Law $\sigma = E\varepsilon$ E = Young's modulus

In terms of stiffness components?

In terms of Compliance components?

Spring Equation $F = k\delta$ k = Spring Constant

How do we get from Spring Eq. to Hooke's Law?

What is the relation between E and k?

Conductance Equation $I = c\,\Delta V$

Conductivity Equation $I/A_\perp = \gamma \frac{\partial V}{\partial x}$

Are these related to the above?

What is the dimension of $\begin{cases} c \\ \gamma \end{cases}$?

Resistance Equation $\Delta V = RI$

Resistivity Equation $\frac{\partial V}{\partial x} = \rho\, I/A_\perp$

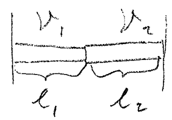
What is the dimension of $\begin{cases} c \\ \gamma \\ R \\ \rho \end{cases}$?

$$\sigma_{ij} = Q_{ijkl}\,\varepsilon_{kl}$$

How about $\begin{cases} ij \neq kl \\ i \neq j \\ k \neq l \end{cases}$ in terms of conductivity?

Composite Structures

Elements in Series



$$I/A = \gamma \frac{\partial V}{\partial x}$$

$$I_1 = I_2 = A_1\gamma_1\left(\frac{\partial V}{\partial x}\right)_1 = A_2\gamma_2\left(\frac{\partial V}{\partial x}\right)_2$$

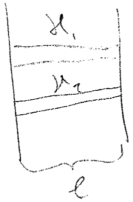
Conductivity Eq. for the Composite system:

$$I/A = \gamma\frac{\Delta V}{\Delta x} = \gamma\frac{\Delta V}{l_1+l_2} = \gamma\frac{\int_0^{l_1}\left(\frac{\partial V}{\partial x}\right)_1 dx + \int_0^{l_2}\left(\frac{\partial V}{\partial x}\right)_2 dx}{l_1+l_2}$$

$$= \gamma\frac{l_1\left(\frac{\partial V}{\partial x}\right)_1 + l_2\left(\frac{\partial V}{\partial x}\right)_2}{l_1+l_2} = \gamma\frac{l_1\frac{I/A_1}{\gamma_1} + l_2\frac{I/A_2}{\gamma_2}}{l_1+l_2}$$

$$\Rightarrow \gamma = \frac{l_1+l_2}{\frac{A\,l_1}{A_1\gamma_1} + \frac{A\,l_2}{A_2\gamma_2}}$$

Elements in Parallel



$$I/A = \gamma\frac{\partial V}{\partial x}$$

$$\left(\frac{\partial V}{\partial x}\right)_1 = \left(\frac{\partial V}{\partial x}\right)_2 = \frac{\partial V}{\partial x} \Rightarrow \frac{I_1}{A_1\gamma_1} = \frac{I_2}{A_2\gamma_2}$$

$$I/A = \frac{I_1+I_2}{A_1+A_2} = \frac{I_1\left(1+\frac{A_2\gamma_2}{A_1\gamma_1}\right)}{A_1\left(1+\frac{A_2}{A_1}\right)} = \gamma\left(\frac{\partial V}{\partial x}\right)_1 = \gamma\frac{I_1}{A_1\gamma_1}$$

$$\gamma = \gamma_1\frac{1+\frac{A_2\gamma_2}{A_1\gamma_1}}{1+\frac{A_2}{A_1}} = \frac{A_1\gamma_1 + A_2\gamma_2}{A}$$

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How do we determine $\left\{\begin{array}{l}\text{stiffness}\\ \text{compliance}\end{array}\right.$ matrices experimentally?

How do we determine mechanical behavior in an arbitrary direction, once $\left\{\begin{array}{l}\text{stiffness}\\ \text{compliance}\end{array}\right.$ matrix is known in the on-axis co-ordinate system?

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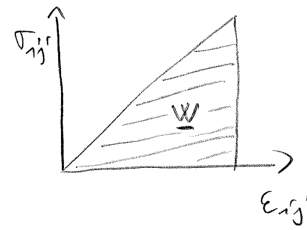
Strain Energy Density

$$d\underline{W} = \sigma_{ij}' d\varepsilon_{ij}' = \sigma_{11} d\varepsilon_{11} + \sigma_{12} d\varepsilon_{12} + \dots$$

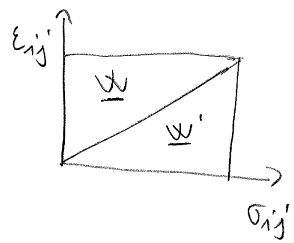
$$\Rightarrow \quad \sigma_{ij}' = \frac{\partial \underline{W}}{\partial \varepsilon_{ij}'}$$

Chain Rule of Partial Derivatives



$$\underline{W} = \frac{1}{2}\sigma_{ij}' \varepsilon_{ij}'$$

Complementary Strain Energy Density



$$d\underline{W}' = \varepsilon_{ij}' d\sigma_{ij}' = \varepsilon_{11} d\sigma_{11} + \dots$$

$$\varepsilon_{ij}' = \frac{\partial \underline{W}'}{\partial \sigma_{ij}'}$$

$$\underline{W} = \underline{W}' \Rightarrow$$

$$\varepsilon_{ij}' = \frac{\partial \underline{W}}{\partial \sigma_{ij}'}$$

(8b)

Symmetry of Compliance and Stiffness

$$W = \frac{1}{2}\sigma_{ij}\varepsilon_{ij} = \frac{1}{2}(Q_{ijkl}\varepsilon_{kl})\varepsilon_{ij}$$

$$\frac{dW}{d\varepsilon_{mn}} = \frac{1}{2} Q_{mnkl}\varepsilon_{kl} + \frac{1}{2} Q_{ijmn}\varepsilon_{ij}$$

$$= \frac{1}{2} Q_{mnkl}\varepsilon_{kl} + \frac{1}{2} Q_{klmn}\varepsilon_{kl}$$

$$= \frac{1}{2}\left(Q_{mnkl} + Q_{klmn}\right)\varepsilon_{kl}$$

On the other hand:

$$\frac{dW}{d\varepsilon_{mn}} = \sigma_{mn} = Q_{mnkl}\varepsilon_{kl}$$

$$\Rightarrow \quad Q_{mnkl} = Q_{klmn}$$

Similarly for Compliance:

$$W = \frac{1}{2}\sigma_{ij}\varepsilon_{ij} = \frac{1}{2}(S_{ijkl}\sigma_{kl})\sigma_{ij}$$

$$\frac{dW}{d\sigma_{mn}} = \frac{1}{2}\left(S_{mnkl} + S_{klmn}\right)\sigma_{kl} = S_{mnkl}\sigma_{kl}$$

$$\Rightarrow \quad S_{mnkl} = S_{klmn}$$

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$$\boxed{\begin{aligned}\varepsilon_{11} &\equiv X_1 \\ \varepsilon_{22} &\equiv X_2\end{aligned}}$$

$$\frac{\partial W}{\partial X_1} = Q_{1111} X_1 + Q_{1122} X_2$$

$$\frac{\partial W}{\partial X_2} = Q_{2211} X_1 + Q_{2222} X_2$$

$$1^\circ \quad W = \frac{1}{2} Q_{1111} X_1^2 + Q_{1122} X_1 X_2 + g(X_2)$$

$$2^\circ \quad W = Q_{2211} X_1 X_2 + \frac{1}{2} Q_{2222} X_2^2 + h(X_1)$$

$$\Rightarrow \begin{cases} g(X_2) = \frac{1}{2} Q_{2222} X_2^2 + C \\ h(X_1) = \frac{1}{2} Q_{1111} X_1^2 + C \\ Q_{1122} = Q_{2211} \end{cases}$$

$$\Rightarrow \quad W = \frac{1}{2} Q_{1111} X_1^2 + \frac{1}{2} Q_{2222} X_2^2 + \frac{1}{2}(Q_{1122} + Q_{2211}) X_1 X_2$$

$$\frac{dW}{dX_1} = Q_{1111} X_1 + Q_{1122} X_2 = \sigma_{11} \quad \%$$

$$\frac{dW}{dX_2} = Q_{2222} X_2 + Q_{2211} X_1 = \sigma_{22} \quad \%$$

strength

Strength $\equiv$ critical stress $\quad (\sigma_{ij})_c$

Critical nominal stress ?

How about multiaxial stress states?

- We may need some multiaxial Failure Criterion.

Von Mises Stress

$$\sigma_m \equiv \frac{1}{\sqrt{2}}\sqrt{(\sigma_{11}-\sigma_{22})^2+(\sigma_{22}-\sigma_{33})^2+(\sigma_{33}-\sigma_{11})^2+6(\sigma_{12}^2+\sigma_{13}^2+\sigma_{23}^2)}$$

For uniaxial tension $\quad \sigma_m = \sigma_{11}$

For biaxial tension $\quad \sigma_m = \frac{1}{\sqrt{2}}\sqrt{(\sigma_{11}-\sigma_{22})^2+\sigma_{22}^2+\sigma_{11}^2}$

$$= \sqrt{\sigma_{11}^2+\sigma_{22}^2+\sigma_{11}\sigma_{22}}$$

For Equibiaxial tension $\quad \sigma_m = \sigma_{ii}$ (no sum)

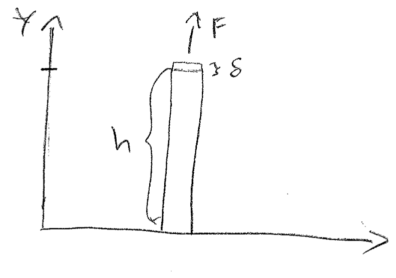
For Tension-compression w. $\sigma_{11} = -\sigma_{22}$ $\quad \sigma_m = \sqrt{3}\,\sigma_{ii}$

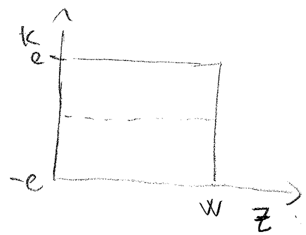
For pure shear in one plane $\quad \sigma_m = \sqrt{3}\,\sigma_{12}$

For Equitriplanar shear $\quad \sigma_m = 3\,\sigma_{ij}$

Failure Criterion $\quad \boxed{\sigma_m = \sigma_c}$ $\quad$ Right or wrong ?

Rigidity in Tension





$$K \equiv \frac{F}{\delta} = \frac{\sigma A_\perp}{\varepsilon h} = \frac{E\,\varepsilon \int_{A_\perp} 1}{\varepsilon h}$$

$$= \frac{E\,(2e)\,w}{h}$$

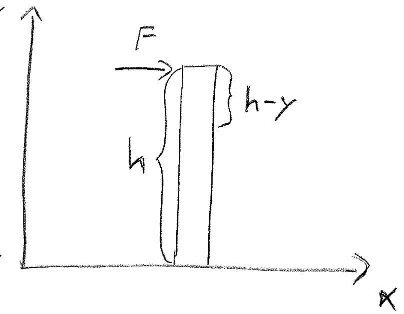
$$K' \equiv \frac{F}{\varepsilon} = E\,(2e)\,w$$

Bending of a Beam

$$EI\frac{dx}{dy} = \int_0^y -M(y')\,dy'$$

$$= F\int_0^y (h-y')\,dy' = F\Big/_0^y \, hy' - \frac{y'^2}{2}$$

$$= Fy\left(h-\frac{y}{2}\right)$$



$M(y) = -F(h-y)$ for $0 \le y \le h$

$$dx = \frac{F}{EI}\left(hy - \frac{y^2}{2}\right)dy \;\Big|\; \int$$

$$\Delta x = \frac{F}{EI}\left(\frac{hy^2}{2} - \frac{y^3}{6}\right) = \frac{Fh^3}{6EI}\left(3\frac{y^2}{h^2} - \frac{y^3}{h^3}\right)$$

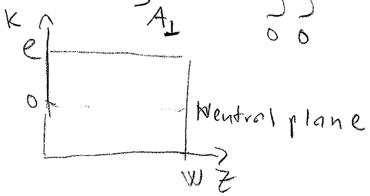
Curvature: $\frac{d^2x}{dy^2}$

Balance of Momenta: $\underbrace{EI\frac{d^2x}{dy^2}}_{\text{Internal}} = \underbrace{-M(y)}_{\text{External}}$

$$\boxed{EI\frac{d^2x}{dy^2} + M(y) = 0}$$

Second Moment of Inertia:

$$I = \int_{A_\perp} k^2 = 2\int_0^e\int_0^w k^2\,dz\,dk = 2w\frac{1}{3}e^3$$



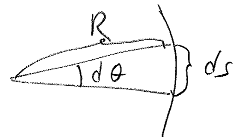
$\uparrow$ $EI = E\frac{(2e)^3 w}{12}$

Bending Rigidity

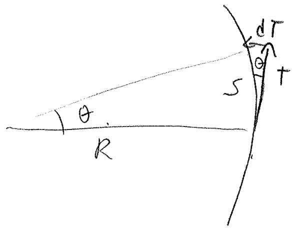
$$EI = \frac{-M(y)}{\frac{d^2x}{dy^2}} = \frac{\text{Momentum}}{\text{Curvature}}$$

Radius of curvature

$$R = \frac{ds}{d\theta}$$



$$\text{Curvature} \equiv \frac{1}{R} = \frac{d\theta}{ds}$$



$$\tan\theta \approx \theta = \frac{S}{R} = \frac{dT}{T}$$

In (x,y) - crd-system

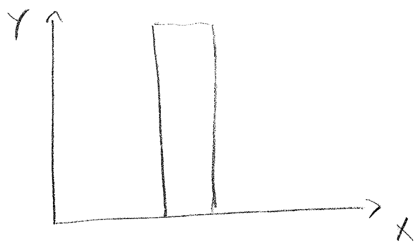
$$\left.\begin{array}{l} dT \to dx \\ T \to dy \end{array}\right\} \quad \tan\theta \approx \theta = \frac{dx}{dy} \;\Big|\; \frac{d}{dy}$$

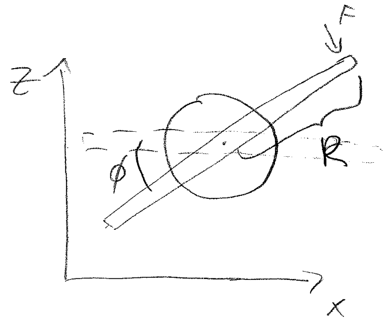
$$\frac{d\theta}{dy} = \frac{d^2x}{dy^2}$$

Small $\theta \Rightarrow S \approx T \equiv y$

$$\frac{d\theta}{dy} \approx \frac{d\theta}{ds} = \frac{1}{R} = \frac{d^2x}{dy^2}$$

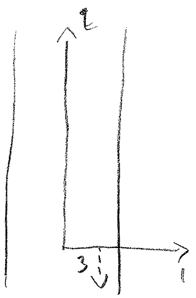
Torsional Rigidity

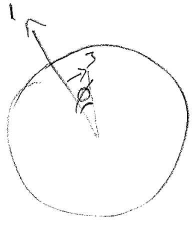


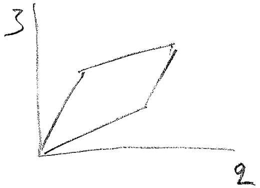


Torque $T = F \cdot R$

Torsional Rigidity $\frac{T}{\phi}$ [Nm] $=$ $\frac{\text{Torque}}{\text{Torsion}}$







$$u_3 = \phi r$$

$$\frac{\partial u_3}{\partial x_2} \equiv \varepsilon_{32} = \frac{\phi r}{\ell_2}$$

$$\sigma_{32} \approx Q_{3232}\,\varepsilon_{32} + Q_{3223}\,\varepsilon_{23}$$

$$= 2\,Q_{3232}\,\varepsilon_{32} = 2\,Q_{3232}\frac{\phi r}{\ell_2} = \frac{dF_3}{dA_2} \qquad \frac{dF_2}{dA_3} = 0$$

$$r\frac{\partial F}{\partial A_2} = 2\,Q_{3232}\frac{\phi r^2}{\ell}$$

$$T = \int_{A_1} 2\,Q_{3232}\frac{\phi r^2}{\ell} = 2\,Q_{3232}\frac{\phi}{\ell} J$$

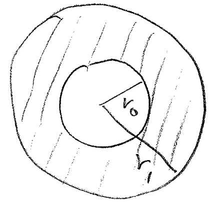
Polar Moment of Inertia

$$J = \int_{A_1} r^2$$

The Area of a Hollow Pipe

$$A = \int_0^{2\pi}\int_{r_0}^{r_1} r\,dr\,d\phi = \int_0^{2\pi} \Big/_{r_0}^{r_1} \tfrac{1}{2}r^2$$

$$= \pi\left(r_1^2 - r_0^2\right)$$



Polar Moment of Inertia

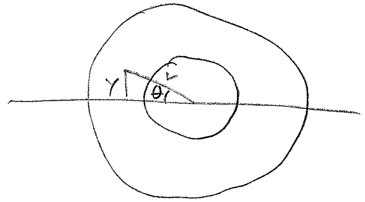
$$J = \int_0^{2\pi}\int_{r_0}^{r_1} r^3\,dr\,d\phi = \int_0^{2\pi} \Big/_{r_0}^{r_1} \frac{r^4}{4}\,d\phi = \frac{\pi}{2}\left(r_1^4 - r_0^4\right)$$

Second Moment of Inertia

$$I = \int_0^{2\pi}\int_{r_0}^{r_1} r^3 \sin^2\theta\,dr\,d\theta$$

$$= \int_0^{2\pi} \Big/_{r_0}^{r_1} \frac{r^4}{4}\sin^2\theta\,d\theta = \frac{r_1^4 - r_0^4}{4}\int_0^{2\pi}\sin^2\theta\,d\theta$$

$$= \frac{r_1^4 - r_0^4}{4}\Big/_0^{2\pi}\frac{1}{2} = \frac{\pi}{4}\left(r_1^4 - r_0^4\right)$$



$Y = r\sin\theta$

$Y^2 = r^2\sin^2\theta$

Mass Density Effects

1^{st} Approximation: the amount of load-carrying material per cross-sectional area unit increases w. density

$\Rightarrow \quad Q_{ijkl} \propto \rho$

2^{st} Appr. for porous material $\quad P \propto \frac{1}{\rho}$

Solid Fraction $\quad S \propto \rho$

$\Rightarrow$ Connectivity of solid elements increases w. ρ

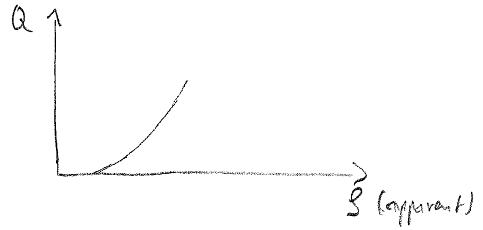
$\Rightarrow$ Specific Stiffness $\quad \frac{Q}{\rho} \propto \rho^{\mu} \Rightarrow Q \propto \rho^{1+\mu}$

$\mu \geq 0$

Percolation and Connectivity

Element sparse in space do not necessarily become connected $\rightarrow$ zero stiffness at finite apparent density

Percolation: formation of a continuous network



What does the Percolation threshold depend on?

For fibers: $\frac{\text{length}}{\text{mass}} \equiv \frac{1}{\text{Coarsenes}}$

Trivial Scaling

Linear Dimensions scaled by q

Object scaled as $\quad q^2 \rightarrow$ Area $\quad q^1 \rightarrow$ line

$q^3 \rightarrow$ Volume

$q^n \rightarrow$ Dimensionality n

Does the scaling exponent have to be an Integer? Would something like $3/2$ be possible? Or $5/3$?

The object would be something between $\begin{cases}\text{line}\\ \text{Area}\end{cases}$ ... $\begin{cases}\text{Area}\\ \text{Volume}\end{cases}$ ...

$2^1 = 2$

$2^{3/2} \approx 2{,}8 \quad$ Magnification w. 2 extends "length" this much.

$2^2 = 4$

$2^{5/3} \approx 5{,}7 \quad$ Magnification w. 2 extends "Area" this much...

Self-Similarity

- exact
- inexact

- w. or w.o. $\begin{cases}\text{lower}\\ \text{higher}\end{cases}$ cutoff

Consequences:

Boundary Lengths, Surface Areas, and Volumes hardly exist in Nature

- only apparent values exist, and those values inherently depend on the magnification of observation

Example:

Specific Surface $\frac{A}{\rho V}$ of pulp fibers scales as (trivially)

$$\frac{A'}{\rho V'} = \frac{q^2 A}{\rho q^3 V} = q^{-1} \frac{A}{\rho V}$$

BUT The fibers do not have an area

$$q^n > q^2$$

The fibers do not have a volume

$$q^m < q^3$$

$$\frac{q^n}{q^m} = q^k > q^{-1}$$

Is ρ scale-invariant?

Size Effect on Strength

Element Failure Probability $P_1(\sigma)$

= cumulative distribution function (cdf) of strength for an Element

pdf = probability density function

Element Survival Probability

$1 - P_1$

Chain Survival Probability

$$1 - P_f = (1 - P_1)^N \quad \Big|\ \ln$$

$$\frac{d}{dp}\ln(1-p) = \frac{d(1-p)}{dp}\frac{d}{d(1-p)}\ln(1-p) = (-1)\frac{1}{1-p}$$

$$\ln(1-P_f) = N \ln(1-P_1)$$

$$f(x) = \sum_{n=0}^{\infty} f^n(0)\, x^n$$

Maclaurin Series

$$\ln(1-P_1) = \ln(1-0) + (-1)\frac{1}{1-0}P_1 + \frac{1}{(1-0)^2}P_1^2 + \dots$$

$$\approx -P_1$$

$$\ln(1-P_f) \approx N(-P_1)$$

$$\Rightarrow P_f \approx 1 - e^{-N P_1(\sigma)} = P_f(\sigma)$$

cdf of strength for the Chain

$N \equiv \frac{V}{V_c}$, $\frac{1}{V_c}P_1(\sigma) \equiv c(\sigma)$ $\Rightarrow$ $\boxed{P_f(\sigma, V) = 1 - e^{-c(\sigma)V}}$

Weibull 1939: $c(\sigma) \approx \frac{1}{V_0}\left\langle \frac{\sigma - \sigma_1}{\sigma_0} \right\rangle^m$

$\langle \text{abs}\, x \rangle = x$

$\langle -\text{abs}\, x \rangle = 0$

$$\Rightarrow \boxed{P_f(\sigma, V) = 1 - e^{-\frac{V}{V_0}\left\langle\frac{\sigma-\sigma_1}{\sigma_0}\right\rangle^m}} \rightarrow 1 - e^{-\frac{V}{V_0}\left(\frac{\sigma}{\sigma_0}\right)^m} \text{ for } \sigma_1 = 0$$

What is the pdf of strength?

$$\frac{d}{d\sigma} P_f = \frac{d\frac{\sigma-\sigma_1}{\sigma_0}}{d\sigma} \frac{d\left(\frac{\sigma-\sigma_1}{\sigma_0}\right)^m}{d\frac{\sigma-\sigma_1}{\sigma_0}} \frac{d}{d\left(\frac{\sigma-\sigma_1}{\sigma_0}\right)^m} P_f$$

$$= \frac{1}{\sigma_0} m \left(\frac{\sigma-\sigma_1}{\sigma_0}\right)^{m-1} \frac{V}{V_0} e^{-\frac{V}{V_0}\left(\frac{\sigma-\sigma_1}{\sigma_0}\right)^m} = p_f$$

What is the mean value of strength?

$$\bar{\sigma} = \int_{\sigma_1}^{\infty} \sigma \, p_f \, d\sigma$$

→ somewhat complicated to integrate

$$\boxed{\frac{dP_f}{d\sigma} = p_f \Rightarrow p_f \, d\sigma = dP_f}$$

$$= \int_0^1 \sigma \, dP_f$$

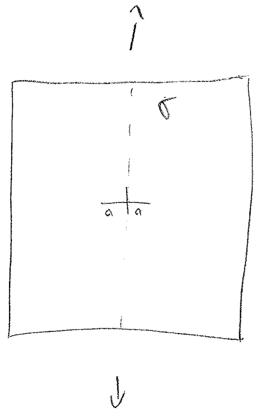
still difficult...

What is the median value of strength?

$$P_f(\sigma, V) = 0,5 \Rightarrow e^{-\frac{V}{V_0}\left(\frac{\sigma-\sigma_1}{\sigma_0}\right)^m} = 0,5$$

$$\Rightarrow \frac{V}{V_0}\left(\frac{\sigma-\sigma_1}{\sigma_0}\right)^m = \ln 2 \Rightarrow \sigma_{0,5} = \sigma_0 \left(\frac{V_0}{V}\ln 2\right)^{\frac{1}{m}} + \sigma_1$$

Fracture Mechanics Size Effect



Failure criterion

$$\underset{<0}{\frac{d\Pi}{da}} + \underset{>0}{\frac{dW_s}{da}} \le 0$$

$$\frac{dW_s}{da} = \frac{d\, 4atG}{da} = 4tG \qquad A \equiv 4ta$$

$$\frac{dW_s}{dA} = G$$

Inglis: $\Pi = \Pi_0 - \frac{\pi\sigma^2 a^2 t}{Q}$

$$\frac{d\Pi}{da} = -\frac{2\pi\sigma^2 a t}{Q}$$

Criticality in LEFM

$$\frac{d\Pi}{da} + \frac{dW_s}{da} = 0$$

$$\frac{dW_s}{da} = -\frac{d\Pi}{da}$$

$$4tG = \frac{2\pi\sigma^2 a t}{Q}$$

$$G = \frac{\pi\sigma^2 a}{2Q} \Rightarrow \sigma_c = \sqrt{\frac{2QG}{\pi a}}$$

LEFM Size Effect

$$\boxed{\sigma_c \propto D^{-\frac{1}{2}}}$$

How about material w. plastic yelding at σ_{pe}?

Let us try a scaling parameter $\beta = \frac{\sigma_{pe}^2}{\sigma_c^2} = \frac{\pi a \sigma_{pe}^2}{2QG}$

w. strength scaling $\sigma_c = \frac{\sigma_{pe}}{\sqrt{1 + \frac{\pi a \sigma_{pe}^2}{2QG}}} = \frac{\sigma_{pe}}{\sqrt{1+\beta}} = \frac{1}{\sqrt{\frac{1}{\sigma_{pe}^2} + \frac{1}{\sigma_c^2}}}$

$$\boxed{\sigma_c \propto (1+\beta)^{-\frac{1}{2}} = \left(1 + \frac{D}{\ell_{ch}}\right)^{-\frac{1}{2}}}$$

Size-Effect Scaling

$$D \equiv \frac{\pi a}{2} \qquad \ell_{ch} \equiv \frac{QG}{\sigma_{pe}^2}$$

Surface Energy γA

$$F = \frac{dW}{dS} = \frac{d\,\gamma A}{dr} = \frac{d\,\gamma 4\pi r^2}{dr} = 8\pi r \gamma$$

stress due to surface tension $\frac{F}{A} = \frac{8\pi r\gamma}{4\pi r^2} = \frac{2\gamma}{r}$

Balance of Forces

$$p_{in}\, 4\pi r^2 = p_{out}\, 4\pi r^2 + 8\pi r\gamma$$

$$\Delta p = \frac{2\gamma}{r} \qquad \text{Laplace Eq.}$$

Internal Energy

$U = TS - pV + \mu N \qquad dU = TdS - pdV + \mu dN$

Gibbs Function

$G = U - TS + pV \qquad dG = -SdT + Vdp + \mu dN$

$\quad = \mu N \qquad\qquad = \frac{\partial G}{\partial T} dT + \frac{\partial G}{\partial p} dp + \frac{\partial G}{\partial N} dN$

$\Rightarrow \mu = \frac{G}{N}$

Molar Gibbs Function

$G_m = \frac{G}{n} = \mu N_A \qquad dG_m = -\frac{S}{n} dT + \frac{V}{n} dp + \frac{\mu}{n} dN$

$\qquad\qquad = -S_m dT + V_m dp + \mu_m dN$

Equilibrium

$\mu_g = \mu_e \Rightarrow G_{mg} = G_{me}$

at $dT = 0$ $\quad V_{mg}\, dp_g = V_{me}\, dp_e = V_{me}\,(dp(r=\infty) + d\Delta p)$

Ideal Gas
$pV_m = RT$

$$\frac{RT}{p_g} dp_g = V_{me}\, dp_\infty + V_{me}\, d\Delta p$$

$$RT \ln p_g = V_{me}\, p_\infty + V_{me}\, \Delta p + C$$

$$p_g = e^{\frac{V_{me} p_\infty}{RT}}\, e^{\frac{V_{me} 2\gamma}{rRT}}\, C_3 \qquad r \to \infty \Rightarrow p_g \to p_\infty$$

$$= C_4\, e^{\frac{V_{me} 2\gamma}{rRT}} = p_\infty\, e^{\frac{2\gamma M}{rRT\rho}}$$

Kelvin Eq.

Set $p_g(r = r_s) = p_s$

$$p_s = p\, e^{\frac{2\gamma M}{r_s RT\rho}} \Rightarrow \frac{p}{p_s} = e^{-\frac{2\gamma M}{r_s RT\rho}}$$

Expansion due to Isotropic pressure

$$\Delta p \rightarrow \sigma'_{11} = \sigma'_{22} = \sigma'_{33} = p$$

$$\varepsilon'_{ij} = C_{ijkl}\, \sigma'_{kl}$$

How do we invert a matrix?
by Gaussian Elimination

Linear transformation $A\begin{pmatrix}x\\y\end{pmatrix} = \begin{pmatrix}x'\\y'\end{pmatrix}$ (1)

$$A^{-1}A\begin{pmatrix}x\\y\end{pmatrix} = A^{-1}\begin{pmatrix}x'\\y'\end{pmatrix} = \begin{pmatrix}x\\y\end{pmatrix} \quad (3)$$

$$\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}x\\y\end{pmatrix} = \begin{pmatrix}x\\y\end{pmatrix}$$

Original transformation

$$\begin{array}{l}1a)\\1b)\end{array}\begin{pmatrix}a&b\\c&d\end{pmatrix}\begin{pmatrix}x\\y\end{pmatrix} = \begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}x'\\y'\end{pmatrix} \Leftrightarrow$$

1a) $ax + by = x'$

1b) $cx + by = y' \quad \Big| \cdot -\frac{a}{c}$

2b) $\left(b - \frac{ad}{c}\right)y = x' - \frac{a}{c}y'$

$$\begin{array}{l}1a)\\2b)\end{array}\begin{pmatrix}a&b\\0&b-\frac{ad}{c}\end{pmatrix}\begin{pmatrix}x\\y\end{pmatrix} = \begin{pmatrix}1&0\\1&-\frac{a}{c}\end{pmatrix}\begin{pmatrix}x'\\y'\end{pmatrix}$$

1a) $ax + by = x' \quad \Big| \cdot \left(-\frac{b-\frac{ad}{c}}{b}\right)$

2b) $\left(b - \frac{ad}{c}\right)y = x' - \frac{a}{c}y'$

2a) $-\frac{a}{b}\left[b - \frac{ad}{c}\right]x = \frac{ad}{cb}x' - \frac{a}{c}y$

$$\begin{array}{l}2a)\\2b)\end{array}\begin{pmatrix}-\frac{a}{b}\left[b-\frac{ad}{c}\right]&0\\0&b-\frac{ad}{c}\end{pmatrix}\begin{pmatrix}x\\y\end{pmatrix} = \begin{pmatrix}\frac{a}{c}&-\frac{a}{c}\\1&-\frac{a}{c}\end{pmatrix}\begin{pmatrix}x'\\y'\end{pmatrix}$$

Inverted Transformation

$$\begin{array}{l}a'\\b'\end{array}\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}x\\y\end{pmatrix} = \begin{pmatrix}-\frac{d}{c}\frac{1}{b-\frac{ad}{c}}&\frac{b}{c}\frac{1}{b-\frac{ad}{c}}\\\frac{1}{b-\frac{ad}{c}}&-\frac{a}{c}\frac{1}{b-\frac{ad}{c}}\end{pmatrix}\begin{pmatrix}x'\\y'\end{pmatrix} = A^{-1}\begin{pmatrix}x'\\y'\end{pmatrix} = \begin{pmatrix}x\\y\end{pmatrix} \quad (3)$$

$$\begin{pmatrix}\frac{d}{ad-bc}&\frac{-b}{ad-bc}\\\frac{-c}{ad-bc}&\frac{a}{ad-bc}\end{pmatrix}$$

How can we check the Inversion is correct?

Moisture Content $\frac{m_w}{m_w + m_o}$

Moisture Ratio $\frac{m_w}{m_o}$

Dryness $\frac{m_o}{m_o + m_w}$

Let us discuss again some thermodynamic potentials:

Internal Energy

$U = TS - pV + \mu N$ (Heat, work, Chem. pot.) $\qquad dU = TdS - pdV + \mu dN$

Enthalpy

$H \equiv U + pV = TS + \mu N \qquad dH = TdS + Vdp + \mu dN$

Gibb's Function

$G \equiv U - TS + pV = \mu N \qquad dG = -SdT + Vdp + \mu dN$

Phase Transition: $dp = dT = 0$

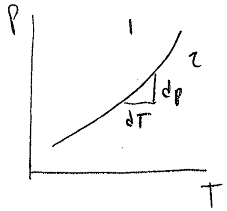
$\Rightarrow \Delta H = T\Delta S$ Change of Heat

Coexistense: $G_1(p,T,N) = G_2(p,T,N)$

$\Delta G_2 - \Delta G_1 = 0$

$\Delta G_1 = -S_1 dT + V_1 dp$

$\Delta G_2 = -S_2 dT + V_2 dp$



$-(S_2 - S_1)dT + (V_2 - V_1)dp = 0$

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

Clausius-Clapeyron Eq.

Clausius-Clapeyron continued

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} \qquad \Delta V \simeq V_{vapor} \qquad pV = nRT \qquad V_{vapor} \approx \frac{nRT}{p}$$

$$\frac{dp}{dT} = \frac{\Delta H p}{nRT^2}$$

$$\frac{dp}{p} = \frac{\Delta H}{nRT^2} dT \quad \Big| \int$$

$$\ln p = \frac{-\Delta H}{nRT} + C = -\frac{\Delta H}{m} \frac{m_{mol}}{RT} + C$$

$m = n\, m_{mol}$

$n = \frac{m}{m_{mol}}$

For Water:

$\frac{\Delta H}{m} \approx 2260\ J/g$

$m_{mol} = 18\ g/mol$

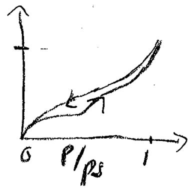
$R = 8{,}31 \frac{J}{mol\,K}$

$$p = e^{-\frac{\Delta H}{m}\frac{m_{mol}}{RT}} e^{c} = C_2\, e^{-\frac{\Delta H}{m}\frac{m_{mol}}{RT}}$$

$\equiv p_s$ SATURATION VAPOR PRESSURE

Relative Vapor Pressure
Water Activity
Relative Humidity } p/p_s $\Rightarrow$ Equilibrium moisture content

Hysteresis



Why does MC Increase w. p/p_s ?

KELVIN Eq II:

$$p_r = p_\infty e^{\frac{V 2\gamma}{RTr}}$$

Vapor pressure in droplet of radius r

p_∞: p_s

γ = surface tension

V = molar volume

For largest droplet

$$1 = \frac{p_\infty}{p_s} e^{\frac{V2\gamma}{RTr}}$$

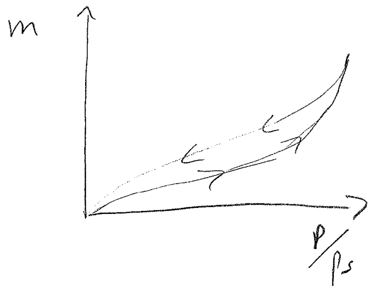
$$\frac{p}{p_s} = e^{-\frac{V2\gamma}{RTr}}$$

$$-\frac{V2\gamma}{RTr} = \ln p/p_s$$

$$r_{max} = -\frac{V2\gamma}{RT \ln p/p_s}$$

Check the Eq. for $\begin{cases} p \to 0 \\ p \to p_s \end{cases}$

ADSORPTION HYSTERESIS

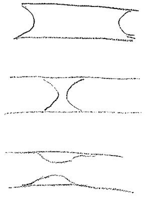


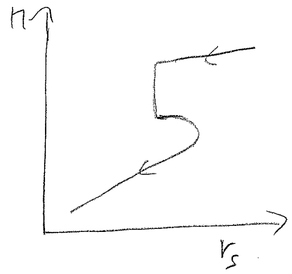
Why does Equilibrium moisture content depend on history?

Kelvin Eq. $\frac{p}{p_s} = e^{-\frac{\gamma 2M}{r_s RST}} \Rightarrow -\ln\frac{p}{p_s} \propto \frac{1}{r_s}$

$$r_s \propto \frac{1}{-\ln p/p_s}$$

Desorption of water from a capillary:





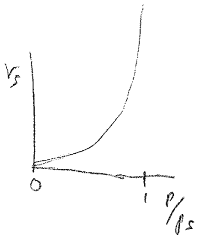
p: $0 \to p_s$

$\frac{p}{p_s}$: $0 \to 1$

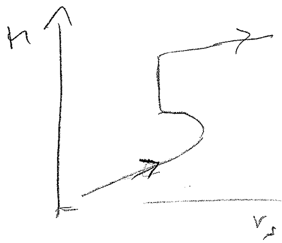
$\ln\frac{p}{p_s}$: $-\infty \to 0$

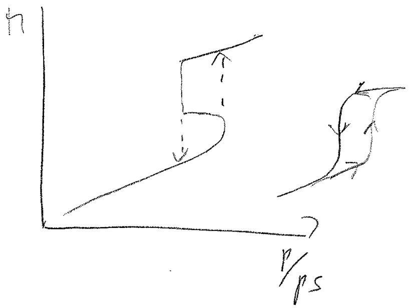
$-\ln\frac{p}{p_s}$: $\infty \to 0$

$\frac{1}{-\ln p/p_s}$: $0 \to \infty$



Adsorption





Determination of FSP through Solute Exclusion Technique

1° Produce a solution of molecules, concentration $c_1 = \frac{m_1}{V_1}$

2° Add wet porous substance, mass of solids in relation to volume of water $c_2 = \frac{m_2}{V_2}$

3° some of the water coming with the substance dilutes the solution, concentration becomes

$$c_3 = \frac{m_1}{V_3}$$

What is now V_3?
That is water volume accessible to the molecules. $V_1 + V_2 = V_3 + V_4$

V_4 is Inaccessible water volume

$$V_4 = V_1 + V_2 - V_3 = \frac{m_1}{c_1} + \frac{m_2}{c_2} - \frac{m_1}{c_3}$$

$$FSP \left[\frac{()}{()}\right] = \frac{V_4 \cdot \rho_w}{m_2} = \rho_w \left[\frac{m_1}{m_2}\left(\frac{1}{c_1} - \frac{1}{c_3}\right) + \frac{1}{c_2}\right]$$

$V_4 \cdot \rho_w$ = mass of water in pores Inaccessible to molecules

Thermal transitions

- changes in thermal properties

First-order transition

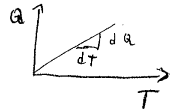
- change in heat capacity
- latent heat involved

Second-order transition

- change in heat capacity only

Heat: thermal energy [J] Q

Heat Capacity: $\frac{dQ}{dT}$

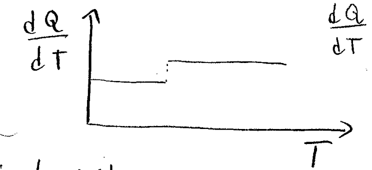


Heat flow rate $\frac{dQ}{dt}$

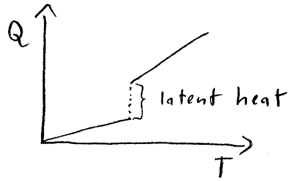
Temperature change rate $\frac{dT}{dt}$

Thermal transition

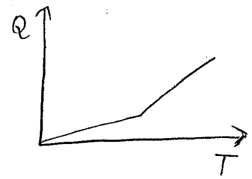
$$\frac{dQ}{dT} = \frac{dQ/dt}{dT/dt}$$



First-order



Second-order



Let us produce heat in a resistor:

Potential difference $\Delta P = P_2 - P_1$ $[V] = \left[\frac{J}{C}\right]$

Current I $[A] = \left[\frac{C}{s}\right]$

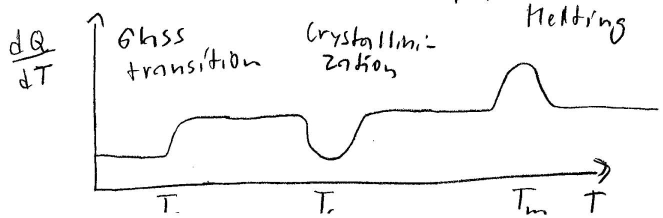
Power $\Delta P\, I \rightarrow \boxed{\frac{dQ}{dt}}$ $\left[\frac{J}{s}\right]$

Work $\int \Delta P\, I\, dt$

$\rightarrow$ dissipated as heat

Calorimetry:
Measurement of Heat flows

Thermal transitions of polymers



How Do we measure Heat Capacity?

$$\frac{dQ}{dT} = \frac{dQ/dt}{dT/dt}$$

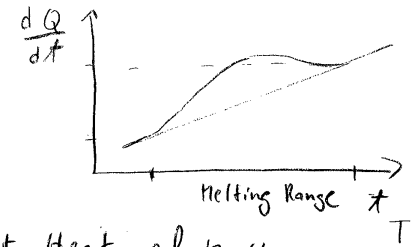
How do we measure Latent Heat?

$\frac{dT}{dt} = \text{constant}$

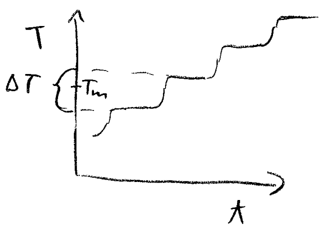
$$\Delta Q = \int \frac{dQ}{dt}\, dt = \Delta Q_c + \Delta H$$

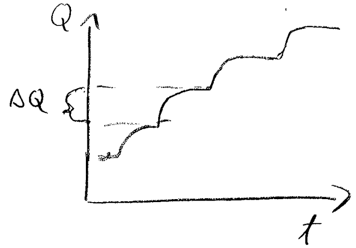
$$= \int \left(\frac{\partial Q}{\partial t}\right)_c dt + \Delta H$$

$$= \int \left(\frac{\partial Q}{\partial T}\right)_c dT + \Delta H$$



How do we measure Latent Heat of Melting at a particular Temperature Range?





$$\Delta Q = \left(\frac{\partial Q}{\partial T}\right)_c \Delta T + \Delta H$$

$$\Delta H(T_m) = \Delta Q(T_m) - \left[\left(\frac{\partial Q}{\partial T}\right)_c\right](T_m)\, \Delta T$$

$$m_{FW}(T_m) = \frac{\Delta H(T_m)}{E_w} \approx \frac{\Delta H(T_m)}{333\ J/g}$$

Non-Freezing Water

$$NFW \equiv \left[m_w - [m_{FW}]_{-\infty\, 0}\right] \frac{1}{m_0}$$

Cell Wall Water

$$m_{cw} = NFW \cdot m_0 + [m_{FW}]_{-\infty\, T_0^-}$$

$$= FSP \cdot m_0 \quad (?)$$

Melting Temperature Spectrum

Coexistence of Solid and Liquid

Chemical potential $\mu = \frac{G}{N}$ must be equal

$$d\mu^s = d\mu^\ell$$

$$dG^s = dG^\ell$$

$$-S^s dT + V^s dp^s = -S^\ell dT + V^\ell dp^\ell$$

$$(S^s - S^\ell)\, dT = V^s dp^s - V^\ell dp^\ell$$

$$-\Delta S\, dT = V^s d(p^\ell + \Delta p) - V^\ell dp^\ell$$

$$-\frac{\Delta H dT}{T} = (V^s - V^\ell)\, dp^\ell + V^s d(\Delta p)$$

$\Delta H = T\Delta S$

$\Delta S = \frac{\Delta H}{T}$

$$\approx V^s d(\Delta p)$$

$$\frac{dT}{T} = \frac{-V^s}{\Delta H} d(\Delta p) \Big/ \int$$

$$\ln T = -\frac{V^s}{\Delta H}\Delta p + C = -\frac{V^s}{\Delta H}\frac{2\gamma}{r} + C$$

$$= -\frac{V^s}{\Delta H}\frac{2\gamma}{r} + \ln T_0$$

$$\ln T - \ln T_0 = \ln\frac{T}{T_0} = -\frac{V^s}{\Delta H}\frac{2\gamma}{r}$$

$$r_m = -\frac{V^s}{\Delta H}\frac{2\gamma}{\ln\frac{T_m}{T_0}}$$

Gibbs-Thomson Eq.

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Divergence Theorem (Gauss)

$$\int_V \nabla\cdot\bar{a}\, dV = \oint_S \bar{a}\cdot d\bar{S} = \oint_S \bar{a}\cdot\hat{n}\, dS$$

$$\nabla = \hat{e}_i \frac{\partial}{\partial x_i} \qquad \nabla\cdot\bar{a} = \frac{\partial a_1}{\partial x_1} + \frac{\partial a_2}{\partial x_2} + \frac{\partial a_3}{\partial x_3}$$

$$\bar{a} = a_1\hat{e}_1 + a_2\hat{e}_2 + a_3\hat{e}_3$$

Fick's First Law

Flux $\bar{J} = -[D]\nabla\cdot\phi \qquad \phi = \dfrac{\partial Q}{\partial V}$

$$J_i = \frac{\partial^2 Q}{\partial t\,\partial A_{\perp i}}$$

$[D]$ = Diffusivity matrix

$$\begin{pmatrix} J_1\hat{e}_1 \\ J_2\hat{e}_2 \\ J_3\hat{e}_3 \end{pmatrix} = \begin{pmatrix} \bar{J}_1 \\ \bar{J}_2 \\ \bar{J}_3 \end{pmatrix} = -\begin{pmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{pmatrix} \begin{pmatrix} \hat{e}_1 \frac{\partial\phi}{\partial x_1} \\ \hat{e}_2 \frac{\partial\phi}{\partial x_2} \\ \hat{e}_3 \frac{\partial\phi}{\partial x_3} \end{pmatrix}$$

Total Flow ~~into~~ out of Volume V

$$-\frac{dQ}{dt} = \oint_S \bar{J}\cdot d\bar{S} = \oint_S -[D]\nabla\cdot\phi\cdot d\bar{S} = \int_V \nabla\cdot\bar{J}\, dV$$

$$Q = \int_V \phi\, dV \qquad \rightarrow \int_V -[D]\nabla^2\phi\, dV$$

$$-\frac{dQ}{dt} = \int_V -\frac{d\phi}{dt}$$

$$\boxed{\frac{d\phi}{dt} = [D]\,\nabla^2\phi}$$

Diffusion Eq.

$$\boxed{\frac{d\phi}{dt} + \nabla\cdot\bar{J} = 0}$$

Continuum Eq.

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Thermal Flux Eq.

$$J_i = -D_i \frac{\partial}{\partial x_i}\phi \quad \text{(no sum)}$$

$$\frac{\partial^2 Q}{\partial t\,\partial A_{\perp i}} = -D_i \frac{\partial^2 Q}{\partial x_i\,\partial V}$$

$$\left[\frac{J}{s\,m^2}\right] \quad \left[\frac{m^2}{s}\right] \left[\frac{J}{m^4}\right]$$

Thermal Diffusivity

$$D_i = -\frac{\partial x_i\,\partial V}{\partial t\,\partial A_{\perp i}} =$$

How about Temperature Gradient as Flux Driving Factor?

Thermal Conductivity Eq.

$$J_i = -k_i \frac{\partial}{\partial x_i} T$$

$$\frac{\partial^2 Q}{\partial t\,\partial A_{\perp i}} = -k_i \frac{\partial}{\partial x_i} T$$

$$\left[\frac{J}{s\,m^2}\right] \quad \left[\frac{J}{m\,s\,K}\right] \left[\frac{K}{m}\right]$$

Thermal Conductivity

$$k_i = -\frac{\partial^2 Q\,\partial x_i}{\partial t\,\partial A_{\perp i}\,\partial T}$$

$$\frac{k_i}{D_i} = \frac{\partial^2 Q\,\partial x_i}{\partial t\,\partial A_{\perp i}\,\partial T}\;\frac{\partial t\,\partial A_{\perp i}}{\partial x_i\,\partial V} = \frac{\partial^2 Q}{\partial T\,\partial V}$$

= Volumetric Heat Capacity

$= C_V$

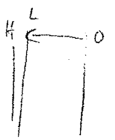
$$k_i = C_V D_i$$

How do we use the Diffusion Eq?

Steady-state problems $\rightarrow \frac{d\phi}{dt} = 0 \Rightarrow$ Laplace Eq.

Transient problems: Fourier series solution

Example: $\frac{\partial u}{\partial t} = D \frac{\partial^2 u}{\partial x^2}$



Heater, $\frac{\text{power}}{\text{Area}} = H$ $\boxed{J(L,t) = -H}$

Wall of thickness $= L$

Outside temperature $u(0,t) = 0$

Initial temperature $u(x,0) = 0$ } Boundary Conditions

Heat Flux at source $-D \frac{\partial u}{\partial x} = -H$ Inhomog.

Potential function transformation: $u(x,t) = v(x,t) + w(x)$

$$D\left(\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 w}{\partial x^2}\right) = \frac{\partial v}{\partial t}$$

$$v(x,0) + w(x) = 0$$

$$v(0,t) + w(0) = 0$$

$$\frac{\partial v(L,t)}{\partial x} + \frac{\partial w(L)}{\partial x} = \frac{H}{D}$$ set $w(x) \equiv \frac{Hx}{D}$

$$\Rightarrow \frac{\partial v(L,t)}{\partial x} = 0$$

$$\frac{\partial v(x,0)}{\partial x} = -\frac{H}{D} \Rightarrow v(x,0) = -\frac{Hx}{D}$$

$$v(0,t) = 0$$

Homogeneous Boundary conditions

Now separate $v(x,t) = X(x)\,T(t)$

$$D \frac{\partial^2 (X(x)\,T(t))}{\partial x^2} = \frac{\partial X(x)\,T(t)}{\partial t}$$

$$D X'' T = X T' \Rightarrow \frac{X''}{X} = \frac{T'}{T}\frac{1}{D} \equiv -\lambda^2$$

$$X'' = -\lambda^2 X \Rightarrow X = a e^{i\lambda x} + b e^{-i\lambda x}$$
$$= A \cos \lambda x + B \sin \lambda x$$

$$T' = -\lambda^2 D T$$
$$\Rightarrow T = c \cdot e^{-\lambda^2 D t}$$

$$v(x,t) = (A \cos \lambda x + B \sin \lambda x)\, e^{-\lambda^2 D t}$$

$$v(0,t) = 0 \Rightarrow A = 0$$

$$v(x,t) = B \sin(\lambda x)\, e^{-\lambda^2 D t}$$

$$\frac{\partial v(L,t)}{\partial x} = 0 \Rightarrow B\lambda \cos(\lambda L) = 0$$

$$\Rightarrow \lambda = \frac{n\pi}{2L}, \quad n = 1, 3, 5, \ldots$$

One Solution:

$$v(x,t) = B \sin\left(\frac{n\pi}{2L} x\right) e^{-\frac{n^2\pi^2}{4L^2} D t}$$

General solution as superposition

$$v(x,t) = \sum_{n\,\text{odd}} B_n \sin\left(\frac{n\pi}{2L} x\right) e^{-\frac{n^2\pi^2}{4L^2} D t}$$

With boundary condition $t = 0$

$$v(x,0) = \sum_{n\,\text{odd}} B_n \sin\left(\frac{2\pi n x}{4L}\right) = -\frac{Hx}{D}$$

Identify Fourier sine series

$$v(x,0) = \sum_{n_{odd}} B_n \sin\left(\frac{n\pi}{2L}x\right) = -\frac{H}{D}x \qquad \Big| \cdot \sin\left(\frac{n\pi}{2L}x\right) \int_{-L}^{L} dx$$

$$\int_{-L}^{L} -\frac{H}{D}x \sin\left(\frac{n\pi}{2L}x\right) dx = B_n \frac{2L}{2}$$

$$B_n = -\frac{H}{DL}\int_{-L}^{L} x \sin\left(\frac{n\pi}{2L}x\right) dx$$

$$= -\frac{H}{DL}\frac{4L^2}{n^2\pi^2}\int_{-\frac{n\pi}{2}}^{\frac{n\pi}{2}} \frac{n\pi x}{2L}\sin\left(\frac{n\pi x}{2L}\right) d\,\frac{n\pi x}{2L}$$

$$= -\frac{H}{D}\frac{8L}{n^2\pi^2}\int_0^{\frac{n\pi}{2}} y \sin y\, dy$$

$$= -\frac{H}{D}\frac{8L}{n^2\pi^2}\left[\underbrace{\Big/_0^{n\frac{\pi}{2}} y(-\cos y)}_{0} - \int_0^{n\frac{\pi}{2}} -\cos y\, dy\right]$$

$$= -\frac{H}{D}\frac{8L}{n^2\pi^2}\Big/_0^{n\frac{\pi}{2}} \sin y\, dy = -\frac{H}{D}\frac{8L}{\pi^2}\frac{1}{n_{odd}^2}(-1)^{\frac{n_{odd}-1}{2}}$$

$$v(x,0) = -\frac{H}{D}\frac{8L}{\pi^2}\sum_{n_{odd}}\frac{(-1)^{\frac{n-1}{2}}}{n^2}\sin\left(n\frac{\pi}{2}\frac{x}{L}\right)$$

$$u(x,t) = w(x) + v(x,t) = \frac{H}{D}x - \frac{H}{D}\frac{8L}{\pi^2}\sum_{n_{odd}}\frac{(-1)^{\frac{n-1}{2}}}{n^2}\sin\left(n\frac{\pi}{2}\frac{x}{L}\right)e^{-\frac{n^2\pi^2 D}{4L^2}t}$$

$$\int_{-L}^{L}\sin^2(Ax)\,dx =$$

$$\frac{1}{A}\int_{-AL}^{AL}\sin^2(Ax)\,d(Ax) =$$

$$\frac{1}{A}\frac{2AL}{2} = \frac{2L}{2}$$

$$\int fg' = \Big/ fg - \int f'g$$

$f = y$

$g' = \sin y$

$g = -\cos y$

n	$\sin(n\frac{\pi}{2})$
1	1
2	0
3	-1
4	0
5	1

$\left\{ \frac{n_{odd}-1}{2} \right.$

0 for n_{even}

What is actually u ?

↳ potential density → Heat density $\frac{Q}{V}$

Temperature $T = \frac{Q}{V} \Big/ \frac{\partial^2 Q}{\partial T \partial V} = u / c_v$

Volumetric Heat capacity

Reduced position $x \to \frac{x}{L} \equiv x'$

Reduced Heat Density $u \to u\frac{D}{HL} \equiv u'$

Reduced Temperature $T \to T c_v \frac{D}{HL} = u\frac{D}{HL} \equiv T' \equiv u'$

Reduced Time $t \to \frac{\pi^2 D}{4L^2}t \equiv t'$

$u' \equiv$

$$u\frac{D}{HL} = \frac{x}{L} - \frac{8}{\pi^2}\sum_{n_{odd}}\frac{(-1)^{\frac{n-1}{2}}}{n^2}\sin\left(n\frac{\pi}{2}x'\right)e^{-n^2 t'}$$

Free variables ; $\{x', t'\}$

x' : $0 \to 1$

t' : $0 \to \infty$

The final Question:

Does our solution satisfy the Diffusion Equation

$$D\frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t} \quad ?$$

$$u(x,t) = v(x,t) + w(x)$$

$$w(x) = \frac{Hx}{D} \qquad \frac{\partial u}{\partial t} = \frac{\partial v}{\partial t}$$

$$\frac{\partial^2 w}{\partial x^2} = 0$$

$$\frac{\partial^2 u}{\partial x^2} = \frac{\partial^2 v}{\partial x^2}$$

$$\frac{\partial v}{\partial x} = -\frac{H}{D}\frac{8L}{\pi^2}\sum_{n_{odd}}\frac{(-1)^{\frac{n-1}{2}}}{n^2}\frac{n\pi}{2L}\cos\left(n\frac{\pi}{2}\frac{x}{L}\right)e^{-\frac{n^2\pi^2}{4L^2}Dt}$$

$$\frac{\partial^2 v}{\partial x^2} = -\frac{H}{D}\frac{4}{\pi}\sum_{n_{odd}}\frac{(-1)^{\frac{n-1}{2}}}{n}(-1)\frac{n\pi}{2L}\sin\left(n\frac{\pi}{2}\frac{x}{L}\right)e^{-\frac{n^2\pi^2 D}{4L^2}t}$$

$$= \frac{H}{D}\frac{2}{L}\sum_{n_{odd}}(-1)^{\frac{n-1}{2}}\sin\left(n\frac{\pi}{2}\frac{x}{L}\right)e^{-\frac{n^2\pi^2 D}{4L^2}t}$$

$$\frac{\partial v}{\partial t} = -\frac{H}{D}\frac{8L}{\pi^2}\sum_{n_{odd}}\frac{(-1)^{\frac{n-1}{2}}}{n^2}\sin\left(n\frac{\pi}{2}\frac{x}{L}\right)\left(-\frac{n^2\pi^2 D}{4L^2}\right)e^{-\frac{n^2\pi^2 D}{4L^2}t}$$

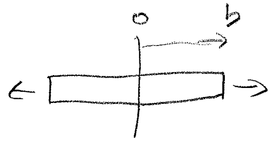
$$= H\frac{2}{L}\sum_{n_{odd}}(-1)^{\frac{n-1}{2}}\sin\left(n\frac{\pi}{2}\frac{x}{L}\right)e^{-\frac{n^2\pi^2 D}{4L^2}t}$$

$$D\frac{\partial^2 v}{\partial x^2} = \frac{\partial v}{\partial t}$$

$$\hookrightarrow \quad D\frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t} \qquad \square$$

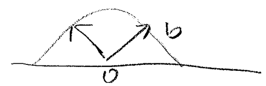
P. K. 29.1.2020

$$\frac{\partial u}{\partial t} = D\frac{\partial^2 u}{\partial x^2}$$



$$u(x,t) = X(x)\,T(t)$$

$$XT' = DX''T$$



$$\frac{X''}{X} = \frac{T'}{T}\frac{1}{D} = -\lambda^2 \Rightarrow \begin{cases} X = A\cos\lambda x + B\sin\lambda x \\ T = C e^{-\lambda^2 D t}\end{cases}$$

$$u(x,t) = \sum_{n=1}^{\infty} A_n \cos\left(\frac{\pi n x}{2b}\right) e^{-\left(\frac{\pi n}{2b}\right)^2 D t}$$

$$\frac{\partial X(0)}{\partial x} = 0$$

$$\frac{\partial X(x)}{\partial x} \le 0 \qquad X(x) \ge 0$$

$$\Rightarrow X(x) = A\cos\left(\frac{\pi n x}{2b}\right)$$

$$n = 1, 3, 5, \dots$$

$$\lambda = \frac{\pi n}{2b}$$

$$u(x,0) = \sum_{n=1}^{\infty} A_n \cos\left(\frac{\pi n x}{2b}\right) \quad \Big| \cdot \cos\left(\frac{\pi m x}{2b}\right) \quad \int_0^b dx$$

$$A_n = \frac{2}{b}\int_0^b u(x,0)\cos\left(\frac{\pi n x}{2b}\right)dx$$

$$= \frac{4}{\pi n}\int_0^{\frac{\pi n}{2}} u(x,0)\cos\left(\frac{\pi n x}{2b}\right) d\frac{\pi n x}{2b}$$

$$= \frac{4\,u(x,0)}{\pi n}(-1)^{\frac{n-1}{2}}, \; n \text{ odd} \xrightarrow{u(x,0)=1} \frac{4}{\pi n}(-1)^{\frac{n-1}{2}}$$

$$u(x,t) = \sum_{n_{odd}} \frac{4}{\pi n}(-1)^{\frac{n-1}{2}} \cos\left(\frac{\pi n x}{2b}\right) e^{-n^2 D\left(\frac{\pi^2}{4b^2}t\right)} \qquad \square$$

31.1.2022

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$$\Delta A = (R+\Delta R)^2 - R^2$$
$$= 2\,\Delta R\,R$$
$$A = R^2$$
$$V = \Delta R\,R^2$$

$$\frac{\partial Q}{\partial t} = {}^{-}A\,\Delta J + {}^{-}J\,\Delta A$$

$$\frac{\partial \phi}{\partial t} = -\frac{\Delta J}{\Delta R} + \frac{{}^{-}J\,2\,\Delta R\,R}{\Delta R\,R^2}$$
$$= -\nabla J + \frac{{}^{-}J\,2}{R}$$
$$= D\nabla^2\phi + \frac{2D\nabla\phi}{R} = D\frac{\partial^2\phi}{\partial r^2} + \frac{2D\frac{\partial\phi}{\partial r}}{R}$$

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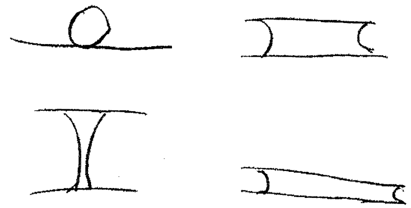
What is the Young's Modulus of Water?

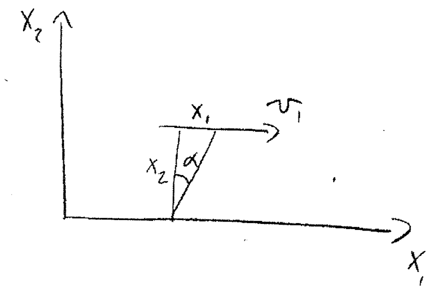
Negative in compression?



$$\sigma_{ij} = \text{function}(\dot\varepsilon_{kl}) = \text{function}\left(\frac{d\varepsilon_{kl}}{dt}\right)$$

Newtonian Viscosity for Isotropic Fluid:

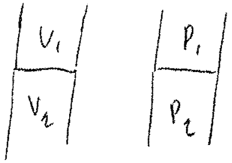
$$\sigma_{ij} = \eta\,\dot\varepsilon_{ij} = \eta\frac{dv_i}{dx_j} = \eta\frac{d^2u_i}{dt\,dx_j} = \eta\frac{d}{dt}\tan\alpha$$



Gravity Drainage Experiment

$dV_1 = -dV_2$

$\Delta P = P_2 - P_1$



$\frac{dV_1}{dt} \propto \Delta P$ Darcy's Law

$\frac{dV_1}{dt} = \frac{\Delta P A}{\eta R}$ $R \equiv$ Filtration Resistance

$b \equiv$ thickness

$R \propto b \Rightarrow R = SFR_b \cdot b$

Specific Filtration Resistance: $R \propto Bw \Rightarrow R = SFR_{Bw} \cdot Bw$

$$\frac{dV_1}{dt} = \frac{\Delta P}{b} \frac{A}{\eta \, SFR_b}$$

towards continuum:

$$\frac{dV_2}{A\,dt} = -\frac{dp}{dx} \frac{1}{\eta \, SFR_b}$$

Can we generalize this?

1-d Fick's Law

$$\frac{\partial^2 Q}{\partial t \, \partial A_\perp} = -D \frac{\partial^2 Q}{\partial x \, \partial V}$$

3-d Fick's Law

$$J_i \equiv \frac{\partial^2 Q}{\partial t \, \partial A_{\perp i}}$$

$$\phi \equiv \frac{\partial Q}{\partial V}$$

$$J_i = -[D] \nabla \cdot \phi = -[D] \hat{e}_i \frac{\partial}{\partial x_i} \phi$$

$$\begin{pmatrix} J_1 \hat{e}_1 \\ J_2 \hat{e}_2 \\ J_3 \hat{e}_3 \end{pmatrix} = \begin{pmatrix} \bar{J}_1 \\ \bar{J}_2 \\ \bar{J}_3 \end{pmatrix} = -\begin{pmatrix} D_1 & 0 & 0 \\ 0 & D_2 & 0 \\ 0 & 0 & D_3 \end{pmatrix} \begin{pmatrix} \hat{e}_1 \frac{\partial \phi}{\partial x_1} \\ \hat{e}_2 \frac{\partial \phi}{\partial x_2} \\ \hat{e}_3 \frac{\partial \phi}{\partial x_3} \end{pmatrix}$$

Flux Equation / Fick's Law

$$\frac{\partial^2 Q}{\partial t \, \partial A_{\perp i}} = -D_i \frac{\partial^2 Q}{\partial x_i \, \partial V} = -D_i \frac{\partial \phi}{\partial x_i}$$

Conductivity Equation

$$\frac{\partial^2 Q}{\partial t \, \partial A_i} = -K_i \frac{\partial T}{\partial x_i}$$

Using the Divergence Theorem

$\rightarrow$ Diffusion Eq. $\frac{d\phi}{dt} = [D] \nabla^2 \phi$

Continuity Eq. $\frac{d\phi}{dt} + \nabla \cdot \bar{J} = 0$

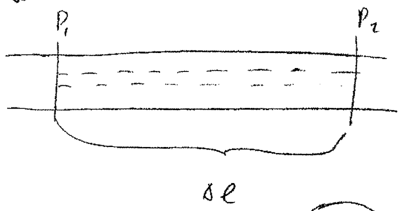
Darcy's Law

$$\frac{\partial^2 V_2}{\partial t \, \partial A_\perp} = -\frac{K}{\eta} \frac{dp}{dK}$$

$\eta \equiv$ viscosity

$K \equiv$ Permeability

Hagen - Poiseulle Law



$$-(P_2-P_1)\,\pi r^2 + \sigma_{lr}\, 2\pi r\, \delta l = 0$$

$$-(P_2-P_1)\,\pi r^2 + \eta\, \dot{\varepsilon}_{lr}\, 2\pi r\, \delta l = 0$$

$$\dot{\varepsilon}_{lr} = \frac{d}{dt}\frac{du}{dr} = \frac{d}{dr}\frac{du}{dt} = \frac{d}{dr} v$$

$$\dot{\varepsilon}_{lr} = \frac{(P_2-P_1)\,r}{2\eta\,\delta l} = \frac{dP}{dl}\frac{r}{2\eta}$$

$$\frac{dv}{dr} = \frac{dP}{dl}\frac{r}{2\eta}$$

$$dv = \frac{dP}{dl}\frac{r}{2\eta}\,dr$$

$$v = \frac{dP}{dl}\frac{r^2}{4\eta} + c$$

$$v(r=R) = 0 \Rightarrow c = -\frac{dP}{dl}\frac{R^2}{4\eta}$$

$$v(r) = \frac{dP}{dl}\frac{r^2-R^2}{4\eta}$$

$$\frac{dV}{dt} = \int_0^R 2\pi r\, v(r)\, dr = -\frac{dP}{dl}\frac{2\pi}{4\eta}\int_0^R rR^2 - r^3\, dr = -\frac{dP}{dl}\frac{2\pi}{4\eta}\Big/_0^R \frac{1}{2}r^2R^2 - \frac{1}{4}r^4$$

$$= -\frac{dP}{dl}\frac{2\pi}{4\eta}\frac{R^4}{4} = -\frac{dP}{dl}\frac{\pi R^4}{8\eta}$$

$$\frac{dV}{A_\perp\, dt} = \frac{1}{\pi R^2}\frac{\partial V}{\partial t} = -\frac{dP}{dl}\frac{R^2}{8\eta}$$

Rewrite Darcy's Law

$$\frac{\partial^2 V}{\partial t\,\partial A_\perp} = -\frac{K}{\eta}\frac{dP}{dl} \qquad K \equiv \text{Permeability}$$

$$K = \frac{1}{SFR_b} = \frac{1}{SFR_{Bw}\frac{Bw}{b}} = \frac{1}{SFR_{Bw}\,\xi}$$

Porosity Effect

$$\frac{\partial}{\partial A_\perp}\frac{\partial V}{\partial t} \equiv \frac{\partial N}{\partial A_\perp}\frac{\partial}{\partial N}\frac{\partial V}{\partial t} = \frac{\mathbb{P}}{\pi R^2}\left[-\frac{\pi R^4}{8\eta}\frac{dP}{dl}\right] = -\mathbb{P}\frac{R^2}{8}\frac{1}{\eta}\frac{dP}{dl}$$

$$\Rightarrow K = \mathbb{P}\frac{R^2}{8} \qquad \mathbb{P} \equiv \text{Porosity}$$

Variable Size of Pores

$$K = \int \mathbb{P}\frac{R^2}{8}\, p(R)\, dR$$

Variable Geometry, Alignment.

$$K \propto \mathbb{P} R_{ch}^2$$

$$SFR_b \propto \frac{1}{\mathbb{P} R_{ch}^2}$$

$$SFR_{Bw} \propto \frac{1}{\xi\,\mathbb{P} R_{ch}^2}$$

$$t_{Bwf} = \frac{\eta\, SFR_{Bw}\,(Bwf)^2}{2\Delta p\, c}$$

$$\propto \frac{\eta\,(Bw)^2}{\Delta p\, c\, \xi\, \mathbb{P} R_{ch}^2}$$

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A Porous System Consisting of Parallel Tubes

$$\frac{dV}{dt} = \left(\frac{dV}{dt}\right)_1 + \left(\frac{dV}{dt}\right)_2 + \dots + \left(\frac{dV}{dt}\right)_n$$

$$\frac{dV}{A\,dt} = \frac{1}{A}\left[\left(\frac{dV}{dt}\right)_1 + \left(\frac{dV}{dt}\right)_2 + \dots + \left(\frac{dV}{dt}\right)_n\right] = \frac{1}{A}\left[A_1\left(\frac{dV}{A\,dt}\right)_1 + \dots\right]$$

If all tubes are of the same size

$$\frac{dV}{A\,dt} = \frac{nA_1}{A}\left(\frac{dV}{A_1\,dt}\right)_1 = -\mathbb{P}\,\frac{R^2}{8\eta}\,\frac{dp}{dl}$$

Tubes of not the same size

$$\frac{dV}{A\,dt} = -\frac{1}{A}\,\frac{dp}{dl}\,\frac{1}{8\eta}\left[A_1R_1^2 + A_2R_2^2 + \dots + A_nR_n^2\right]$$

$$= -\frac{A_p}{A}\frac{dp}{dl}\frac{1}{8\eta}\;\frac{A_1R_1^2 + A_2R_2^2 + \dots + A_nR_n^2}{A_p}$$

$$\frac{dV}{A\,dt} = -\mathbb{P}\,\frac{dp}{dl}\,\frac{1}{8\eta}\int P(A)\,R^2\,dA$$

$$= -\mathbb{P}\,\frac{dp}{dl}\,\frac{1}{8\eta}\int P(A)\,R^2\,2\pi R\,dR$$

$$= -\mathbb{P}\,\frac{dp}{dl}\,\frac{1}{8\eta}\int P(R)\,R^2\,dR$$

$$\int P(A)\,dA = 1$$

$$\int P(A)\,d(\pi R^2) = 1$$

$$\frac{d\pi R^2}{dR} = 2\pi R$$

$$d\pi R^2 = 2\pi R\,dR$$

$$\int P(A)\,2\pi R\,dR = 1$$

$$P(R) = P(A)\,2\pi R$$

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Time-dependent Mechanical Behavior – Linear Viscoelasticity

$$\varepsilon_{ij} = S_{ijkl}\,\sigma_{kl}$$

$$\Rightarrow\quad d\varepsilon_{ij}(t) = C_{ijkl}(t-\tau)\,d\sigma_{kl}(\tau)$$

$$\varepsilon_{ij}(t) = \int_{\sigma(\tau=-\infty)}^{\sigma(\tau=t)} C_{ijkl}(t-\tau)\,d\sigma_{kl}(\tau)$$

$$= \int_{-\infty}^{t} C_{ijkl}(t-\tau)\,\frac{d\sigma_{kl}}{d\tau}\,d\tau$$

$C_{ijkl}(t) \equiv$ Creep Compliance

$$\sigma_{ij} = Q_{ijkl}\,\varepsilon_{kl}$$

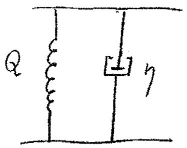
$$\Rightarrow\quad d\sigma_{ij}(t) = R_{ijkl}(t-\tau)\,d\varepsilon_{kl}(\tau)$$

$$\sigma_{ij}(t) = \int_{-\infty}^{t} R_{ijkl}(t-\tau)\,\frac{d\varepsilon_{kl}(\tau)}{d\tau}\,d\tau$$

$R_{ijkl}(t) \equiv$ Relaxation Modulus

What kind of a function is the Creep Compliance?

Voigt Element



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

$$\frac{d\sigma}{dt} = 0 \Rightarrow \dot{\varepsilon} Q + \ddot{\varepsilon}\eta = 0$$

write $\dot{\varepsilon} \equiv a \Rightarrow aQ + \dot{a}\eta = 0$

$$aQ = -\frac{da}{dt}\eta$$

$$-\frac{Q}{\eta}dt = \frac{da}{a} \quad \Big| \int$$

$$-\frac{Q}{\eta}t = \ln a + C \quad \Big| \exp()$$

$$a = \dot{\varepsilon} = C_2 e^{-\frac{Q}{\eta}t} \approx \frac{\sigma}{\eta} e^{-\frac{t}{\tau}}$$

$$\frac{d\varepsilon}{dt} = \frac{\sigma}{\eta} e^{-\frac{t}{\tau}}$$

$$d\varepsilon = \frac{\sigma}{\eta} e^{-\frac{Q}{\eta}t} dt \quad \Big| \int$$

$$\varepsilon = -\frac{\sigma}{Q} e^{-\frac{t}{\tau}} + C_3$$

$$\varepsilon(t=0) = -\frac{\sigma}{Q} + C_3 = 0 \Rightarrow C_3 = \frac{\sigma}{Q}$$

$$\varepsilon = \frac{\sigma}{Q}\left(1 - e^{-t/\tau}\right) \Rightarrow \boxed{C(t) = C_\infty\left(1 - e^{-t/\tau}\right)}$$

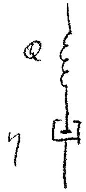
Voigt Elements in Series:

$$\varepsilon = \sum_i (C_\infty)_i \left(1 - e^{t/\tau_i}\right) \sigma$$

$$C(t) = \int_0^\infty (C_\infty)_i \left(1 - e^{-t/\tau_i}\right) di = \int_0^\infty C_\infty(\tau)\left(1 - e^{-t/\tau}\right)\frac{di}{d\tau}\, d\tau$$

What kind of a function is the Relaxation Modulus?

Maxwell Element



$$\sigma = Q\varepsilon_1 = \eta\dot{\varepsilon}_2$$

$$\varepsilon = \varepsilon_1 + \varepsilon_2$$

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt} = 0$$

$$\frac{1}{Q}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0$$

$$\frac{d\sigma}{\sigma} = -\frac{Q}{\eta}dt$$

$$\ln \sigma = -\frac{Q}{\eta}t + C$$

$$\sigma = C_2 e^{-\frac{Q}{\eta}t} = R_0 \varepsilon e^{-t/\tau}$$

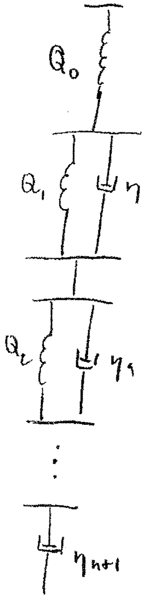
$$R(t) = R_0 e^{-t/\tau}$$

Maxwell elements in parallel:

$$\sigma = \sum_i \sigma_i = \sum_i R_i(t)\varepsilon = \varepsilon \sum_i (R_0)_i e^{-t/\tau_i}$$

$$R(t) = \int_i (R_0)_i e^{-t/\tau_i} di = \int_0^\infty (R_0)_i e^{-t/\tau_i}\frac{di}{d\tau}\, d\tau$$

What if two of the Voigt elements are degenerate?



$$C(t) = C_0 + \int_0^{\infty} (C_\infty)_i (1 - e^{-t/\tau}) \frac{dn_i}{d\tau} d\tau + \frac{t}{\eta}$$

$$= \boxed{C_0} + \int_{-\infty}^{\infty} \boxed{L(\tau)} (1 - e^{-t/\tau}) \, d(\ln \tau) + t/\boxed{\eta}$$

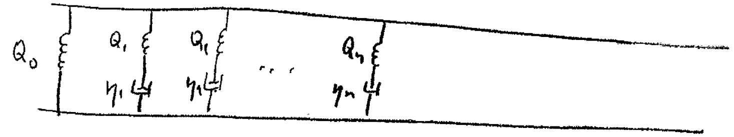
Glassy Compliance — Retardation Spectrum — Steady-state Viscosity

{ Steady-state Compliance?
Equilibrium
Rubbery

only if $\eta \to \infty$

$$C(\infty) = C_0 + \int_{-\infty}^{\infty} L(\tau) \, d(\ln \tau)$$

What if some of the elements are degenerate?



$$R(t) = Q_0 + \sum_i (R_0)_i \, e^{-t/\tau_i}$$

$$= Q_0 + \int_0^{\infty} (R_0)_i \, e^{-t/\tau_i} \frac{dn_i}{d\tau} d\tau$$

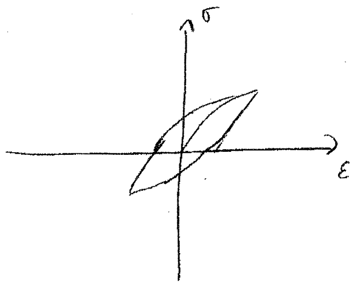
$$= \boxed{R_\infty} + \int_{-\infty}^{\infty} \boxed{H(\tau)} e^{-t/\tau} \, d(\ln \tau)$$

Equilibrium Modulus — Relaxation Spectrum

Glassy modulus:

$$R(t=0) = R_\infty + \int_{-\infty}^{\infty} H(\tau) \, d(\ln \tau) \equiv R_0$$

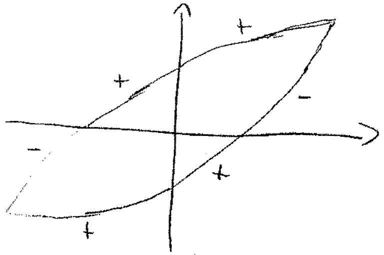
Cyclical Experiment



Strain Energy Density

$$\dot{W} = \frac{1}{2}\sigma\varepsilon = \frac{1}{2} Q \varepsilon^2$$

$$\frac{d\dot{W}}{d\varepsilon} = \sigma$$



Where does the work (energy) go ?

Stress – Strain – Time – Temperature – Moisture - relations

Crosslinked polymers:

Equilibrium Elasticity exist

$$\sigma = \varepsilon\left[R_\infty + \sum_i (R_0)_i \, e^{-t/\tau_i} \right]$$

Noncrosslinked: Liquid-like flow $(R_\infty = 0)$

Liquid-like flow

$$\varepsilon = \sigma\left[\quad \dots + t/\eta \right] \qquad \eta < \infty$$

Amorphous Polymers:

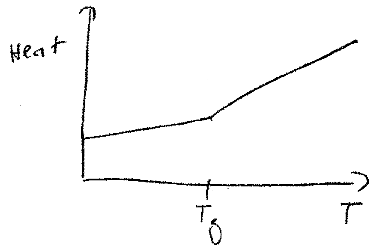
1/ Large-deformation Equilibrium properties

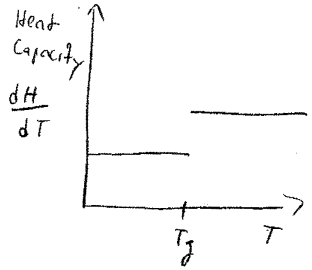
2/ Small-deformation nonequilibrium properties (viscoelastic)

3/ Large-deformation time-dependent properties

Amorphous Polymers:

Glass Transition – second-order transition

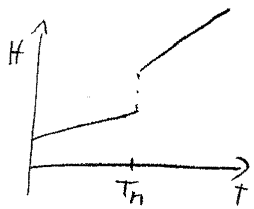




Crystalline polymers:

Melting – first-order transition

First-order transition



1/ Large-deformation Equilibrium properties

From kinetic theory:

$$\sigma = \rho k T \left(\varepsilon - \varepsilon^{-2}\right)$$

Eng. tensile stress
— " — strain

Shear Modulus $G = \rho k T$

How to approach this behavior?

- increase time
  = reduce straining rate
- speed up relaxation (temperature, moisture, ...)

Time-Temperature Equivalency

- All characteristic times similarly affected by temperature change

Thermorheologically simple materials:

$$C(T,t) = C\left(T_0, \frac{t}{a(T)}\right)$$

$$R(T,t) = R\left(T_0, \frac{t}{b(T)}\right)$$

$$b(T) \approx a(T) \quad (?)$$

$$T > T_0 \Rightarrow t < \frac{t}{a(T)}$$

$$\Rightarrow a(T) < 1$$

$$T < T_0 \Rightarrow t > \frac{t}{a(T)}$$

$$\Rightarrow a(T) > 1$$

$$\boxed{\text{Reduced time} \equiv \frac{t}{a(T)}}$$

WLF:

$$\log a(T) = -\frac{C_1(T-T_0)}{C_2+T-T_0} \approx \frac{-8{,}86\,(T-T_0)}{101{,}6+T-T_0}$$

$$\log a = \frac{\ln a}{\ln 10}$$

$$10^{\log a} = a = 10^{-\frac{C_1(T-T_0)}{C_2+T-T_0}}$$