STRUCTURE AND PROPERTIES OF WOOD-BASED MATERIALS 7

Structure
- Atomic
- Molecular
- Fibrillar
- Cellular
- Macroscopic

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

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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

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

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

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

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

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

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

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

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

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

Total of $9 \times 9 = 81$ components

$$\left.\begin{array}{l} \begin{array}{ccccc} \text{stress vector} & & \text{stiffness matrix} & & \text{strain vector} \\ \bar{\sigma} & = & [Q] & \cdot & \bar{\varepsilon} \end{array} \\ \text{In component form} \\ \sigma_{ij} = Q_{ijkl}\, \varepsilon_{kl} \end{array}\right\} \text{Linear elasticity}$$

→ page 8

$$\left.\begin{array}{l}\text{Orthotropic symmetry} \\ \text{On-axis crd}\end{array}\right\} \Rightarrow \left\{\begin{array}{l} Q_{ijkl} = Q_{klij} \\ \left\{\begin{array}{l} Q_{ijkl} = Q_{jikl} = Q_{ijlk} = Q_{jilk} \\ \sigma_{ij} = \sigma_{ji} \qquad \varepsilon_{kl} = \varepsilon_{lk} \end{array}\right. \\ Q_{iikl} = Q_{iikl}\,\delta_{kl} \quad \text{(no sum)} \\ Q_{ijil} = Q_{ijil}\,\delta_{jl} \quad \text{(no sum)} \end{array}\right.$$

9 independent components! $\Leftarrow$

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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 $I/A_\perp = \nu \frac{\partial V}{\partial x}$

Are these related to the above?

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

Resistance Equation $\Delta V = RI$

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

What is the dimension of $\begin{cases} \text{[illegible]} \\ R \\ \rho \end{cases}$?

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

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

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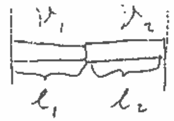
Composite Structures

Elements in Series



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

$$I_1 = I_2 = A_1\nu_1\left(\frac{\partial V}{\partial x}\right)_1 = A_2\nu_2\left(\frac{\partial V}{\partial x}\right)_2$$

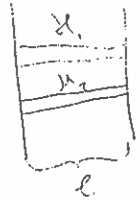
Conductivity Eq. for the Composite system:

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

$$= \nu\frac{l_1\left(\frac{\partial V}{\partial x}\right)_1 + l_2\left(\frac{\partial V}{\partial x}\right)_2}{l_1+l_2} = \nu\frac{l_1\frac{I/A_1}{\nu_1} + l_2\frac{I/A_2}{\nu_2}}{l_1+l_2}$$

$$\Rightarrow \nu = \frac{l_1+l_2}{\frac{A l_1}{A_1\nu_1} + \frac{A l_2}{A_2\nu_2}}$$

Elements in Parallel



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

$$\left(\frac{\partial V}{\partial x}\right)_1 = \left(\frac{\partial V}{\partial x}\right)_2 = \frac{\partial V}{\partial x} \Rightarrow \frac{I_1}{A_1\nu_1} = \frac{I_2}{A_2\nu_2}$$

$$I/A = \frac{I_1+I_2}{A_1+A_2} = \frac{I_1\left(1+\frac{A_2\nu_2}{A_1\nu_1}\right)}{A_1\left(1+\frac{A_2}{A_1}\right)} = \nu\left(\frac{\partial V}{\partial x}\right)_1 = \nu\frac{I_1}{A_1\nu_1}$$

$$\nu = \nu_1\frac{1+\frac{A_2\nu_2}{A_1\nu_1}}{1+\frac{A_2}{A_1}} = \frac{A_1\nu_1 + A_2\nu_2}{A}$$

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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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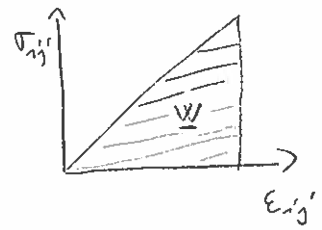
Strain Energy Density

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

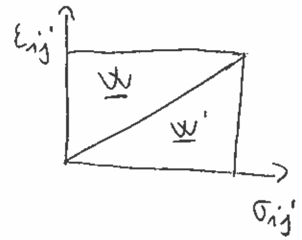
$$\Rightarrow \sigma_{ij} = \frac{\partial \underline{W}}{\partial \varepsilon_{ij}}$$

Chain Rule of Partial Derivatives



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

Complementary Strain Energy Density



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

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

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

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

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Symmetry of Compliance and Stiffness

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

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

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

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

On the other hand:

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

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

Similarly for Compliance:

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

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

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

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$$\boxed{\begin{array}{l}\varepsilon_{11} \equiv X_1 \\ \varepsilon_{22} \equiv X_2\end{array}}$$

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

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

$1°$ $W = \frac{1}{2}Q_{1111}X_1^2 + Q_{1122}X_1X_2 + g(X_2)$

$2°$ $W = Q_{2211}X_1X_2 + \frac{1}{2}Q_{2222}X_2^2 + h(X_1)$

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

$$\Rightarrow \quad W = \frac{1}{2}Q_{1111}X_1^2 + \frac{1}{2}Q_{2222}X_2^2 + \frac{1}{2}(Q_{1122} + Q_{2211})X_1X_2$$

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

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

Strength

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

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 $\quad \sigma_m = \sigma_{ii}$

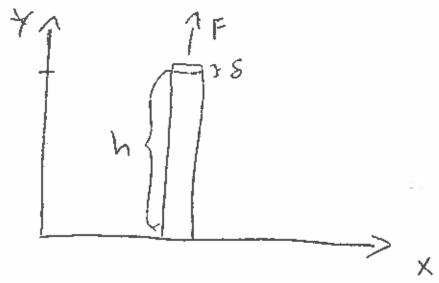
For Tension-Compression w. $\sigma_{11} = -\sigma_{22}$ $\quad \sigma_m = \sqrt{3}\,\sigma_{ii}$

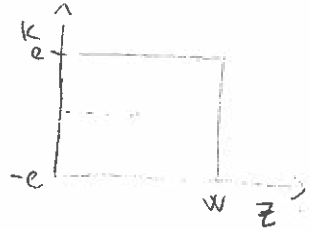
For pure shear in one plane $\quad \sigma_m = \sqrt{3}\,\sigma_{12}$

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

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

Rigidity in Tension





$$K \equiv \frac{F}{\delta} = \frac{\sigma A_\perp}{\varepsilon h} = \frac{E\,\sigma\, S_{A_\perp}}{h} = \frac{E\,(2e)\,w}{h}$$

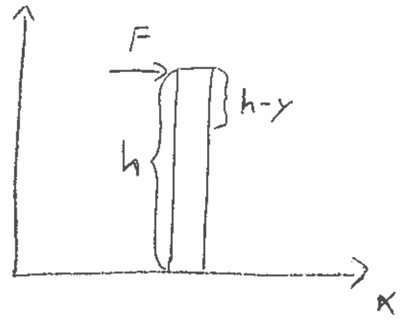
$$K' \equiv \frac{F}{\varepsilon} = E\,(2e)\,w$$

Bending of a Beam

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

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

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



$$M(y) = -F(h-y) \quad \text{for} \quad 0 \le y \le h$$

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

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

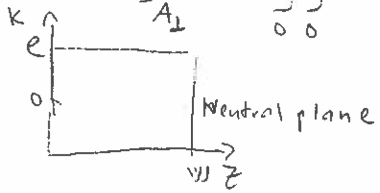
Curvature: $\frac{d^2x}{dy^2}$

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

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

Second Moment of Inertia:

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



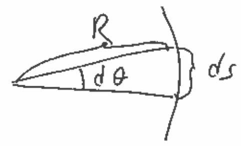
$$\uparrow \quad EI = E\frac{(2e)^3 w}{12}$$

Bending Rigidity

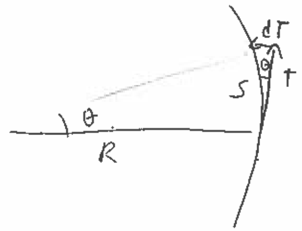
$$EI = \frac{-M(y)}{\frac{d^2x}{dy^2}} = \frac{\text{Momentum}}{\text{Curvature}}$$

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

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

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

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

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

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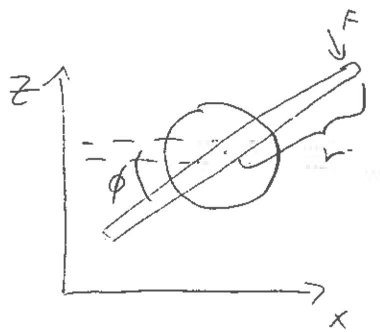
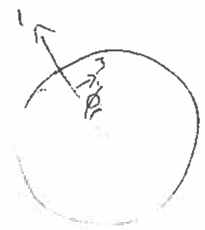
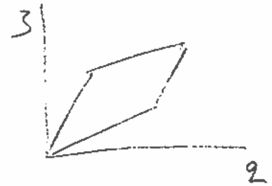
Torsional Rigidity



Torque $T = F \cdot r$

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





$u_3 = \phi r$

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

$$\sigma_{32} + \sigma_{23} = Q_{3232}\varepsilon_{32} + Q_{2323}\varepsilon_{23}$$

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

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

$$T = \int_{A_2} 2Q_{3232}\frac{\phi r^2}{\ell} = 2Q_{3232}\frac{\phi}{\ell}J$$

Polar Moment of Inertia

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

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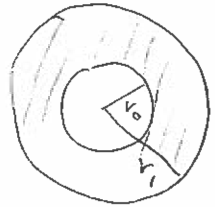
The Area of a Hollow Pipe

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

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



Polar Moment of Inertia

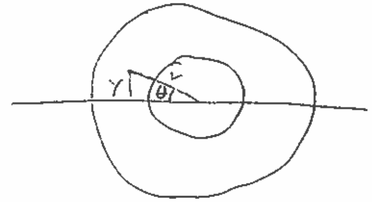
$$J = \int_0^{2\pi}\int_{r_0}^{r_1} r^3\,dr\,d\phi = \int_0^{2\pi} \Big/_{r_0}^{r_1} \frac{r^4}{4}\,d\phi = \frac{\pi}{2}(r_1^4 - r_0^4)$$

Second Moment of Inertia

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

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

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



$Y = r\sin\theta$

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

Mass Density Effects

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

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

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

Solid Fraction $\quad S \propto \rho$

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

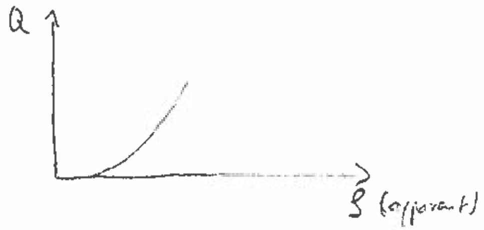
$\Rightarrow$ Specific Stiffness $\quad \frac{Q}{\rho} \propto \rho^{\mu} \Rightarrow Q \underset{\sim}{\propto} \rho^{1+\mu}$

$\mu \geq 0$

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: $\frac{\text{length}}{\text{mass}} \equiv \frac{1}{\text{Coarsene.}}$

Trivial Scaling

Linear Dimensions scaled by q

Object scaled as $\quad q^2 \rightarrow$ Area $\qquad q^1 \rightarrow$ 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 $\begin{cases} \text{line} \\ \text{Area} \end{cases}$ ... $\begin{cases} \text{Area} \\ \text{Volume} \end{cases}$ ...

$2^1 = 2$

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

$2^2 = 4$

$2^{5/3} \cong 5{,}7 \quad$ 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

$$q^m < q^3$$

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

$\boxed{\text{Is } \rho \text{ scale-invariant?}}$

Size Effect on Strength

Element Failure Probability $P_1(\sigma)$

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

$\boxed{\text{pdf = probability density function}}$

Element Survival Probability

$$1 - P_1$$

Chain Survival Probability

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

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

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

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

$$\ln(1 - P_1) = \ln(1-0) + (-1)\frac{1}{1-0}P_1 + \ldots$$

$$\approx -P_1$$

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

$$\Rightarrow P_f \approx 1 - e^{-NP_1(\sigma)} = P_f(\sigma) \quad \text{cdf of strength for the chain}$$

$$\left.\begin{array}{l} N \equiv \frac{V}{V_c} \\ \frac{1}{V_c}P_1(\sigma) \equiv c(\sigma) \end{array}\right\} \Rightarrow \boxed{P_f(\sigma, V) = 1 - e^{-c(\sigma)V}}$$

Weibull 1939: $c(\sigma) \approx \frac{1}{V_0}\left\langle\frac{\sigma - \sigma_1}{\sigma_0}\right\rangle^m$ $\quad \langle \text{abs } x\rangle = x$, $\langle -\text{abs } x\rangle = 0$

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

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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...

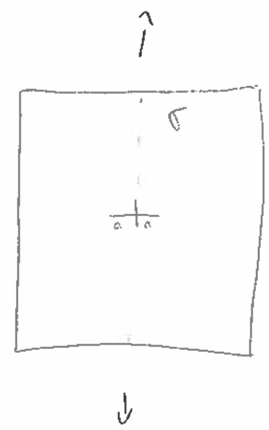
What is the median value of strength?

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

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

(20)

Fracture Mechanics Size Effect



Failure criterion

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

$$\frac{dW_s}{da} = \frac{d\, 4at\mathcal{G}}{da} = 4t\mathcal{G}$$

$$\frac{dW_s}{dA} = \mathcal{G} \qquad A \equiv 4ta$$

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

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

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

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

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

LEFM Size Effect

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

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

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

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

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

Size-Effect Scaling

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

Surface Energy γA

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

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

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

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

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

Molar Gibbs Function

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

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

Equilibrium

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

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

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)

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

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

Original transformation

$\begin{matrix}1a\\1b\end{matrix}\begin{pmatrix}a&b\\c&d\end{pmatrix}\begin{pmatrix}x\\y\end{pmatrix}=\begin{pmatrix}1&0\\0&1\end{pmatrix}\begin{pmatrix}x'\\y'\end{pmatrix}\iff$ 1a) $ax+by=x'$
1b) $cx+by=y' \quad |\cdot -\frac{a}{c}$

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

$\begin{matrix}1a\\2b\end{matrix}\begin{pmatrix}a&b\\0&b-\frac{ab}{c}\end{pmatrix}\begin{pmatrix}x\\y\end{pmatrix}=\begin{pmatrix}1&0\\1&-\frac{a}{c}\end{pmatrix}\begin{pmatrix}x'\\y'\end{pmatrix}$

1a) $ax+by=x' \quad \left|\cdot\left(-\frac{b-\frac{ab}{c}}{b}\right)\right.$
2b) $\left(b-\frac{ab}{c}\right)y=x'-\frac{a}{c}y'$

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

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

Inverted Transformation

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

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

$U=\underset{\text{Heat}}{TS}\ \underset{\text{work}}{-pV}\ \underset{\text{Chem. pot.}}{+\mu N}$ $\quad dU=TdS-pdV+\mu dN$

Enthalpy

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

Gibb's Function

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

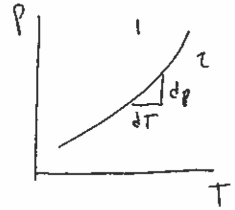
Phase Transition: $dp=dT=0$

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

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

$\Delta G_2-\Delta G_1=0$

$\Delta G_1=-S_1dT+V_1dp$
$\Delta G_2=-S_2dT+V_2dp$



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

$\frac{dp}{dT}=\frac{\Delta S}{\Delta V}=\frac{\Delta H}{T\Delta V}$ Clausius–Clapeyron Eq.

(25)

Clausius - Clapeyron Continued

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

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

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

$m = n\, m_{mol}$

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

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

For Water:

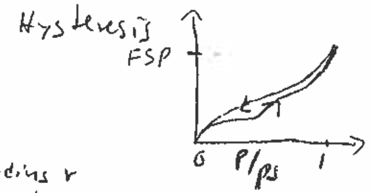
$$p = e^{-\frac{\Delta H}{m}\frac{m_{mol}}{RT}}\, e^{c} = C_2\, e^{-\frac{\Delta H}{m}\frac{m_{mol}}{RT}}$$

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

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

$\equiv p_s$ SATURATION VAPOR PRESSURE $\qquad R = 8.31 \frac{J}{mol\,K}$

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



Why does MC Increase w. p/p_s ?

KELVIN Eq II: Vapor pressure in droplet of radius r

$$p_r = p_\infty\, e^{\frac{V 2\gamma}{RTr}} \quad \Big|\, : p_s \qquad \gamma = \text{surface tension},\ V = \text{molar volume}$$

for largest droplet $\qquad 1 = \frac{p_\infty}{p_s}\, e^{\frac{V2\gamma}{RTr}}$

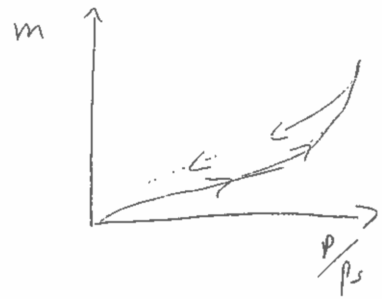
$$\frac{p}{p_s} = e^{-\frac{V2\gamma}{RTr}}$$

$$-\frac{V2\gamma}{RTr} = \ln p/p_s \qquad \text{check the Eq. for } \begin{cases} p \to 0 \\ p \to p_s \end{cases}$$

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

(26)

ADSORPTION HYSTERESIS

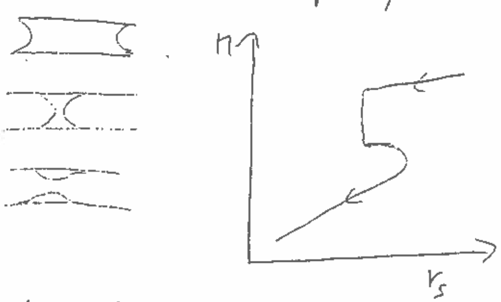


Why does Equilibrium moisture content depend on history?

Kelvin Eq. $\quad \frac{p}{p_s} = e^{-\frac{V2\gamma}{r_s RT}} \Rightarrow -\ln\frac{p}{p_s} \propto \frac{1}{r_s}$

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

Desorption of water from a capillary:



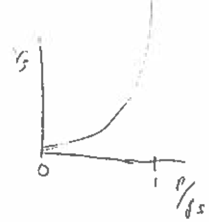
p: $0 \to p_s$

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

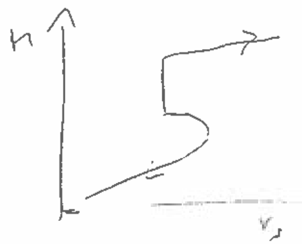
$\ln\frac{p}{p_s}$: $-\infty \to 0$

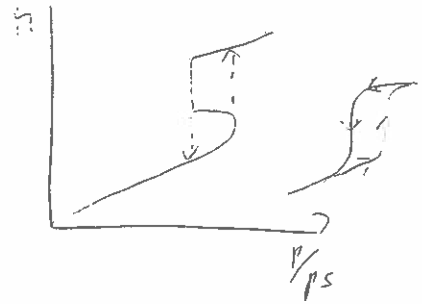
$-\ln p/p_s$: $\infty \to 0$

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



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

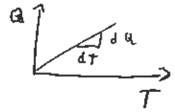
Thermal transitions

- 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: $\frac{dQ}{dT}$

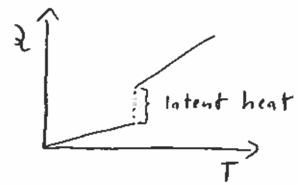
Heat flow rate $\frac{dQ}{dt}$

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

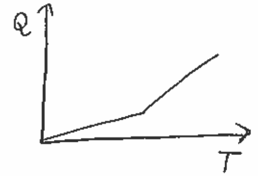
Thermal transition

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

First-order



Second-order



Let us produce heat in a resistor:

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

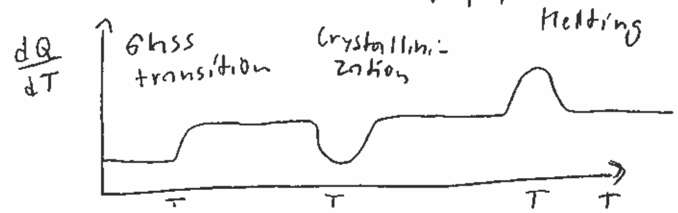
Current I $[A] = \left[\frac{C}{s}\right]$

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

Work $\int \Delta P\, I\, dt$ → dissipated as heat

Calorimetry: Measurement of Heat flows

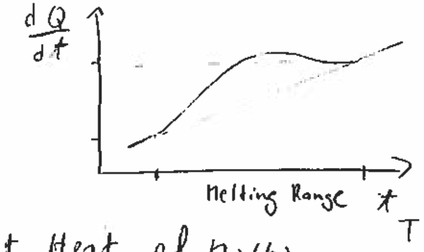
Thermal transitions of polymers



How Do we measure Heat Capacity?

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

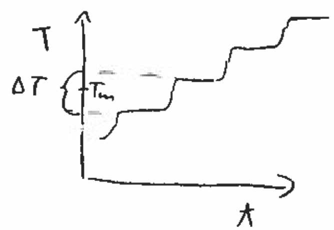
How do we measure Latent Heat?

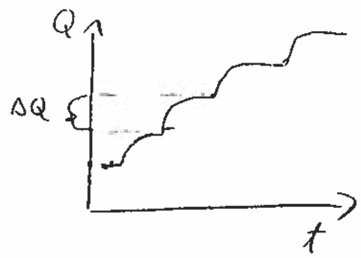


$\frac{dT}{dt} = \text{constant}$

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

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





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

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

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

Non-Freezing Water

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

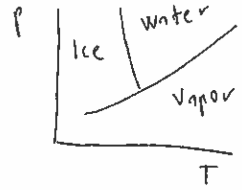
Cell Wall Water

$$m_{cw} = NFW \cdot m_o + [m_{FW}]_{-\infty T_0^-}$$
$$= FSP \cdot m_o \ (?)$$

An application: melting temperature spectrum of cell wall water

Clausius - Clapeyron

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta V} = \frac{H_2 - H_1}{T(V_2 - V_1)} < 0!$$



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

$$p = \frac{\Delta H}{\Delta V} \ln T + C$$

$$\ln T = p \frac{\Delta V}{\Delta H} + C_2$$

$$T_m = C_3\, e^{p \frac{\Delta V}{\Delta H}} = C_3\, e^{-p \left|\frac{\Delta V}{\Delta H}\right|}$$

$$\frac{T_m}{T_o} = \frac{e^{p \frac{\Delta V}{\Delta H}}}{e^{p_\infty \frac{\Delta V}{\Delta H}}} = \frac{e^{(p_\infty + \Delta p) \frac{\Delta V}{\Delta H}}}{e^{p_\infty \frac{\Delta V}{\Delta H}}} = e^{\Delta p \frac{\Delta V}{\Delta H}} = e^{-\frac{2\gamma}{r}\left|\frac{\Delta V}{\Delta H}\right|}$$

$$-\frac{2\gamma}{r}\left|\frac{\Delta V}{\Delta H}\right| = \ln \frac{T_m}{T_o}$$

$$r = -\frac{2\gamma |\Delta V|}{\Delta H \ln \frac{T_m}{T_o}}$$

Gibbs - Thompson Eq.

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

$$J_i = \frac{\partial^2 Q}{\partial t\,\partial A_{\perp i}} \qquad [D] = \text{Diffusivity matrix}$$

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

Total Flow ~~into~~ out of Volume V

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

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

$$Q = \int_V \phi\, dV$$

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

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

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

Thermal Flux Eq.

$$J_i = -D_i \frac{\partial}{\partial x_i} \phi$$

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

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

Thermal Diffusivity

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

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

$= C_V$

$$k_i = C_V D_i$$

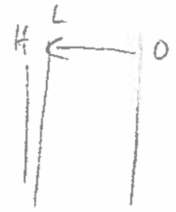
How do we use the Diffusion Eq?

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

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

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

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

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

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

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

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

Homogeneous Boundary conditions

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

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

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

$$X'' = -\lambda^2 X \quad \Rightarrow \quad X = a e^{i\lambda x} + b e^{-i\lambda x}$$

$$T' = -\lambda^2 D T \qquad = A\cos\lambda x + B\sin\lambda x$$

$$\Rightarrow T = c \cdot e^{-\lambda^2 D t}$$

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

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

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

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

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

One Solution:

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

General solution as superposition

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

With boundary condition $t = 0$

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

Identify Fourier sine series

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

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

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

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

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

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

$$= -\frac{H}{D}\frac{8L}{n^2\pi^2}\Big/_{0}^{n\frac{\pi}{2}} \sin y \, dy = -\frac{H}{D}\frac{8L}{\pi^2}\frac{1}{n_{odd}^2}(-1)^{\frac{n_{odd}-1}{2}}$$

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

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

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

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

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

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

$$f = y$$

$$g' = \sin y$$

$$g = -\cos y$$

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

$$\begin{cases} \frac{n_{odd}-1}{2} \\ 0 \text{ for } n_{even} \end{cases}$$

What is actually u ?

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

Temperature $T = \frac{Q}{V} \Big/ \underbrace{\frac{\partial^2 Q}{\partial T \partial V}}_{\text{Volumetric Heat capacity}} = u / c_v$

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

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

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

$$w(x) = \frac{Hx}{D}$$

$$\frac{\partial u}{\partial t} = \frac{\partial v}{\partial t}$$

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

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

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

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

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

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

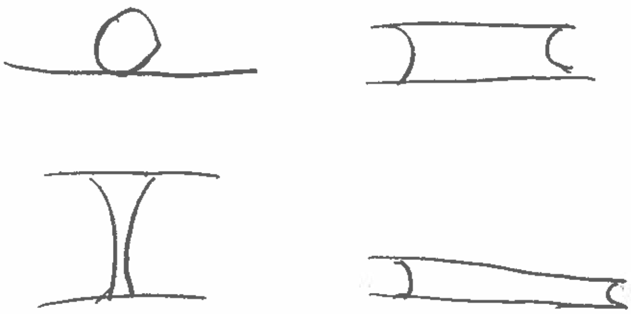
$$= H\frac{2}{L}\sum_{n_{odd}}(-1)^{\frac{n-1}{2}}\sin\left(n\frac{\pi}{2}\frac{x}{L}\right)e^{-\frac{n^2\pi^2 D}{4L^2}t}$$

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

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

What is the Young's Modulus of Water?

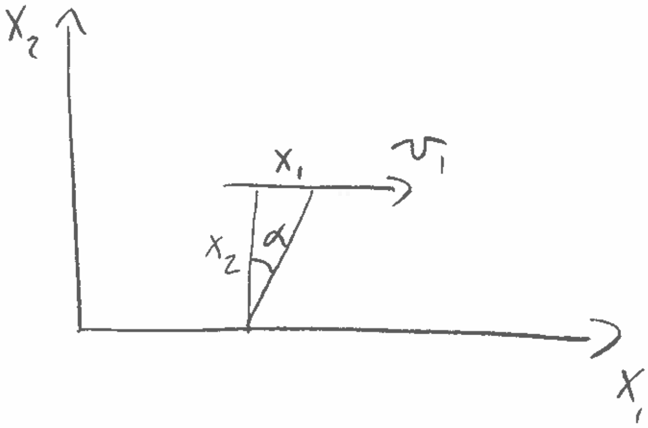
Negative in compression?



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

Newtonian Viscosity for Isotropic Fluid:

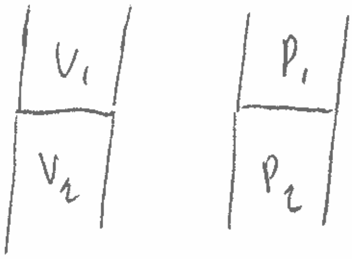
$$\sigma_{ij} = \eta\,\dot{\varepsilon}_{ij} = \eta \frac{dv_i}{dx_j} = \eta \frac{d^2 u_i}{dt\,dx_j} = \eta \frac{d}{dt}\tan\alpha$$



Gravity Drainage Experiment

$dV_1 = -dV_2$

$\Delta P = P_2 - P_1$



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

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

$R \equiv$ 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. $\quad \frac{d\phi}{dt} = [D]\, \nabla^2 \phi$

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

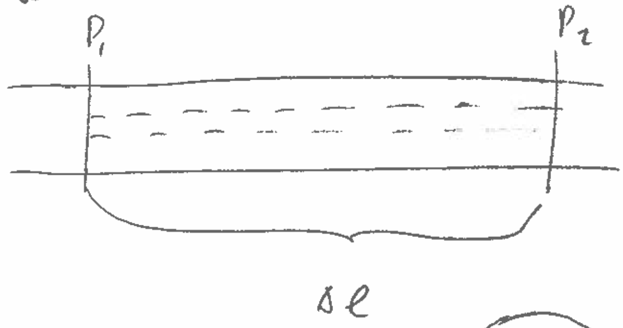
Darcy's Law

$$\frac{\partial^2 V_x}{\partial t\, \partial A_\perp} = -\frac{k}{\eta} \frac{dp}{dx}$$

$\eta \equiv$ viscosity

$k \equiv$ Permeability

Hagen-Poiseuille Law



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

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

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

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

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

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

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

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

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

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

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

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

Rewrite Darcy's Law

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

$K \equiv$ Permeability

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

Porosity Effect

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

$$\Rightarrow \quad K = \mathbb{P} \frac{R^2}{8}$$

$\mathbb{P} \equiv$ Porosity

Variable Size of Pores

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

Variable Geometry, Alignment

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

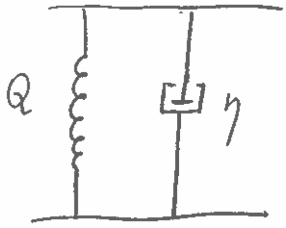
$$\Rightarrow \quad d\sigma_{ij}(t) = R_{ijkl}(t-\tau) \, d\varepsilon_{kl}(\tau)$$

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

$R_{ijkl}(t) \equiv$ 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 $\dot{\varepsilon} \equiv a \Rightarrow aQ + \dot{a}\eta = 0$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

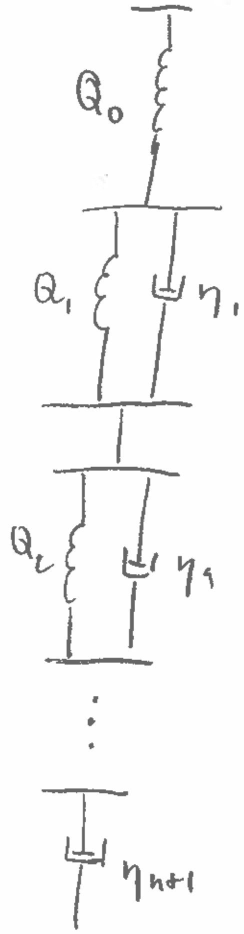
$$R(t) = R_0\, e^{-t/\tau}$$

Maxwell elements in parallell:

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

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

What if two of the Voigt elements are degenerate?



$$c(t) = C_0 + \int_0^{\infty} (C_\infty)_\tau (1 - e^{-t/\tau}) \frac{d\lambda}{d\tau} d\tau + \frac{t}{\eta}$$

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

Glassy Compliance

Retardation Spectrum

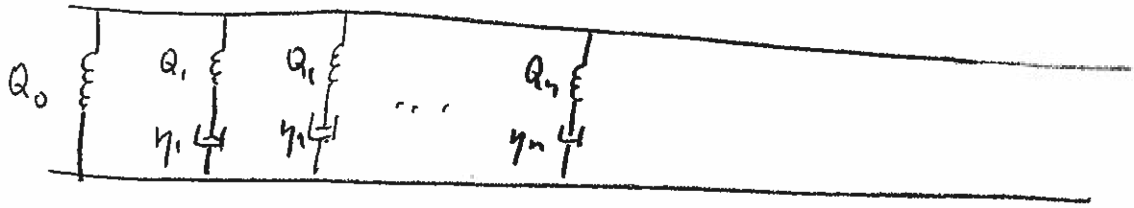
Steady-state Viscosity

$\left\{ \begin{array}{l} \text{Steady-state Compliance?} \\ \text{Equilibrium} \\ \text{Rubbery} \end{array} \right.$

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?



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

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

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

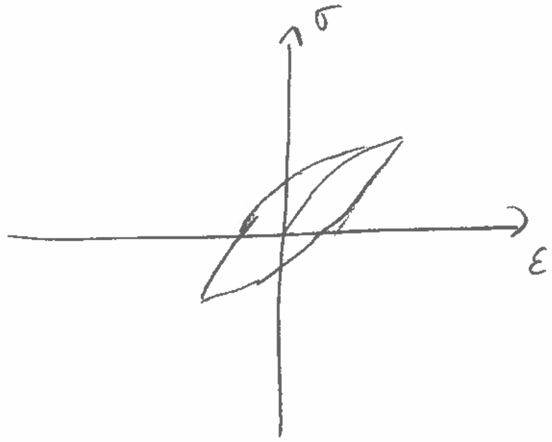
Equilibrium Modulus

Relaxation Spectrum

Glassy modulus:

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

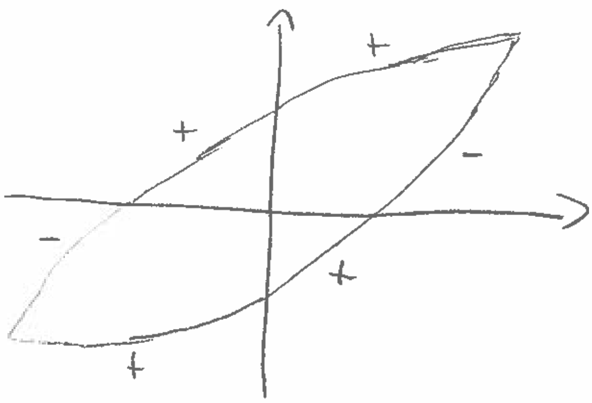
Cyclical Experiment



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

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

Amorphous Polymers:

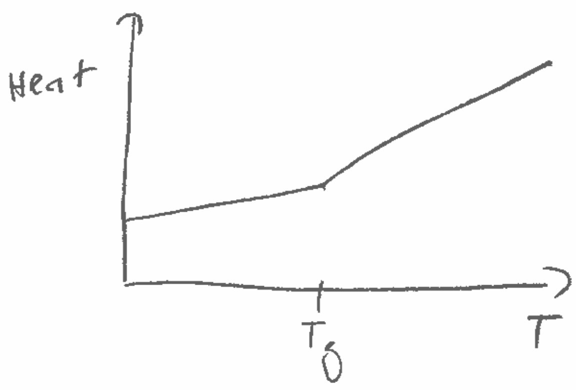
1/ Large-deformation Equilibrium properties

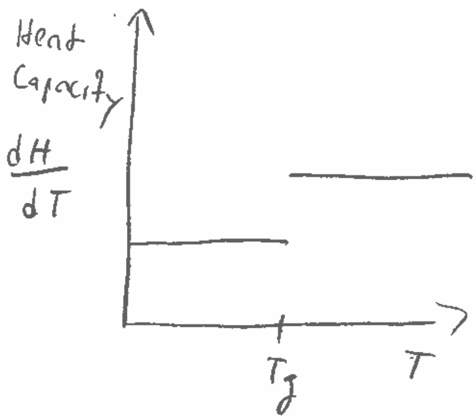
2/ Small-deformation nonequilibrium properties (viscoelastic)

3/ Large-deformation time-dependent properties

Amorphous Polymers:

Glass Transition - second-order transition

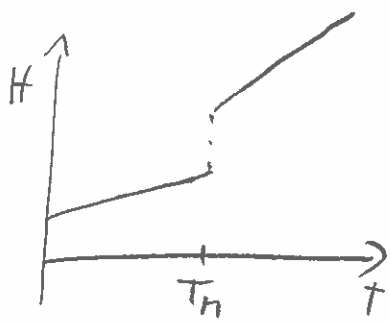




Crystalline polymers:

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:

$$C(T,t) = C\left(T_0, \, t/a(T)\right)$$

$$R(T,t) = R\left(T_0, \, t/b(T)\right)$$

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

$$T > T_0 \Rightarrow t < t/a(T)$$

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

$$T < T_0 \Rightarrow t > t/a(T)$$

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

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

WLF:

$$\log a(T) = -\frac{c_1 (T-T_0)}{c_2 + T - T_0} \approx \frac{-8{,}86\,(T-T_0)}{101{,}6 + T - T_0}$$

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

$$10^{\log a} = a = 10^{-\frac{c_1 (T-T_0)}{c_2 + T - T_0}}$$