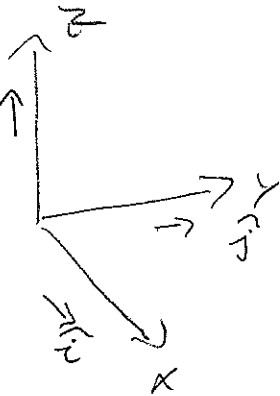


Measurement, Scaling, Instrumentation

⑦

Measurement of Volume

- 1^o Stereometric $\left\{ \begin{array}{l} \text{Determine some boundaries} \\ \text{Adopt shape assumptions} \\ \text{Compute volume} \end{array} \right.$
- 2^o Fluid Replacements
- 3^o Buoyancy



Vectors and line elements

$$L = \int_A^B \vec{l} \cdot d\vec{r} = \int_A^B dl = \int_A^B \hat{l} \cdot d\vec{r}$$

$$= \int_A^C \vec{l} \cdot d\vec{i} + \int_C^B \vec{l} \cdot d\vec{j} = \hat{l} \cdot \left[\int_A^C d\vec{i} + \int_C^B d\vec{j} \right]$$

$$= \int_A^C \cos\theta dx + \int_C^B \sin\theta dy$$

$$= |C-A| \cos\theta + |B-C| \sin\theta$$

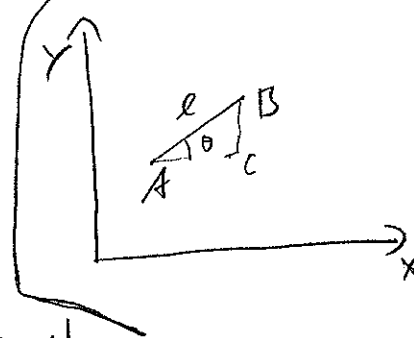
$$= |C-A| \frac{|C-A|}{|B-A|} + |B-C| \frac{|B-C|}{|B-A|} = |B-A|$$

$$|B-A|^2 = |C-A|^2 + |B-C|^2$$

$$dl^2 = dx^2 + dy^2$$

$$dl = \sqrt{dx^2 + dy^2} = dx \sqrt{1 + \left(\frac{dy}{dx}\right)^2}$$

$$\begin{aligned} d\vec{l} &= \hat{l} dl \\ d\vec{i} &= \hat{i} dx \\ d\vec{j} &= \hat{j} dy \\ d\vec{k} &= \hat{k} dz \end{aligned}$$



Surface Area Element

(2)

$$d\vec{S} = \hat{n} dS$$

Surface Area Element in xy-plane

$$\begin{aligned} d\vec{S}_{xy} &= \hat{k} dS_{xy} = \hat{k} (\hat{k} \cdot d\vec{S}) = \hat{k} (\hat{k} \cdot \hat{n}) dS = \hat{k} \cos\theta dS \\ &= \hat{k} dx dy = d\vec{i} \times d\vec{j} = \hat{i} dx \times \hat{j} dy \\ &= \hat{k} dx dy \end{aligned}$$

Area $A = \int \hat{n} \cdot d\vec{S} = \int dS$

In xy-plane

$$A_{xy} = \int \hat{k} \cdot d\vec{S}_{xy} = \int dS_{xy} = \iint dx dy = \int \hat{k} \cdot \hat{n} dS = \int \cos\theta dS$$

$$\vec{A} \times \vec{B} = A_i B_j \vec{e}_k \epsilon_{ijk}$$

$$= \begin{bmatrix} e_i & e_j & e_k \\ A_i & A_j & A_k \\ B_i & B_j & B_k \end{bmatrix}$$

$$\hat{i} \times \hat{j} = \begin{bmatrix} \hat{e}_i & \hat{e}_j & \hat{e}_k \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$= \hat{e}_k = \hat{k}$$

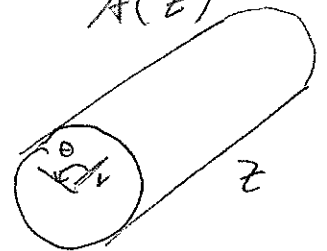
Volume

$$V = \int_V dV = \iiint dx dy dz = \int A_{\perp}(z) dz = \int A_{xy}(z) dz =$$

$$dz \equiv d(\cos\theta z')$$

$$\int A(z) \cos\theta dz'$$

$A(z')$



In Cylindrical co-ordinates

$$A = \int_0^{2\pi} \int_0^r r' dr' d\theta = \int_0^{2\pi} \frac{1}{2} r^2 d\theta = \pi r^2$$

If r constant

$$V = \int_0^z A(z) dz$$

Let us compute the volume of a cylinder

(3)

$$V = \int_0^l A(z) dz = \int_0^l \pi r^2 dz = \pi r^2 l$$

And the volume of a cone: $r = az$ $\left\{ \begin{array}{l} \Rightarrow r_l = al \\ \Rightarrow a = \frac{r_l}{l} \end{array} \right.$

$$V = \int_0^l A(z) dz = \int_0^l \pi (az)^2 dz = \pi a^2 \left| \frac{1}{3} z^3 \right|_0^l = \frac{\pi a^2 l^3}{3} = \frac{\pi r_l^2 l}{3}$$

The volume of a frustum of a cone

$$r = r_0 + az$$

$$\begin{aligned} V &= \int_0^l A(z) dz = \int_0^l \pi (r_0 + az)^2 dz = \pi \int_0^l (r_0^2 + 2r_0 az + a^2 z^2) dz \\ &= \pi \left[r_0^2 z + r_0 a z^2 + \frac{1}{3} a^2 z^3 \right]_0^l = \pi \left[r_0^2 l + r_0 a l^2 + \frac{1}{3} a^2 l^3 \right] \end{aligned}$$

What is $r(l)$? $r(l) = r_0 + al \Rightarrow a = \frac{r_l - r_0}{l}$ \int

$$V = \pi l \left[r_0^2 + r_0(r_l - r_0) + \frac{1}{3} (r_l - r_0)^2 \right]$$

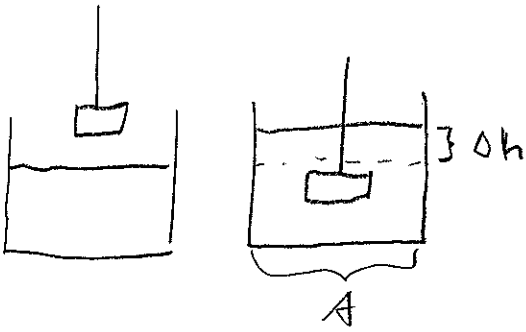
$$= \frac{\pi l}{3} [r_l^2 + r_0 r_l + r_0^2] = \frac{\pi l}{12} [d_l^2 + d_0 d_l + d_0^2]$$

What if our object is not strictly a frustum of a cone?

- Within any small section, shape difference will be negligible...
- The same applies even for a cylinder...

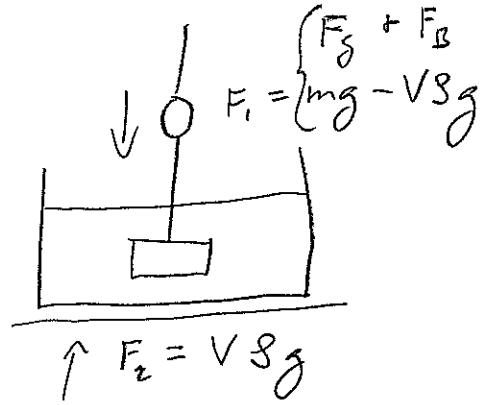
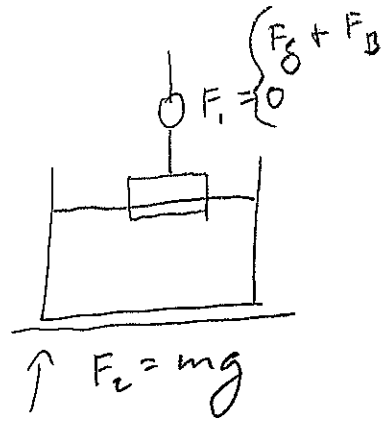
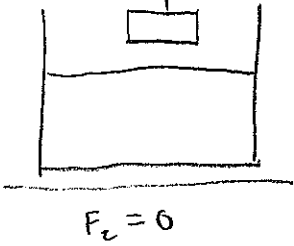
2° Fluid Replacement

(4)



$$V = A \Delta h$$

3° Buoyancy



Measurement of mass

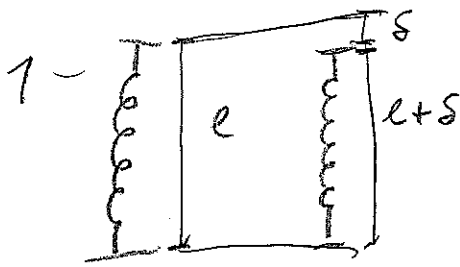
1° Spring displacement

2° Balance of forces

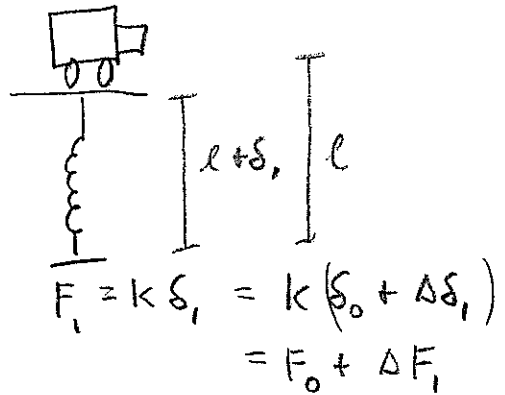
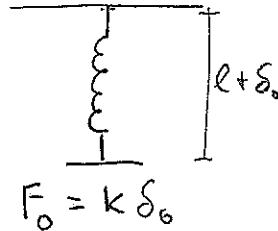
3° Balance of torque momenta

4° Buoyancy - fluid replacement

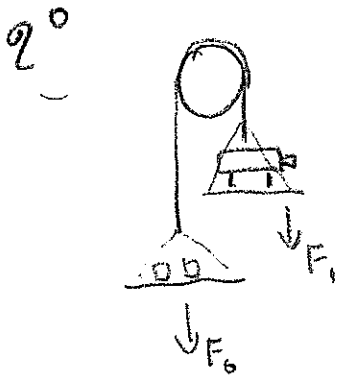
- others



Spring Equation $F = k \delta$



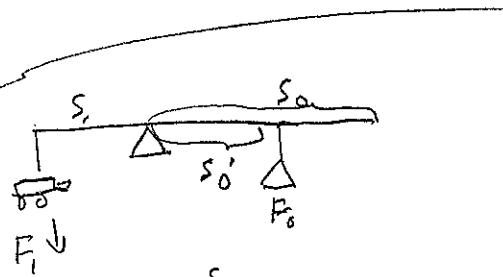
$$\Delta F_1 = k \Delta \delta_1$$



$$F_1 = F_0$$

$$mg = m_0 g$$

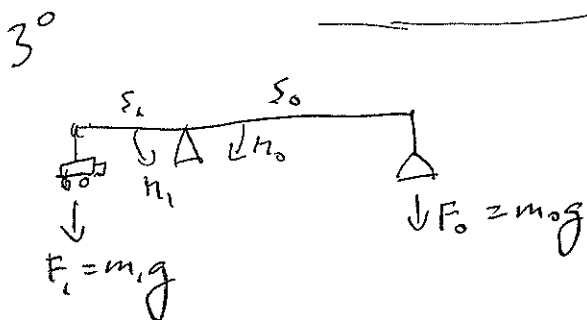
$$m_i = m_o$$



$$M_i = s_1 m g + \int_0^{s_1} \frac{dm}{ds} g s ds$$

$$M_o = s_0' m_0 g + \int_0^{s_0} \frac{dm}{ds} g s ds$$

$$m_i = \frac{s_0' m_0 + \int_0^{s_0} \frac{dm}{ds} s ds - \int_0^{s_1} \frac{dm}{ds} s ds}{s_1}$$



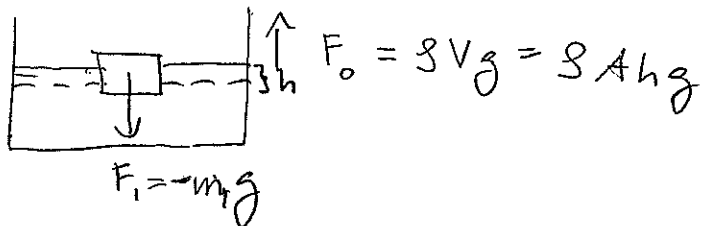
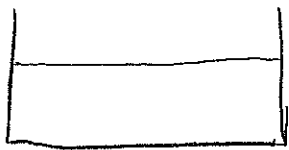
$$M_i = M_o$$

$$s_1 m_1 g = s_0 m_0 g \Rightarrow m_i = \frac{s_0}{s_1} m_o$$

Measurement of mass contd

(6)

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$$F_0 + F_1 = 0 \Rightarrow F_1 = -F_0$$

$$m_1 = \rho A h$$

Why $F_1 = -\rho A h g$?

Since $F_1 = -\rho p A = -\rho g h A$

$$V = \rho h A \Rightarrow F_1 = -\rho g V$$

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 some thermodynamic potentials:

Internal Energy

$$U = TS - pV + \mu N$$

Heat work Chem. pot.

$$dU = TdS - pdV + \mu dN$$

Enthalpy

$$H \equiv U + pV = TS + \mu N$$

$$dH = TdS + Vdp + \mu dN$$

Gibb's Function

$$G \equiv U - TS + pV = \mu N$$

$$dG = -SdT + Vdp + \mu dN$$

Phase Transition: $dp = dT = 0$

$$\Rightarrow \Delta H = T\Delta S$$

Change of Heat

Coexistence: $dG_1(p, T, N) = dG_2(p, T, N)$

$$\Delta G_2 - \Delta G_1 = 0$$

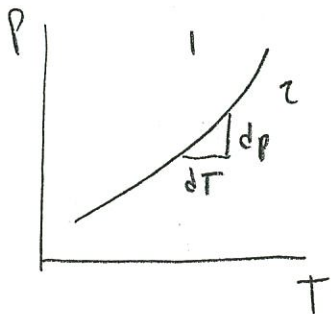
$$\Delta G_1 = -S_1 dT + V_1 dp$$

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

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

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

Clausius - Clapeyron Eq.



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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

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

$$\Delta P = P_{in} - P_{out} = \frac{2\gamma}{r} \quad \text{Laplace Eq.}$$

Molar Gibbs Function

$$G_m = \frac{G}{n} = \mu N_A$$

$$\begin{aligned} dG_m &= -\frac{S}{n} dT + \frac{V}{n} dp + \frac{\mu}{n} dN \\ &= -S_m dT + V_m dp + \mu_m dN \end{aligned}$$

Equilibrium of liquid w. Ideal Gas

$$\mu_g = \mu_l \Rightarrow G_{m,g} = G_{m,l}$$

at $dT = dN = 0$

$$V_{m,g} dp_g = V_{m,l} dp = V_{m,l} (dp(r=\infty) + d\Delta P)$$

Ideal Gas: $pV_m = RT$

$$\frac{RT}{p} dp_g = V_{m,l} dp_{\infty} + V_{m,l} d\Delta P$$

$$\begin{aligned} RT \ln p_g &= V_{m,l} p_{\infty} + V_{m,l} \Delta P + C \\ &= V_{m,l} p_{\infty} + V_{m,l} \frac{2\gamma}{r} + C \end{aligned}$$

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$$\begin{aligned} p_g &= e^{\frac{V_{me} p_\infty}{RT}} e^{\frac{V_{me} 2\gamma}{rRT}} C_2 \\ &= C_3 e^{\frac{V_{me} 2\gamma}{rRT}} \\ &= p_\infty e^{\frac{V_{me} 2\gamma}{rRT}} \\ &= p_\infty e^{\frac{2\gamma M}{rRTS}} \end{aligned}$$

$$\begin{cases} r \rightarrow \infty \Rightarrow \\ e^{\frac{1}{r}} \rightarrow 1, p_g \rightarrow p_\infty \end{cases}$$

KELVIN Eq.

Set $p_g (r=r_s) = p_s$

$$p_s = p e^{\frac{2\gamma M}{r_s R T S}} \Rightarrow \frac{p}{p_s} = e^{-\frac{2\gamma M}{r_s R T S}}$$

Clausius - Clapeyron Continued

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

$$\Delta V \approx V_{\text{vapor}}$$

$$pV = nRT$$

$$V_{\text{vapor}} \approx \frac{nRT}{p}$$

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

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

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

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

$\equiv p_s$

SATURATION VAPOR PRESSURE

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

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

For Water:

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

$$m_{\text{mol}} = 18 \frac{\text{g}}{\text{mol}}$$

$$R = 8.31 \frac{\text{J}}{\text{mol K}}$$

Relative Vapor Pressure
Water Activity
Relative Humidity

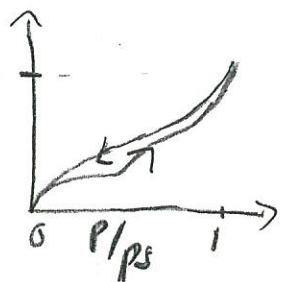
$$\frac{p}{p_s}$$

\Rightarrow

Equilibrium moisture content

Hysteresis

FSP



Why does MC increase w. p/p_s ?

KELVIN Eq II:

$$p_r = p_{\infty} e^{\frac{V_2 \gamma}{RT r}}$$

vapor pressure in droplet of radius r

p_s

γ = surface tension

V = molar volume

For largest droplet

$$1 = \frac{p_{\infty}}{p_s} e^{\frac{V_2 \gamma}{RT r}}$$

$$\frac{p}{p_s} = e^{-\frac{V_2 \gamma}{RT r}}$$

$$-\frac{V_2 \gamma}{RT} = \ln \frac{p}{p_s}$$

$$r_{\text{max}} = -\frac{V_2 \gamma}{RT \ln \frac{p}{p_s}}$$

check the Eq. for $\begin{cases} p \rightarrow 0 \\ p \rightarrow p_s \end{cases}$

What happens to water activity as a function of Temperature?

(11)

$$\frac{(p/p_s)_2}{(p/p_s)_1} = \frac{p/p_{s2}}{p/p_{s1}} = \frac{p_{s1}}{p_{s2}} = \frac{e^{-\frac{\Delta H}{m} \frac{m_{mol}}{RT_1}}}{e^{-\frac{\Delta H}{m} \frac{m_{mol}}{RT_2}}} = e^{\frac{\Delta H}{m} \frac{m_{mol}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

$$\text{Say, } \begin{cases} T_1 = 293 \text{ K} \\ T_2 = 373 \text{ K} \end{cases} \Rightarrow \frac{1}{T_2} - \frac{1}{T_1} = \left(\frac{1}{373} - \frac{1}{293} \right) \frac{1}{\text{K}} \approx (268 \cdot 10^{-5} - 341 \cdot 10^{-5}) \frac{1}{\text{K}}$$
$$\approx -73 \cdot 10^{-7} \frac{1}{\text{K}}$$

$$\frac{(p/p_s)_2}{(p/p_s)_1} = e^{-2260 \frac{1}{\text{g}} \frac{18 \text{ g/mol}}{8,31 \frac{\text{J}}{\text{mol K}} \cdot 1366 \text{ K}}} \approx e^{-3,58} \approx 0,028$$
$$\approx -\frac{1}{1366 \text{ K}}$$

Measurement of RH

- Hygrometers
- Psychrometers
- Dew - Point Sensors
 - Determine Dew Point Temperature, then use Clausius - Clapeyron

$$\frac{P}{P_s} = \frac{e^{-\frac{\Delta H}{m} \frac{m_{mol}}{RT_0}}}{e^{-\frac{\Delta H}{m} \frac{m_{mol}}{RT}}} = e^{-\frac{\Delta H}{m} \frac{m_{mol}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right)}$$

Measurement of Moisture Content

- Gravimetry
- Distillation
- NMR
- Resistivity / conductivity
- Neutron Moderation / γ -absorption

Determination of Equilibrium Moisture Content

- Determine RH
- Determine MC at equilibrium
- RH can be arranged using a saturated salt solution at $RH \leq 95\%$.
- For higher humidities, a wet specimen is placed on the top of a porous plate, a known pressure difference arranged to run some water from the specimen through the plate.
 - Water Desorption Isotherm

Which $\frac{p}{p_0}$ corresponds to Fiber Saturation Point ? → Solution from

Kelvin Eq $\frac{p}{p_s} = e^{-\frac{2\gamma h}{r_s RT S}}$

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

$$V_4 = V_1 + V_2 - V_3 = \frac{m_1}{C_1} + \frac{m_2}{C_2} - \frac{m_1}{C_3}$$

$$FSP \left[\frac{(1)}{(1)} \right] = \frac{V_4 \cdot \rho_w}{m_2} = \rho_w \left[\frac{m_1}{m_2} \left(\frac{1}{C_1} - \frac{1}{C_3} \right) + \frac{1}{C_2} \right]$$

$V_4 \cdot \rho_w \approx$ mass of water in pores inaccessible to molecules

Moisture Content and Electrical Conductivity

spring Eq.

$$F = k \delta$$

$$\left[\frac{N}{m} \right] \left[m \right]$$

Hooke's Law

$$\frac{F}{A} = E \frac{\delta}{l}$$

$$\left[\frac{N}{m^2} \right] \left[\frac{N}{m^2} \right] \left[\right]$$

Potential difference Eq.

$$\Delta Q = R I$$

$$\left[\frac{J}{C} \right] \left[\frac{J \cdot s}{C^2} \right] \left[\frac{C}{s} \right]$$

$$\left[\Omega \right]$$

Specific Resistance Eq.

$$\frac{\Delta Q}{s} = \rho \frac{l}{A}$$

$$\left[\frac{V}{m} \right] \left[\frac{V \cdot m}{A} \right] \left[\frac{A}{m^2} \right]$$

$$\left[\Omega m \right]$$

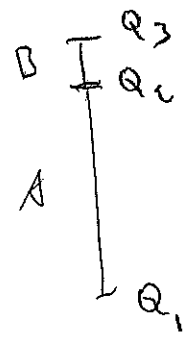
Conductivity Eq.

$$\frac{I}{A} = \frac{1}{\rho} \frac{\Delta Q}{s} = C \frac{\Delta Q}{s}$$

$$\left[\frac{A}{m^2} \right] \left[\frac{1}{\Omega m} \right] \left[\frac{V}{m} \right]$$

How do we measure conductivity?

Conductors A and B in series



$$\bar{I}_A = \bar{I}_B$$

$$(Q_3 - Q_2) C_B = (Q_2 - Q_1) C_A$$

$$C_A = \frac{Q_3 - Q_2}{Q_2 - Q_1} C_B$$

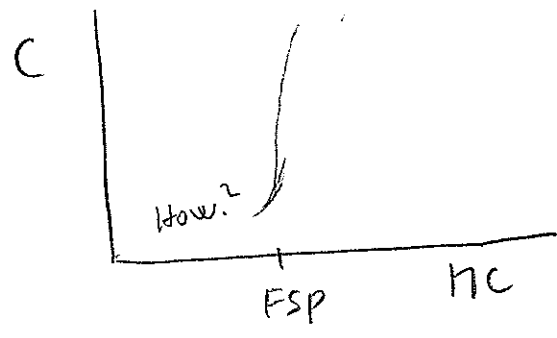
some specific Resistances

Dry Wood	$10^{12} \Omega m$	} $C = C (mC)$
Distilled Water	$5 \cdot 10^3 \Omega m$	

=> specific conductivities

$$10^{-12} \frac{1}{\Omega m}$$

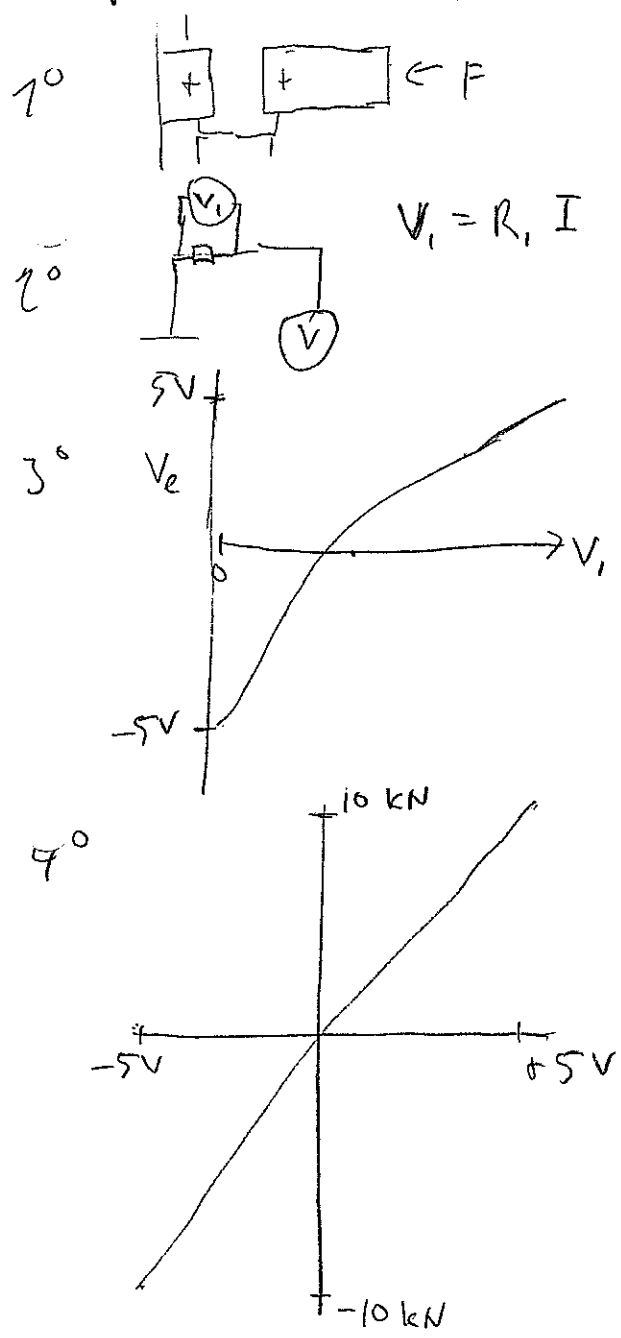
$$2 \cdot 10^{-9} \frac{1}{\Omega m}$$



Signal Processing

- Signal generator
- Input transducer
- Signal modifier
- Output transducer

- Displacement due to force
- Electrical signal
- Conversion to linear Voltage $\pm 5V$
- Conversion to Newtons



Eventual problems

- Signal generator displacement \rightarrow specimen displacement
- Finite signal generator stiffness
- Finite mounting system stiffness
- Signal dampening
- Temperature-dependence
- Hysteresis

$$\begin{aligned} \delta &= \delta_1 + \delta_2 \\ &= \frac{F}{k_1} + \frac{F}{k_2} \end{aligned}$$

$$\begin{aligned} F &= k_1 \delta_1 = k_2 \delta_2 \\ \text{Effective } k: \\ k_e &= \frac{F}{\delta} = \frac{F}{\delta_1 + \delta_2} \\ &= \frac{F}{\frac{F}{k_1} + \frac{F}{k_2}} = \frac{1}{\frac{1}{k_1} + \frac{1}{k_2}} \end{aligned}$$

Solutions / Actions

- Calibration
 - Full range
 - Zero offset
- Temperature compensation
- Signal Generator Displacement Compensation

Noise

Signal-to-Noise-Ratio $\frac{S}{N} = \frac{\text{Signal Amplitude}}{\text{Noise Amplitude}}$
 → Detection limit

Fundamental Noise

- Thermal - thermal movement of charge carriers
- Shot - Impacts by individual charge carriers
- Flicker - (?)

Environmental Noise

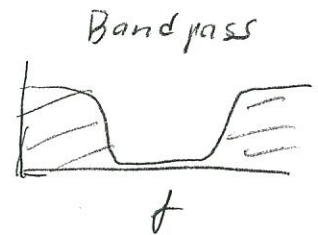
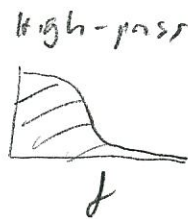
- Electric & Magnetic fields
- Radiation
- Mechanical vibration
- Others...

Car → Heart rate meter
 { Subway → computer screen
 mobile phone → ↑

Solutions - Actions

$\frac{S}{N} \uparrow$

Filtering



Integration

- Boxcar
- Ensemble Averaging
- Moving-Average Smoothing
- Weighted Moving-Average Smoothing

Dirac δ

$$\int \delta(x) dx = 1 \quad (19)$$

$$\delta(0) = \infty$$

$$\int f(x) \delta(x-a) dx = f(a)$$

$$\delta(x) = 0$$

for $x \neq 0$

Fourier Transform

$$\mathcal{F}(w) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-iwx} dx \rightarrow \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(u) e^{-iwu} du$$

Inverse Fourier Transform

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathcal{F}(w) e^{iwx} dw$$

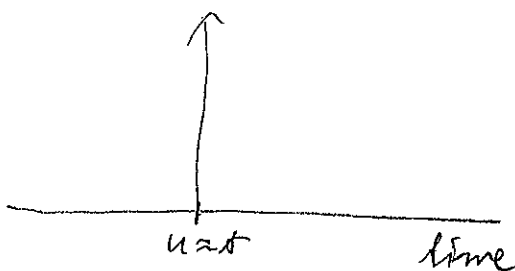
$$= \int_{-\infty}^{\infty} du f(u) \left\{ \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega(x-u)} d\omega \right\}$$

$$\Rightarrow \left\{ \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i\omega(x-u)} d\omega \right\} = \delta(u-x)$$

Euler Identity

$$e^{i\omega(x-u)} = \cos[\omega(x-u)] + i \sin[\omega(x-u)]$$

~~xxxxx~~ Fourier Transform compresses a whole spectrum of harmonic waves into a narrow range $u \approx x$ in the time domain!



Cumulative Distribution:



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$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \tilde{f}(\varphi) e^{i\varphi x} d\varphi$$

$$\begin{aligned} \tilde{f}(\omega) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-i\omega x} dx \\ &= \int_{-\infty}^{\infty} d\varphi \tilde{f}(\varphi) \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\varphi(x-\omega)} dx \right\} \end{aligned}$$

$$\Rightarrow \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\varphi(x-\omega)} dx \right\} = \delta(\varphi - \omega)$$

\Rightarrow (Inverse) Fourier transform compresses a whole spectrum of functions into a narrow range $\omega \approx \varphi$ in the frequency domain!

Some Fourier Transformations

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$$\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-it\omega} dt = \delta(\omega)$$

$$\frac{1}{2\pi} \int_{-\infty}^{\infty} e^{-it(\omega - \omega_0)} dt = \delta(\omega - \omega_0)$$

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-it\omega} dt = \boxed{\sqrt{2\pi} \delta(\omega) = \mathcal{F}(1)}$$

$$\mathcal{F}[\mathcal{F}(1)] = 1$$

$$\mathcal{F}[\sqrt{2\pi} \delta(\omega)] = 1 \Rightarrow \boxed{\mathcal{F}[\delta(\omega)] = \frac{1}{\sqrt{2\pi}}}$$

$$\mathcal{F}[e^{it\varphi}] = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{it\varphi} e^{-it\omega} dt$$

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$$= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-it(\omega-\varphi)} dt = \sqrt{2\pi} \delta(\omega-\varphi)$$

$$\mathcal{F}[e^{-it\varphi}] = \sqrt{2\pi} \delta(\omega+\varphi)$$

$$\cos(\varphi t) = \frac{e^{i\varphi t} + e^{-i\varphi t}}{2}$$

$$\mathcal{F}[\cos(\varphi t)] = \mathcal{F}\left[\frac{e^{i\varphi t} + e^{-i\varphi t}}{2}\right] = \frac{\sqrt{\pi}}{\sqrt{2}} \left[\delta(\omega-\varphi) + \delta(\omega+\varphi) \right]$$

Spectroscopy

- Monitoring a spectrum of something
- Affected by interaction with matter
 - Electromagnetic radiation
 - Mechanical waves
 - Particles

Absorption Spectroscopy
 Emission Spectroscopy
 Scattering Spectroscopy

Photon Energy $E = h\nu = \frac{hc}{\lambda}$
 Discrete Energy levels
 → Oscillations between states
 - several modes of vibration

Classical Wave Equation

$$\frac{\partial^2}{\partial z^2} A = \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2}$$

One Solution: $A = A_0 \cos(kz - \omega t)$

Verification:

$$\frac{\partial}{\partial z} A = -k A_0 \sin(kz - \omega t)$$

$$\frac{1}{c^2} \frac{\partial A}{\partial t} = \frac{-\omega}{c^2} A_0 [-\sin(kz - \omega t)]$$

$$\frac{\partial^2}{\partial z^2} A = -k^2 A_0 \cos(kz - \omega t)$$

$$\frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = -\frac{\omega^2}{c^2} A_0 \cos(kz - \omega t)$$

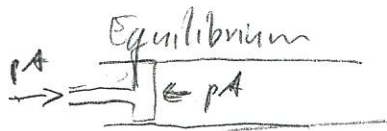
$$\Rightarrow \boxed{k^2 = \frac{\omega^2}{c^2}}$$

Intensity \propto (Field density)² = $A^2 = A_0^2 \cos^2(kz - \omega t)$

Frequency spectrum of Intensities $A^2(\omega) = \mathcal{F}(A^2(x))$

Longitudinal Mechanical Waves

Fluid in a tube



Momentum - Impulse theorem

$$\Delta P + I = 0$$

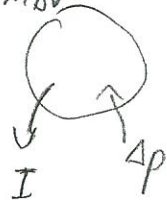
$$\Delta P = -I$$

$$I = F \Delta t$$

$$P = mv = m \frac{\Delta s}{\Delta t}$$

$$F \Delta t = m \frac{\Delta v}{\Delta t} \Delta t$$

$$\Delta P = m \Delta v$$

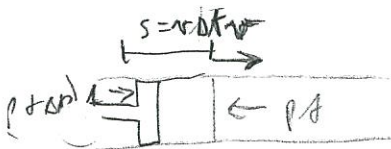


Additional pressure ΔP applied for time Δt

\Rightarrow Acceleration of a Fluid Element of length

$$s = v \Delta t$$

$v =$ velocity of the front face of the element



$v_z =$ velocity of the piston
 \approx velocity of the element

Impulse by the Fluid element:

$$I = -A \Delta p \Delta t$$

Momentum change by the Fluid element:

Fractional volume change of the Fluid element:

$$\Delta P = (\rho v \Delta t A) v_z$$

Bulk modulus $\equiv \frac{-\Delta P}{\frac{\Delta V}{V}} = B$

$$\frac{\Delta V}{V} = -\frac{v_z \Delta t A}{v \Delta t A} = -\frac{v_z}{v}$$

$$\Rightarrow \Delta P = -B \frac{\Delta V}{V} = B \frac{v_z}{v}$$

$$\Delta P = -I$$

$$\rho v \Delta t A v_z = A \Delta p \Delta t$$

$$\rho v v_z = B \frac{v_z}{v}$$

$$v^2 = \frac{B}{\rho} \Rightarrow v = \sqrt{\frac{B}{\rho}}$$

$$v = \sqrt{\frac{B}{\rho}}$$

Uniaxial strain

$\frac{B}{\rho}$

Intensity of longitudinal wave

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Differential work

$$\begin{aligned} dW &= \frac{\partial W}{\partial x_1} dx_1 + \frac{\partial W}{\partial x_2} dx_2 + \frac{\partial W}{\partial x_3} dx_3 \\ &= F_1 dx_1 + F_2 dx_2 + F_3 dx_3 \\ &= F_i dx_i \end{aligned}$$

Force in one dimension

$$\rightarrow dW = F_i dx_i = F dx$$

Power $\frac{dW}{dt} = \frac{F dx}{dt} = F \frac{dx}{dt} = Fv$

$$\begin{aligned} \frac{dW}{dt} &= Fv_z = \Delta p A v_z = B \frac{v_z}{v} A v_z \rightarrow Fv_z \\ &= B \frac{v_z^2}{v} A \end{aligned}$$

$$v_z \equiv \frac{d\Delta}{dt}$$

$$\text{Intensity} = \frac{\text{Power}}{\text{Area}} = \frac{dW}{A dt} = B \frac{v_z^2}{v} = B \left(\frac{d\Delta}{dt} \right)^2 \frac{1}{\sqrt{\frac{B}{S}}} = \sqrt{BS} \left(\frac{d\Delta}{dt} \right)^2$$

Say $\Delta(x,t) = A_\Delta \sin(\omega t - kz) = A_\Delta \sin \omega \left(t - \frac{z}{v} \right)$

$$\frac{d\Delta}{dt} = A_\Delta \omega \cos(\omega t - kz)$$

$$\begin{aligned} \omega &= 2\pi f = \frac{2\pi}{T} \\ k &= \frac{\omega}{v} = \frac{2\pi}{\lambda} \end{aligned}$$

$$\left(\frac{d\Delta}{dt} \right)^2 = A_\Delta^2 \omega^2 \cos^2(\omega t - kz)$$

$$\text{Intensity} = \sqrt{BS} A_\Delta^2 \omega^2 \cos^2(\omega t - kz)$$

Cycle

$$\begin{aligned} \text{Average Intensity} &= \frac{1}{T} \int_0^T \sqrt{BS} A_\Delta^2 \omega^2 \cos^2(\omega t - kz) dt = \frac{1}{2} \sqrt{BS} A_\Delta^2 \omega^2 \\ &= \frac{1}{2} \rho v A_\Delta^2 \omega^2 \end{aligned}$$

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How to determine A_Δ ?

$$\Delta p = B \frac{v_z}{v} = B \frac{d\Delta}{dt} \frac{1}{v}$$

$$\text{If } \frac{d\Delta}{dt} = A_\Delta \omega \cos(\omega t - kz)$$

$$\Delta p = \frac{B}{v} A_\Delta \omega \cos(\omega t - kz) = A_p \cos(\omega t - kz)$$

$$\Rightarrow A_p = \frac{B}{v} A_\Delta \omega \Rightarrow A_\Delta = A_p \frac{v}{B\omega} = A_p \frac{1}{\sqrt{B\rho} \omega}$$

→ Measure pressure amplitude, compute displacement amplitude!

Thermal transitions

- changes in thermal properties

First-order transition

- change in heat capacity
- latent heat involved

Second-order transition

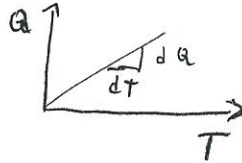
- change in heat capacity only

Unit: thermal energy [J] Q

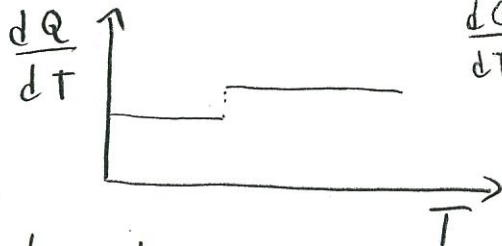
Heat Capacity: $\frac{dQ}{dT}$

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

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



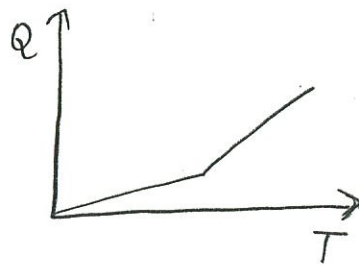
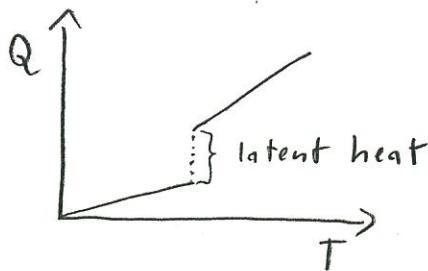
Thermal transition



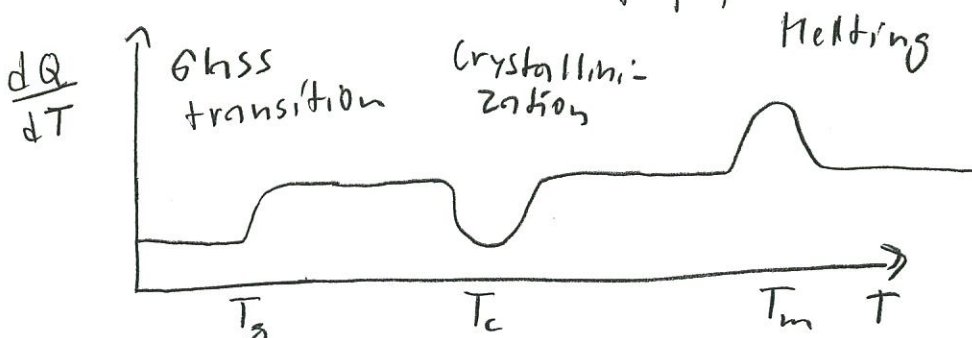
$$\frac{dQ}{dT} = \frac{\frac{dQ}{dt}}{\frac{dT}{dt}}$$

First-order

Second-order



Thermal transitions of polymers



Let us produce heat in a resistor:

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

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

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

Heat energy $\int \Delta P I dt$
 \rightarrow dissipated as heat

Calorimetry:
Measurement of Heat flows

Melting Temperature Spectrum

Coexistence of Solid and Liquid

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

$$d\mu^s = d\mu^l$$

$$dG^s = dG^l$$

$$-S^s dT + V^s dp^s = -S^l dT + V^l dp^l$$

$$(S^s - S^l) dT = V^s dp^s - V^l dp^l$$

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

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

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

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

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

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

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

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

Melting Temperature Spectrum → pore size distribution

T [°C]	D [nm]
-30	1,4
-10	4,2
-5	8,6
-2,5	17
-1,2	36
-0,6	72
-0,3	144
-0,2	216
-0,1	433

Mass of freezing water

in pores of diameter D_1 and D_2 ^{between}

$$[m_{FW}]_{D_1, D_2} = \frac{1}{\Delta H_m} \int_{T_1(D_1)}^{T_2(D_2)} \frac{dQ}{dT} dT = \frac{1}{\Delta H_m} \int_{x_1(T_1)}^{x_2(T_2)} \frac{dQ}{dx} dx$$

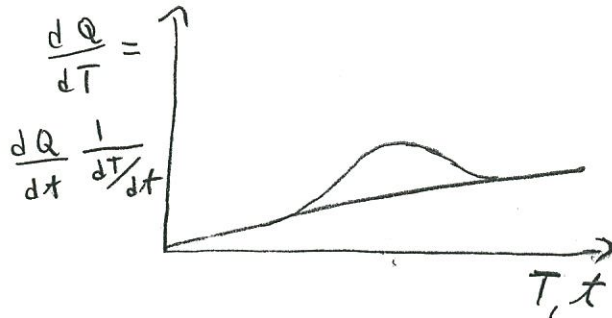
$$\Delta H_m \approx 333 \frac{J}{g}$$

How about the effect of Heat Capacity?

$$Q = Q_T(\text{transition}) + Q_S(\text{temperature increment}) \Rightarrow Q_T = Q - Q_S$$

$$[m_{FW}]_{D_1, D_2} = \frac{1}{\Delta H_m} \int_{T_1(D_1)}^{T_2(D_2)} \left(\frac{dQ}{dT} - \frac{dQ_S}{dT} \right) dT \approx \frac{1}{\Delta H_m} \left[\int_{T_1}^{T_2} \frac{dQ}{dT} dT - \frac{dQ_S}{dT} (T_2 - T_1) \right]$$

How to determine Heat Capacity $\frac{dQ_S}{dT}(T)$?



Non-Freezing Water

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

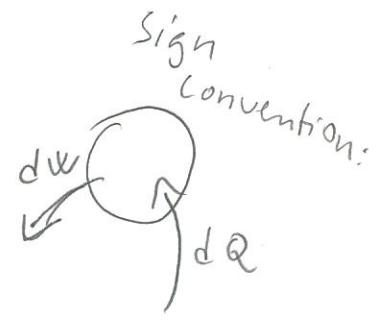
Total Cell Wall Water

$$m_{CW} = NFW + [m_{FW}]_{-\infty T_0^-} \approx FSP \cdot m_0 (?)$$

Internal Energy

$$U = U(S, V, N)$$

Energy $dE = \overset{\text{Heat}}{dQ} - \overset{\text{Work}}{dW}$



$$dU = dE + \mu dN$$

$$= dQ - dW + \mu dN$$

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, N} dS + \left(\frac{\partial U}{\partial V}\right)_{S, N} dV + \left(\frac{\partial U}{\partial N}\right)_{S, V} dN$$

Chain Rule of partial derivatives
 → Total Differential

$$dU = T dS - p dV + \mu dN$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, N}$$

$$-p = \left(\frac{\partial U}{\partial V}\right)_{S, N}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S, V}$$

Maxwell Relations (some)

$$dE = TdS - pdV$$

$$T = \left(\frac{\partial E}{\partial S} \right)_V \quad \left| \frac{\partial}{\partial V} \right. \Rightarrow \frac{\partial^2 E}{\partial V \partial S} = \left(\frac{\partial T}{\partial V} \right)_S$$

$$-p = \left(\frac{\partial E}{\partial V} \right)_S \quad \left| \frac{\partial}{\partial S} \right. \Rightarrow \frac{\partial^2 E}{\partial S \partial V} = - \left(\frac{\partial p}{\partial S} \right)_V$$

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \quad \boxed{(S, V) - \text{system}}$$

Gibbs Function

$$\Theta \equiv U - TS + pV$$

$$d\Theta = dU - TdS - SdT + pdV + Vdp = -SdT + Vdp + \mu dN$$

$$S = - \left(\frac{\partial \Theta}{\partial T} \right)_{p, N} \quad \left| \frac{\partial}{\partial p} \right. \Rightarrow - \frac{\partial^2 \Theta}{\partial p \partial T} = \left(\frac{\partial S}{\partial p} \right)_{T, N}$$

$$V = \left(\frac{\partial \Theta}{\partial p} \right)_{T, N} \quad \left| \frac{\partial}{\partial T} \right. \Rightarrow \frac{\partial^2 \Theta}{\partial T \partial p} = \left(\frac{\partial V}{\partial T} \right)_{p, N}$$

$$\left(\frac{\partial S}{\partial p} \right)_{T, N} = - \left(\frac{\partial V}{\partial T} \right)_{p, N} \quad \boxed{(T, p, N) - \text{system}}$$

Kelvin's Thermoelastic Eq.

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$$dQ = T dS$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

(T, P) -system

Isothermal process $\Rightarrow dT = 0$

$$dQ = T dS = T \left(\frac{\partial S}{\partial P} \right)_T dP = -T \left(\frac{\partial V}{\partial T} \right)_P dP$$

$$dP = -\frac{\Delta F}{A}$$

$$\delta V = \Delta V = A \Delta l$$

Uniaxial elongation

$$\frac{\delta l/l}{\delta T} = \frac{\Delta l/l}{\Delta T} = \alpha$$

Linear
Thermal expansion
coefficient

$$\frac{1}{\Delta T} = \alpha \frac{l}{\Delta l}$$

$$\Delta Q = -T A \Delta l \alpha \frac{l}{\Delta l} \left(-\frac{\Delta F}{A} \right) = T \alpha l \Delta F$$

$$\frac{\Delta Q}{\Delta F} = T \alpha l$$

$$\frac{\Delta Q/V}{\Delta \sigma} = T \alpha$$

$$\left. \begin{aligned} \Delta \sigma &= \frac{\Delta F}{A} \\ V &= A l \end{aligned} \right\} \rightarrow$$

Energy Change in Thermoelastic Uniaxial Straining

$$\begin{aligned} dE &= dQ - dW \\ &= T\alpha l dF + F dS \end{aligned}$$

$$\frac{dF/A}{dS/l} = \frac{d\sigma}{d\varepsilon} \equiv Y$$

$$\begin{aligned} F dS &= Fl d\varepsilon \\ &= Al\sigma d\varepsilon \\ &= VY\varepsilon d\varepsilon \end{aligned}$$

$$dF = Y A d\varepsilon$$

$$dE = T\alpha V Y d\varepsilon + V Y \varepsilon d\varepsilon$$

$$= V Y [T\alpha d\varepsilon + \varepsilon d\varepsilon] \quad / S$$

$$\Delta E = V Y \left[\underbrace{T\alpha \varepsilon}_{\text{Heat}} + \underbrace{\frac{1}{2} \varepsilon^2}_{\text{Work}} \right] \quad \left| \frac{d}{dt} \right.$$

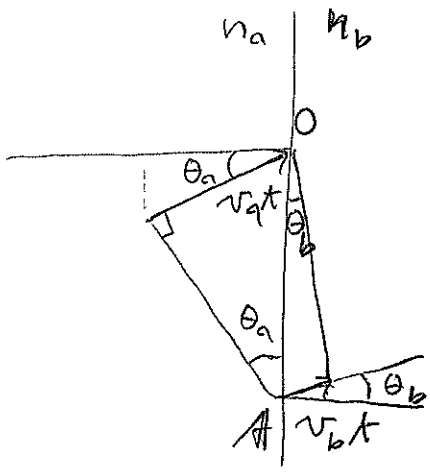
$$\dot{E} = V Y [T\alpha \dot{\varepsilon} + \varepsilon \dot{\varepsilon}]$$

What if there is an Irreversible process?

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$$dU \leq Tds - pdV + \mu dN$$

Snell's Law of Refraction

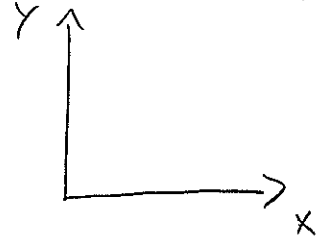


$$\sin \theta_a = \frac{v_a t}{AO} \Rightarrow AO = \frac{v_a t}{\sin \theta_a}$$

$$\sin \theta_b = \frac{v_b t}{AO} \Rightarrow AO = \frac{v_b t}{\sin \theta_b}$$

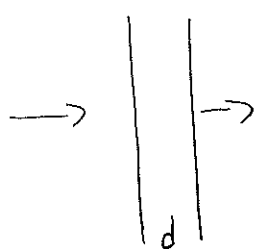
$$\frac{\sin \theta_a}{\sin \theta_b} = \frac{v_a}{v_b} = \frac{c/n_b}{c/n_a} = \frac{n_b}{n_a}$$

Birefringence: Anisotropic Index of Refraction



$$n_x = \frac{c}{v_x} \neq n_y = \frac{c}{v_y}$$

Passage through a layer d



Passage Time difference

$$t = \frac{d}{v}$$

$$\Delta t = d \left(\frac{1}{v_x} - \frac{1}{v_y} \right)$$

Path Difference (after crossing the layer)

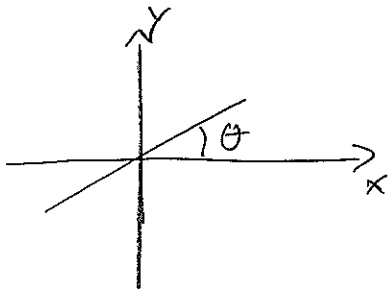
$$p = \Delta t c = d \left(\frac{c}{v_x} - \frac{c}{v_y} \right) = d (n_x - n_y)$$

Phase Difference

$$\delta = 2\pi \frac{p}{\lambda} = 2\pi \frac{d}{\lambda} (n_x - n_y)$$

Birefringence

Apply linearly polarized light



$$A = A_0 \sin \omega t$$

$$A_x = A \cos \theta = A_0 \cos \theta \sin(\omega t)$$

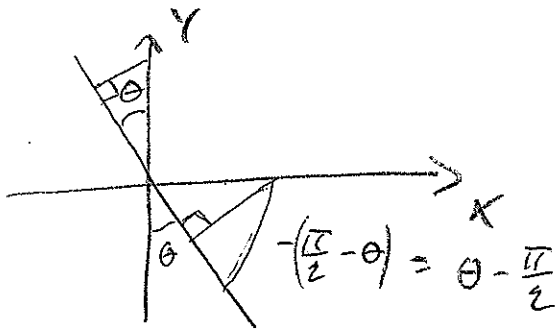
$$A_y = A \sin \theta = A_0 \sin \theta \sin(\omega t)$$

After passage of layer d

$$A'_x = A_0 \cos \theta \sin(\omega t)$$

$$A'_y = A_0 \sin \theta \sin(\omega t + \delta)$$

Projections to Analyzer, perpendicular to polarizer



$$S = \cos \theta A'_y - \cos \left(\theta - \frac{\pi}{2} \right) A'_x$$

$$= \cos \theta \sin \theta \sin(\omega t + \delta) A_0$$

$$- \sin \theta \cos \theta \sin(\omega t) A_0$$

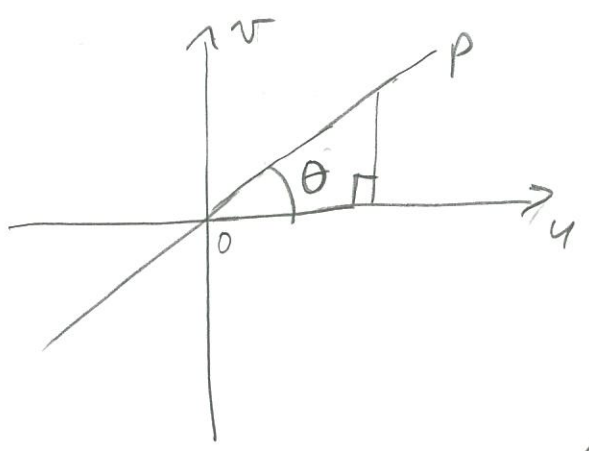
$$= \sin \theta \cos \theta \left[\sin(\omega t + \delta) - \sin(\omega t) \right] A_0$$

$$= \frac{A_0}{2} \sin(2\theta) \left[\sin(\omega t + \delta) - \sin(\omega t) \right]$$

$$\left[\sin\left(\omega t + 2\pi \frac{d}{\lambda}\right) - \sin(\omega t) \right]$$

$$\left[\sin\left[\omega t + 2\pi \frac{d}{\lambda}(n_x - n_y)\right] - \sin(\omega t) \right]$$

Elliptical Polarization



Apply linearly polarized light (along OP)

$$A = A_0 \sin \omega t$$

$$\Rightarrow A_x = A \cos \theta = A_0 \sin \omega t \cos \theta$$

$$A_y = A \sin \theta = A_0 \sin \omega t \sin \theta$$

Passing through birefringent material induces phase retardation

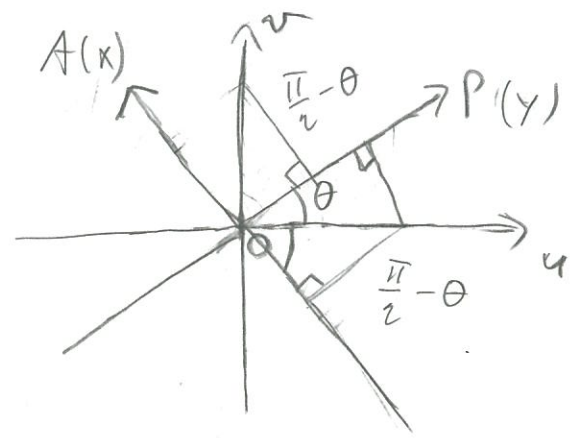
$$A'_x = A_0 \cos \theta \sin(\omega t - \delta)$$

$$A'_y = A_0 \sin \theta \sin(\omega t)$$

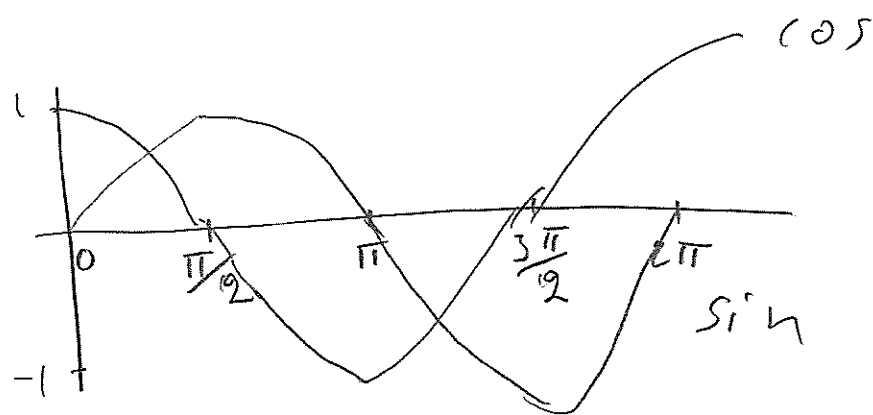
Project into (P, A) - coord-system

$$A_y = -A'_x \sin\left(\frac{\pi}{2} - \theta\right) + A'_y \cos\left(\frac{\pi}{2} - \theta\right)$$

$$A_x = -A'_x \underbrace{\cos\left(\frac{\pi}{2} - \theta\right)}_{\cos \theta} + A'_y \sin\left(\frac{\pi}{2} - \theta\right)$$



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$$\cos(\theta) = \sin\left(\theta + \frac{\pi}{2}\right)$$

$$\sin(\theta) = \cos\left(\theta - \frac{\pi}{2}\right) = \cos\left(\frac{\pi}{2} - \theta\right)$$

$$\sin\left(\frac{\pi}{2} - \theta\right) = -\sin\left(\theta - \frac{\pi}{2}\right) = \cos(\theta)$$

$$\cos\left(\frac{\pi}{2} - \theta\right) = \sin(\theta)$$

$$A_y = A_u \cos(\theta) + A'_v \sin(\theta)$$

$$A_x = -A'_u \sin(\theta) + A'_v \cos(\theta)$$

$$A_y = A_0 \left[\cos^2 \theta \sin(\omega t - \delta) + \sin^2 \theta \sin(\omega t) \right]$$

$$A_x = A_0 \left[-\sin(\theta) \cos(\theta) \sin(\omega t - \delta) + \sin(\theta) \cos(\theta) \sin(\omega t) \right]$$

Some Trigonometry

$$\sin(a-b) = \sin(a)\cos(b) - \sin(b)\cos(a)$$

$$\sin(2a) = 2\sin(a)\cos(a)$$

$$\cos(a-b) = \cos(a)\cos(b) + \sin(a)\sin(b)$$

$$\cos(2a) = 2\cos^2 a - 1 = 1 - 2\sin^2 a$$

$$1 - \cos(2a) = 2\sin^2 a$$

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A Special Case: $\theta = \frac{\pi}{4}$

$$\Rightarrow \sin(\theta) = \cos(\theta) = \frac{1}{\sqrt{2}}$$

$$A_y = \frac{A_0}{2} [\sin(\omega t) + \sin(\omega t - \delta)]$$

$$A_x = \frac{A_0}{2} [\sin(\omega t) - \sin(\omega t - \delta)]$$

$$A_y = \frac{A_0}{2} [\sin(\omega t) + \sin(\omega t)\cos(\delta) - \sin(\delta)\cos(\omega t)]$$

$$= \frac{A_0}{2} \left[\sin(\omega t) (1 + \cos \delta) - \cos(\omega t) \cdot 2 \sin\left(\frac{\delta}{2}\right) \cos\left(\frac{\delta}{2}\right) \right]$$

$$= \frac{A_0}{2} \left[\sin(\omega t) \cdot 2 \cos^2\left(\frac{\delta}{2}\right) - \cos(\omega t) \cdot 2 \sin\left(\frac{\delta}{2}\right) \cos\left(\frac{\delta}{2}\right) \right]$$

$$= A_0 \left[\sin(\omega t) \cos\left(\frac{\delta}{2}\right) - \cos(\omega t) \sin\left(\frac{\delta}{2}\right) \right] \cos\left(\frac{\delta}{2}\right)$$

$$= A_0 \sin\left(\omega t - \frac{\delta}{2}\right) \cos\left(\frac{\delta}{2}\right)$$

(40)

$$A_x = \frac{A_0}{2} [\sin(\omega t) - \sin(\omega t - \delta)]$$

$$= \frac{A_0}{2} [\sin(\omega t) - \sin(\omega t)\cos(\delta) + \sin(\delta)\cos(\omega t)]$$

$$= \frac{A_0}{2} [\sin(\omega t)(1 - \cos\delta) + 2\sin\left(\frac{\delta}{2}\right)\cos\left(\frac{\delta}{2}\right)\cos(\omega t)]$$

$$= \frac{A_0}{2} \left[\sin(\omega t) 2\sin^2\left(\frac{\delta}{2}\right) + 2\sin\left(\frac{\delta}{2}\right)\cos\left(\frac{\delta}{2}\right)\cos(\omega t) \right]$$

$$= A_0 \left[\sin(\omega t)\sin\left(\frac{\delta}{2}\right) + \cos(\omega t)\cos\left(\frac{\delta}{2}\right) \right] \sin\left(\frac{\delta}{2}\right)$$

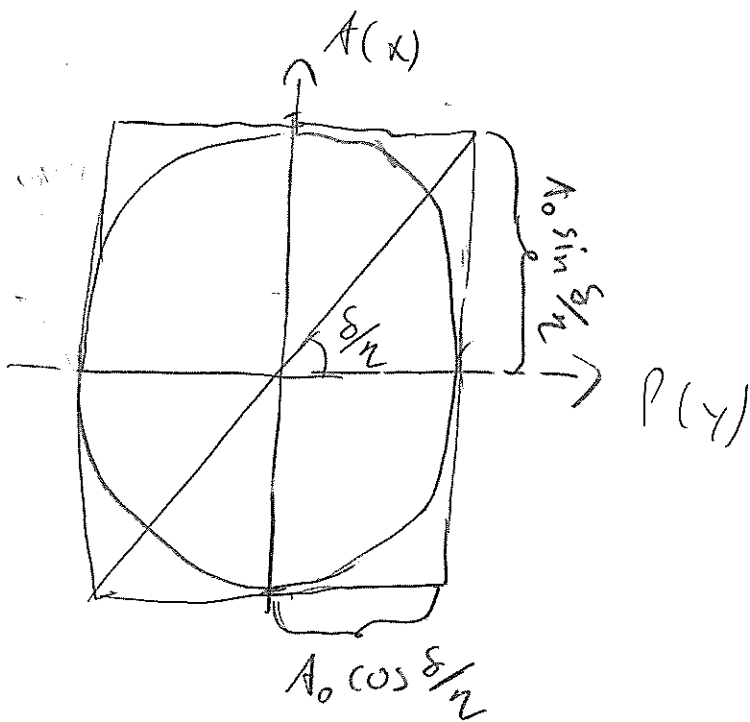
$$= A_0 \cos\left(\omega t - \frac{\delta}{2}\right) \sin\left(\frac{\delta}{2}\right)$$

Square, normalize and add.

$$\frac{A_x^2}{A_0^2 \sin^2\left(\frac{\delta}{2}\right)} + \frac{A_y^2}{A_0^2 \cos^2\left(\frac{\delta}{2}\right)} = \cos^2\left(\omega t - \frac{\delta}{2}\right) + \sin^2\left(\omega t - \frac{\delta}{2}\right) = 1$$

ELLIPTICAL POLARIZATION!

(91)



Rewrite still once:

$$A_x = A_0 \sin\left(\frac{\delta}{2}\right) \cos\left(\omega t - \frac{\delta}{2}\right)$$

$$= A_0 \sin\frac{\delta}{2} \sin\left(\omega t - \frac{\delta}{2} + \frac{\pi}{2}\right)$$

$$A_y = A_0 \cos\frac{\delta}{2} \sin\left(\omega t - \frac{\delta}{2}\right)$$

\Rightarrow There always is an (x, y) -phase difference of $\frac{\pi}{2}$! $\left(\theta = \frac{\pi}{4}\right)$

Could we get rid of it?

If yes, we would have

a linearly polarized wave in the direction $\psi = \frac{\delta}{2}$

i.e. $\frac{A_x}{A_y} = \tan \frac{\delta}{2} = \tan \psi$

This angle can be determined by turning the analyzer to extinction:

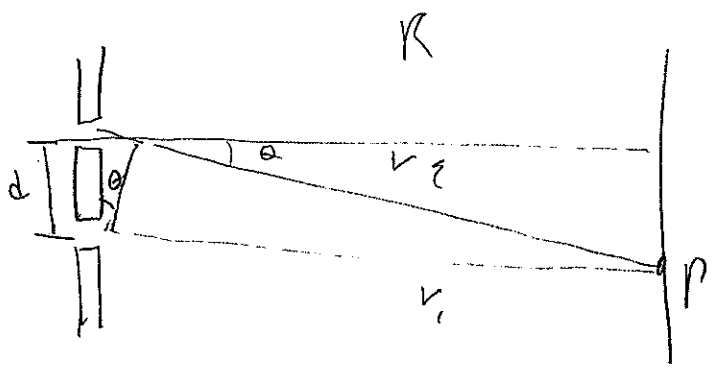
$$\delta = 2\psi = 2\pi \frac{P}{\lambda} = 2\pi \frac{d}{\lambda} (n_u - n_v)$$

How?

Use a Quarter Wave Plate ...

→ de Sénarmont Compensator

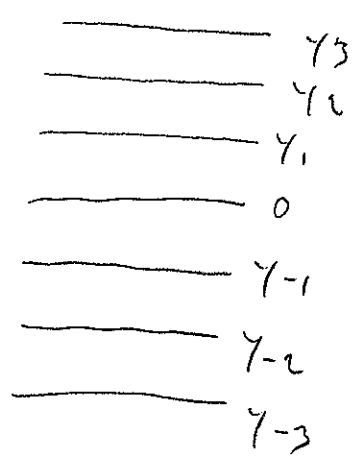
Interference \rightarrow Diffraction



Positive Interference: $d \sin \theta = m \lambda$

Destructive Interference: $d \sin \theta = (m + \frac{1}{2}) \lambda$ $m = 0, \pm 1, \pm 2, \dots$

Interference Pattern:



$$\frac{y_m}{R} \approx \tan \theta_m \approx \sin \theta_m$$

$$y_m \approx R \sin \theta_m = R \frac{m \lambda}{d}$$