

Measurement, Scaling, Instrumentation

Measurement of Volume

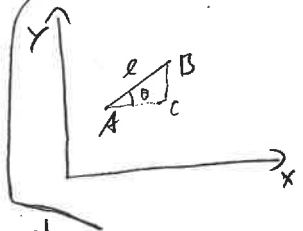
- 1^o Stereometry
 - Determine some boundaries
 - Adopt shape assumptions
 - compute volume
- 2^o Fluid Replacement
- 3^o Buoyancy



Vectors and line elements

$$\begin{aligned}
 l &= \int_A^B \hat{l} \cdot d\vec{e} = \int_A^B dl = \hat{l} \cdot \int_A^B d\vec{e} \\
 &= \int_A^C \hat{l} \cdot d\vec{i} + \int_C^B \hat{l} \cdot d\vec{j} \\
 &= \int_A^C \cos\theta dx + \int_C^B \sin\theta dy \\
 &= |C-A| \cos\theta + |B-C| \sin\theta \\
 &= |C-A| \frac{|C-A|}{|B-A|} + |B-C| \frac{|B-C|}{|B-A|} = |B-A| \\
 |B-A|^2 &= |C-A|^2 + |B-C|^2
 \end{aligned}$$

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



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

①

Surface Area Element

②

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

Surface Area Element in xy-plane

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

$$\begin{aligned}
 \vec{A} \times \vec{B} &= A_i B_j \hat{e}_k \epsilon_{ijk} \\
 &= \begin{bmatrix} e_i & e_j & e_k \\ A_i & A_j & A_k \\ B_i & B_j & B_k \end{bmatrix} \\
 \hat{i} \times \hat{j} &= \begin{bmatrix} \hat{e}_i & \hat{e}_j & \hat{e}_k \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} \\
 &= \hat{e}_k = \hat{k}
 \end{aligned}$$

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

In xy-plane

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

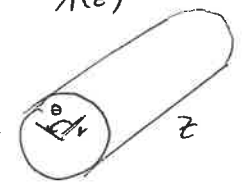
Volume

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

$$dz \equiv d(\cos\theta z') \quad \int A(z) \cos\theta dz'$$

In Cylindrical co-ordinates

$$\begin{aligned}
 A &= \int_0^{2\pi} \int_0^r r' dr' d\theta = \int_0^{2\pi} \frac{1}{2} r^2 d\theta = \pi r^2 \\
 &\quad \uparrow \\
 &\quad \text{If } r \text{ constant}
 \end{aligned}$$



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

$$A = \int dS = \int r dr d\theta$$



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: $r = az \Rightarrow r_l = al \Rightarrow a = \frac{r_l}{l}$

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

The volume of a frustum of a cone $r = r_0 + az$

$$V = \int_0^l A(z) dz = \int_0^l \pi (r_0 + az)^2 dz = \pi \int_0^l (r_0^2 + 2r_0 az + a^2 z^2) dz$$

$$= \pi \left[r_0^2 z + r_0 a z^2 + \frac{1}{3} a^2 z^3 \right]_0^l = \pi \left[r_0^2 l + r_0 a l^2 + \frac{1}{3} a^2 l^3 \right]$$

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

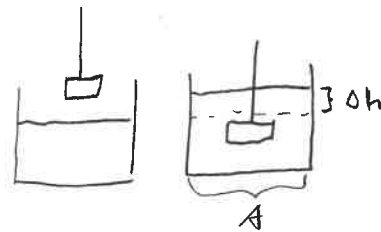
$$V = \pi l \left[r_0^2 + r_0(r_l - r_0) + \frac{1}{3} (r_l - r_0)^2 \right]$$

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

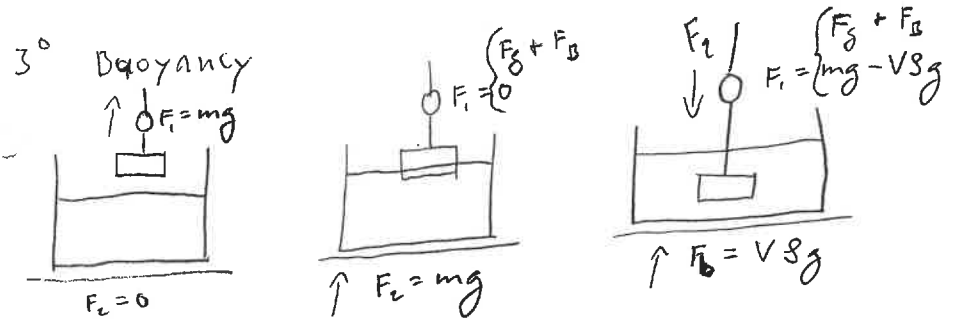
What if our object is not strictly a frustum of a cone?

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

2° Fluid Replacement (4)



$$V = A \Delta h$$



$$F_3 + F_B = 0$$

$$-|F_3| + F_B = 0$$

$$F_2 + F_3 + F_B = 0$$

$$-|F_2| + -|F_3| + F_B = 0$$

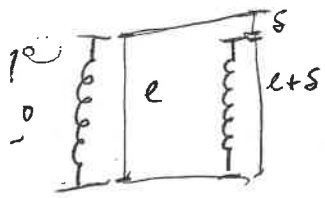
$$-|F_2| + -|mg| + \rho g V = 0$$

$$V = \frac{|F_2| + |mg|}{\rho g} = \frac{mg - F_2}{\rho g}$$

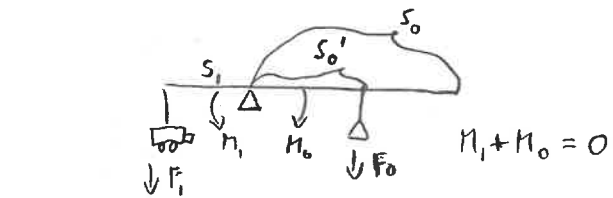
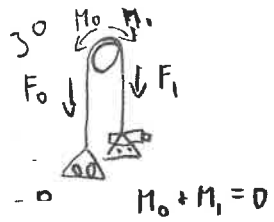
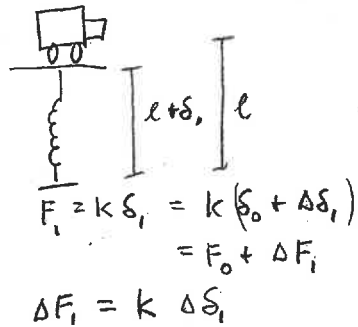
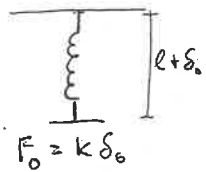
Measurement of mass

⑤
24.3.2021

- 7° Spring displacement
- 2° Balance of forces
- 3° Balance of torque moments
- 1° Buoyancy - fluid replacement
- others



Spring Equation $F = k\delta$



$$M_1 + M_0 = 0$$

$$s_1 m_1 g + s_0 m_0 g = 0$$

$$m_1 = \frac{-s_0}{s_1} m_0$$

$$M_1 = s_1 m_1 g + \int_0^{s_1} \frac{dm}{ds} s g ds$$

$$M_0 = s_0' m_0 g + \int_0^{s_0'} \frac{dm}{ds} s g ds$$

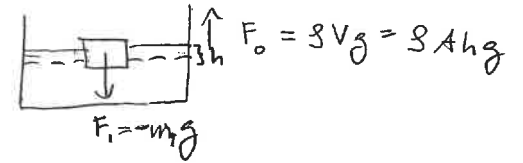
$$m_1 = \frac{-s_0' m_0 g - \int_0^{s_0'} \frac{dm}{ds} s g ds - \int_{s_1}^0 \frac{dm}{ds} s g ds}{s_1}$$

$$= \frac{-s_0' m_0 + \frac{1}{2} \frac{dm}{ds} [s_0'^2 - s_1^2]}{s_1} = \frac{s_0' m_0 + \frac{dm}{2 ds} [s_0'^2 - s_1^2]}{|s_1|}$$

Measurement of mass contd

⑥

4°



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

$$m_1 = \rho A h$$

Why $F_0 = -\rho A h g$?

Since $F_0 = -\rho p A = -\rho g h A$

$$V = h A \Rightarrow F_0 = -\rho g V$$

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

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

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

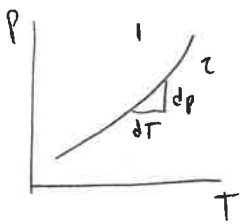
$$\Delta G_1 = -S_1 dT + V_1 dp$$

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

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

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

Clausius - Clapeyron Eq.



Surface Energy γA

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

Stress due to surface tension

$$\frac{F}{A} = \frac{8\pi r \gamma}{4\pi r^2} = \frac{2\gamma}{r}$$

Balance of Forces

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

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

Molar Gibbs Function

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

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

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

Equilibrium of liquid w. Ideal Gas

$$p_g = p_l \Rightarrow G_{m,g} = G_{m,l}$$

at $dT = dN = 0$

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

Ideal Gas: $pV_m = RT$

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

$$RT \ln p_g = V_{m,l} p_l + V_{m,l} \Delta p + C$$

$$= V_{m,l} p_l + V_{m,l} \frac{2\gamma}{r} + C$$

$$\begin{aligned}
 p_0 &= e^{\frac{V_{mc} p_0}{RT}} e^{\frac{V_{mc} \gamma}{rRT}} C_2 \\
 &= C_3 e^{\frac{V_{mc} \gamma}{rRT}} \\
 &= p_0 e^{\frac{V_{mc} \gamma}{rRT}} \\
 &= p_0 e^{\frac{\gamma V_m}{rRT}}
 \end{aligned}$$

$$\left\{ \begin{aligned} r &\rightarrow \infty \Rightarrow \\ e^{\frac{\gamma}{r}} &\rightarrow 1, p_0 \rightarrow p_0 \end{aligned} \right.$$

KELVIN Eq.

Set $p_g(r=r_s) = p_s$

$$p_s = p_0 e^{\frac{\gamma V_m}{r_s RT}} \Rightarrow \frac{p}{p_s} = e^{-\frac{\gamma V_m}{r RT}}$$

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Clausius-Clapeyron Continued

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

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

$$pV = nRT$$

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

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

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

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

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

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

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

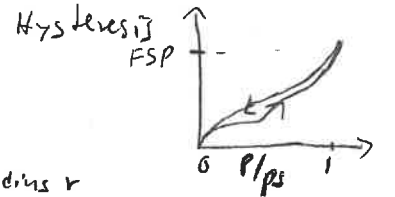
$$n = \frac{m}{m_{\text{mol}}}$$

For Water:

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

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

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



Why does FIC increase w. p/p_s ?

KELVIN Eq II: Vapor pressure in droplet of radius r
 $p_r = p_0 e^{\frac{\gamma V_m}{rRT}} \quad | \quad p_s$
 $\gamma = \text{surface tension}$
 $V = \text{molar volume}$

For largest droplet $1 = \frac{p_0}{p_s} e^{\frac{\gamma V_m}{rRT}}$

$$\frac{p}{p_s} = e^{-\frac{\gamma V_m}{rRT}}$$

$$-\frac{\gamma V_m}{rRT} = \ln \frac{p}{p_s}$$

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

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

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What happens to water activity as a function of Temperature?

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

Say, $\begin{cases} T_1 = 293 \text{ K} \\ T_2 = 373 \text{ K} \end{cases} \Rightarrow \frac{1}{T_2} - \frac{1}{T_1} = \left(\frac{1}{373} - \frac{1}{293}\right) \frac{1}{K} \approx \left(\frac{268 \cdot 10^5 - 391 \cdot 10^5}{1366}\right) \frac{1}{K}$

$$\approx -73 \cdot 10^{-7} \frac{1}{K}$$

$$\approx -\frac{1}{1366 \text{ K}}$$

$$\frac{(P/P_s)_2}{(P/P_s)_1} = e^{-2260 \frac{1}{8} \frac{18 \text{ g/mol}}{2,71 \frac{J}{mol \cdot K} 1366 \text{ K}}} \approx e^{-3,58} \approx 0,028$$

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

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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

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

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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 ?

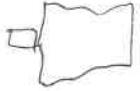
That is water volume accessible to the molecules. $V_1 + V_2 = V_3 + V_4$

V_4 is Inaccessible water volume

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

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

$V_4 \cdot S_w$ = mass of water in pores inaccessible to molecules



Moisture Content and Electrical Conductivity

spring Eq.

$$F = k \delta$$

$[N] \quad [N/m] \quad [m]$

Hooke's Law

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

$[N/m^2] \quad [N/m^2] \quad [m]$

Potential difference Eq.

$$\Delta Q = R I$$

$[V] \quad [A] \quad [A]$
 $[C] \quad [C/s] \quad [C/s]$
 $[Ω]$

Specific Resistance Eq.

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

$[V/m] \quad [V/A \cdot m] \quad [A/m^2]$
 $[Ωm]$

Conductivity Eq.

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

$[A/m^2] \quad [1/Ωm] \quad [V/m]$

How do we measure conductivity?

Conductors A and B in series



$$I_A = I_B$$

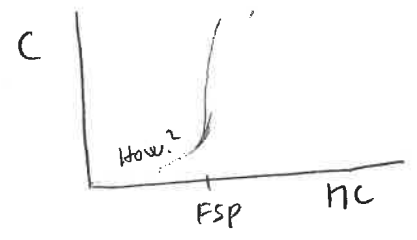
$$\frac{(Q_3 - Q_2) C_B}{S_B} = \frac{(Q_2 - Q_1) C_A}{S_A}$$

$$\frac{S_B}{C_A} = \frac{S_A (Q_3 - Q_2)}{C_B (Q_2 - Q_1)}$$

some specific Resistances

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

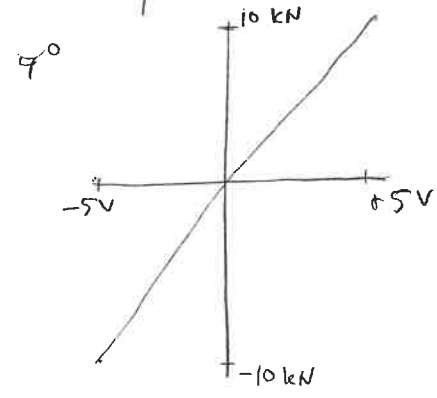
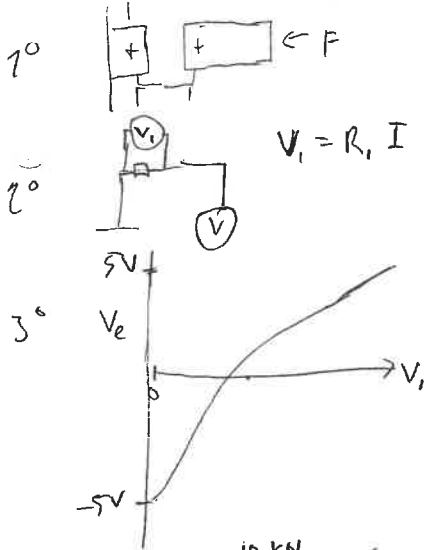
=> specific conductivities $10^{-12} \frac{1}{\Omega m}$
 $2 \cdot 10^{-4} \frac{1}{\Omega m}$



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

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

Solutions/Actions

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

Noise

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

\rightarrow Detection limit

Fundamental Noise

- Thermal - thermal movement of charge carriers
- Shot - Impacts by individual charge carriers
- Flicker - (1)

Environmental Noise

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

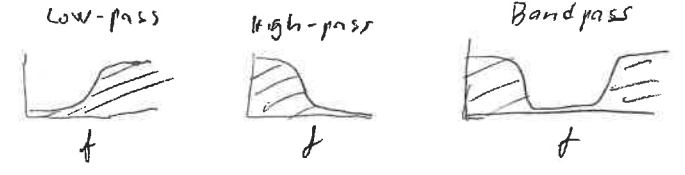
Car \rightarrow Heart rate meter
 Subway \rightarrow computer screen
 mobile phone \rightarrow

Solutions-Actions

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

Filtering

Integration



- Boxcar
- Ensemble Averaging
- Moving-Average smoothing
- Weighted Moving-Average smoothing

Dirac δ

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

$$\int \delta(x) dx = 1 \quad (19)$$
$$\delta(0) = \infty$$
$$\delta(x) = 0$$

for $x \neq 0$

Some Fourier Transformations

(219)

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

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

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

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

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

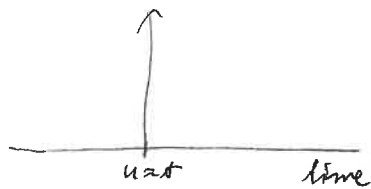
$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-itw} dt = \boxed{\sqrt{2\pi} \delta(w) = \mathcal{F}(1)}$$

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

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

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

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



Cumulative Distribution:



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

21b

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

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

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

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

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

$$\mathcal{F}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-i\omega x} dx$$

$$= \int_{-\infty}^{\infty} d\vartheta \mathcal{F}(\vartheta) \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{it(\vartheta-\omega)} dt \right\} e^{-it(\omega-\vartheta)}$$

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

\Rightarrow (Inverse) Fourier transform compresses a whole spectrum of functions into a narrow range of the time domain

range $\omega \approx \vartheta$ in the frequency domain!

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:

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

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

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

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

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

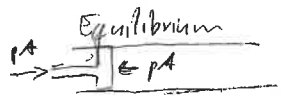
Intensity $\propto (\text{Field density})^2 = A^2 = A_0^2 \cos^2(kz - \omega t)$

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

Longitudinal Mechanical Waves

Fluid in a tube

Momentum - Impulse theorem



$$\Delta P + I = 0$$

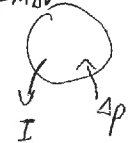
$$\Delta P = -I$$

$$I = F \Delta t$$

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

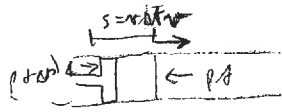
$$F \Delta t = m \frac{\Delta v}{\Delta t} \Delta t$$

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



Additional pressure ΔP applied for time Δt

⇒ Acceleration of a fluid element of length $s = v \Delta t$, $v = \text{velocity of the frontier of the element}$



$v_z = \text{velocity of the piston}$
 $\approx \text{velocity of the element}$

Impulse by the fluid element: $I = -\Delta P \Delta t$

Momentum change by the fluid element:

Fractional volume change of the fluid element: $\Delta P = (\gamma \Delta t A) v_z$
 $\frac{\Delta V}{V} = -\frac{v_z \Delta t A}{v \Delta t A} = -\frac{v_z}{v}$

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

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

$$\Delta P = -I$$

$$\gamma v \Delta t A v_z = \Delta P \Delta t$$

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

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



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 $\frac{dW}{dt} = \frac{F dx}{dt} = F \frac{dx}{dt} = F v$

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

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

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

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

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

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

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

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

Average Intensity $= \frac{1}{T} \int_0^T \sqrt{BS} A_\Delta^2 \omega^2 \cos^2(\omega t - kz) dt = \frac{1}{2} \sqrt{BS} A_\Delta^2 \omega^2$

$$= \frac{1}{2} \rho v A_\Delta^2 \omega^2$$

(25)

How to determine A_Δ ?

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

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

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

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

→ 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

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Lat: thermal energy [J] Q

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

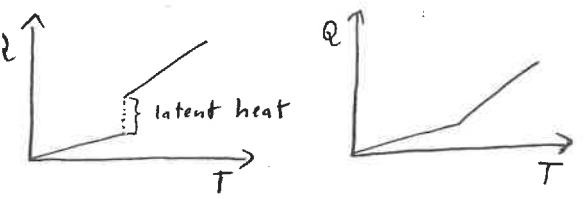
Heat flow rate $\frac{dQ}{dt}$

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

Thermal transition

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

First-order Second-order



Let us produce heat in a resistor:

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

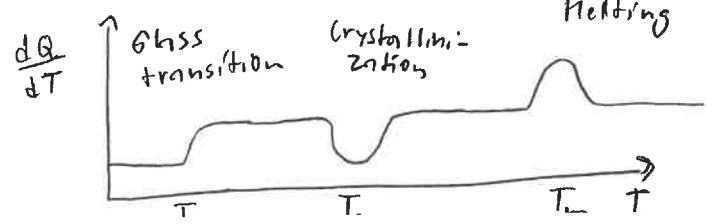
Current I
 $[A] = \left[\frac{C}{s}\right]$

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

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

Calorimetry:
Measurement of Heat flows

Thermal transitions of polymers



Melting Temperature Spectrum

Coexistence of Solid and Liquid

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

$$d\mu^s = d\mu^e$$

$$dG^s = dG^e$$

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

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

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

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

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

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

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

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

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

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

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

Melting Temperature Spectrum
 → pore size distribution

Mass of freezing water
 in pores of diameter D_1 and D_2 between $T_2(T_0)$ and $T_1(T_0)$

$$[m_{FW}]_{D_1, D_2} = \frac{1}{\Delta H_m} \int_{T_1(D_1)}^{T_2(D_2)} \frac{dQ_e}{dT} dT = \frac{1}{\Delta H_m} \int_{T_1(T_0)}^{T_2(T_0)} \frac{dQ_e}{dT} dT$$

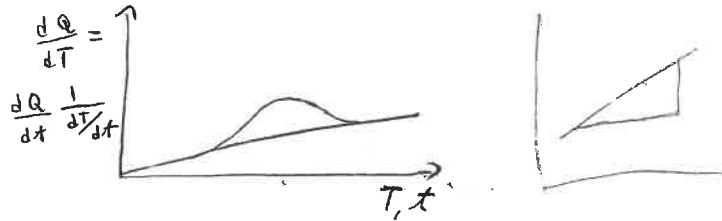
$$\Delta H_m \approx 333 \frac{J}{g}$$

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

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

Total Cell Wall Water

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

(28)

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	432

(29)

Internal Energy

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

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



$$dU = dE + \mu dN$$

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

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

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)

(30)

$$dE = TdS - pdV$$

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

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

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

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.

(31)

$$dQ = TdS$$

$$dS = \left(\frac{\partial S}{\partial T} \right)_p dT + \left(\frac{\partial S}{\partial p} \right)_T dp \quad \boxed{(T, p) - \text{system}}$$

Isothermal process $\Rightarrow dT = 0$

$$dQ = TdS = T \left(\frac{\partial S}{\partial p} \right)_T dp = -T \left(\frac{\partial V}{\partial T} \right)_p dp$$

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

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

Uniaxial elongation

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

Linear
Thermal expansion
coefficient

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

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

$$\boxed{\frac{\Delta Q}{\Delta F} = T \alpha \ell}$$

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

$$\Delta \sigma = \frac{\Delta F}{A}$$

$$V = A \ell$$



Energy Change in Thermoelastic
Uniaxial Straining

$$dE = dQ - dW$$

$$= T\alpha l dF + F dS$$

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

$$F dS = Fl d\varepsilon$$

$$= Al \sigma d\varepsilon$$

$$= V Y \varepsilon d\varepsilon$$

$$dF = Y A d\varepsilon$$

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

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

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

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

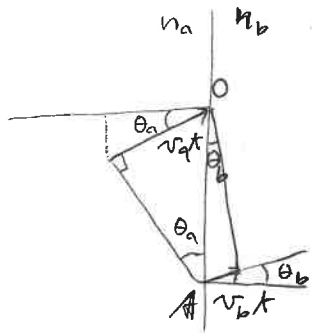
(32)

What if there is an Irreversible
process?

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

(33)

Snell's Law of Refraction



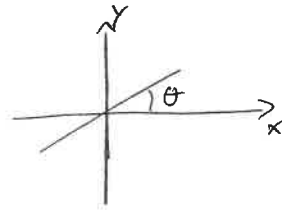
$$\sin \theta_a = \frac{v_a t}{AO} \Rightarrow AO = \frac{v_a t}{\sin \theta_a}$$

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

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

(34)

Apply linearly polarized light



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

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

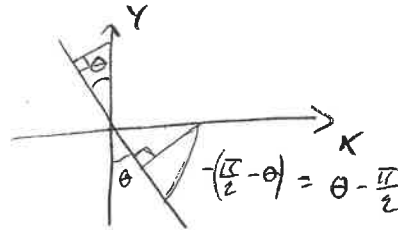
$$A_y = A \sin \theta = A_0 \sin \theta \sin(\omega t)$$

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



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

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

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

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

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

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

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

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

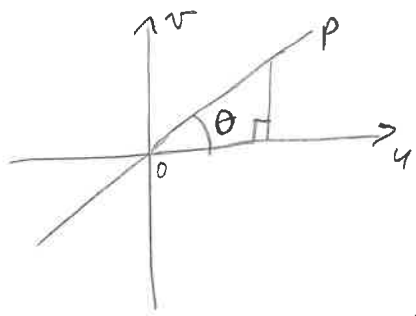
$$\delta = 2\pi \frac{p}{\lambda} = 2\pi \frac{d}{\lambda} (n_x - n_y)$$

Birefringence

(35)

Elliptical Polarization

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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

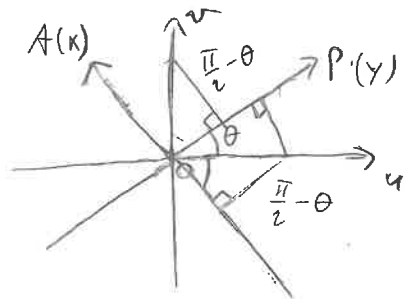
$$A'_x = A_0 \cos \theta \sin(\omega t - \delta) \rightarrow \sin(\omega t)$$

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

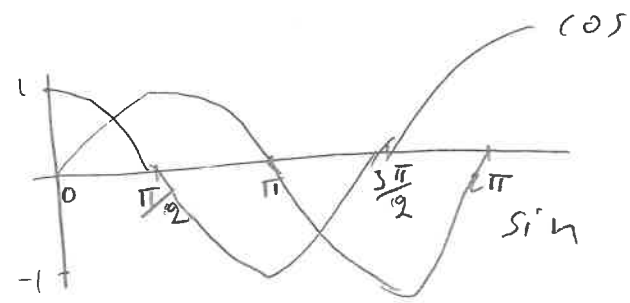
Project into (P, A) - coord-system

$$A_y = A'_x \cos \theta + A'_y \sin \theta$$

$$A_x = -A'_x \sin \theta + A'_y \cos \theta$$



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

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

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

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

$$A_y = A_x \cos(\theta) + A'_y \sin(\theta)$$

$$A_x = -A'_x \sin(\theta) + A'_y \cos(\theta)$$

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

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

Some Trigonometry

(38)

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

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

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

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

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

(39)

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

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

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

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

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

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

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

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

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

(40)

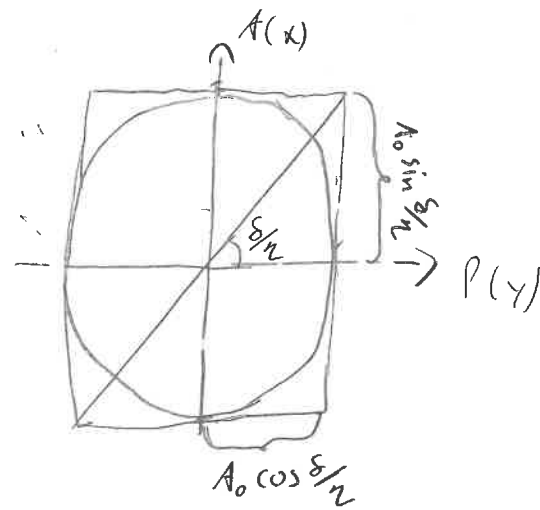
$$\begin{aligned}
 A_x &= \frac{A_0}{2} [\sin(\omega t) - \sin(\omega t - \delta)] \\
 &= \frac{A_0}{2} [\sin(\omega t) - \sin(\omega t)\cos(\delta) + \sin(\delta)\cos(\omega t)] \\
 &= \frac{A_0}{2} \left[\sin(\omega t)(1 - \cos\delta) + 2 \sin\left(\frac{\delta}{2}\right)\cos\left(\frac{\delta}{2}\right)\cos(\omega t) \right] \\
 &= \frac{A_0}{2} \left[\sin(\omega t) 2 \sin^2\left(\frac{\delta}{2}\right) + 2 \sin\left(\frac{\delta}{2}\right)\cos\left(\frac{\delta}{2}\right)\cos(\omega t) \right] \\
 &= A_0 \left[\sin(\omega t) \sin\left(\frac{\delta}{2}\right) + \cos(\omega t) \cos\left(\frac{\delta}{2}\right) \right] \sin\left(\frac{\delta}{2}\right) \\
 &= A_0 \cos\left(\omega t - \frac{\delta}{2}\right) \sin\left(\frac{\delta}{2}\right)
 \end{aligned}$$

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!

(41)



Rewrite still once:

$$\begin{aligned}
 A_x &= A_0 \sin\left(\frac{\delta}{2}\right) \cos\left(\omega t - \frac{\delta}{2}\right) \\
 &= A_0 \sin\frac{\delta}{2} \sin\left(\omega t - \frac{\delta}{2} + \frac{\pi}{2}\right) \\
 A_y &= A_0 \cos\frac{\delta}{2} \sin\left(\omega t - \frac{\delta}{2}\right)
 \end{aligned}$$

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

Could we get rid of it?

(92)

If yes, we would have
 a linearly polarized wave in the
 direction $\nu = \frac{\delta}{\lambda}$

i.e. $\frac{A_x}{A_y} = \tan \frac{\delta}{\lambda} = \tan \nu$

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

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

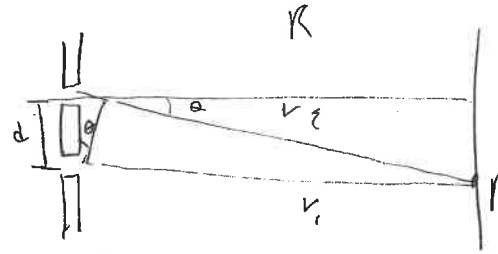
How?

Use a Quarter Wave Plate ...

→ de Sénarmont Compensator

(93)

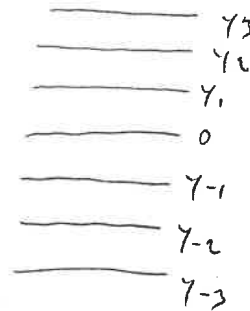
Interference → Diffraction



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:



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

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