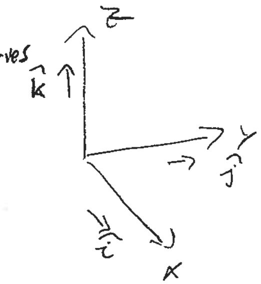
Measurement, Scaling, Instrumentation

Measurement of Volume

1° Stereometrie
- Determine some boundaries
- Adopt shape assumptions
- Compute volume

2° Fluid Replacement

3° Buoyancy



Vectorial line elements

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

$$= \int_A^C \hat{\ell}\cdot d\bar{i} + \int_C^B \hat{\ell}\cdot d\bar{j}$$

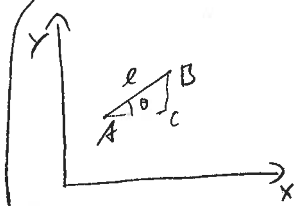
$$= \int_A^C \cos\theta\, dx + \int_C^B \sin\theta\, dy$$

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

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

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

$$d\bar{\ell} = \hat{\ell}\, d\ell$$
$$d\bar{i} = \hat{i}\, dx$$
$$d\bar{j} = \hat{j}\, dy$$
$$d\bar{k} = \hat{k}\, dz$$



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

Surface Area Element

$$d\bar{S} = \hat{n}\, dS$$

Surface Area Element in xy-plane

$$d\bar{S}_{xy} = \hat{k}\, dS_{xy} = \hat{k}(\hat{k}\cdot d\bar{S}) = \hat{k}(\hat{k}\cdot\hat{n})dS = \hat{k}\cos\varphi\, dS$$
$$= \hat{k}\, dx\, dy = d\bar{i}\times d\bar{j} = \hat{i}\,dx \times \hat{j}\,dy$$
$$= \hat{k}\, dx\, dy$$

$$\bar{A}\times\bar{B} = A_i B_j \hat{e}_k \varepsilon_{ijk} = \begin{vmatrix} e_i & e_j & e_k \\ A_i & A_j & A_k \\ B_i & B_j & B_k \end{vmatrix}$$

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

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

In xy-plane

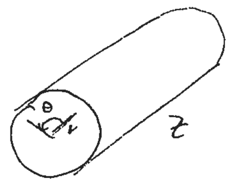
$$A_{xy} = \int \hat{k}\cdot d\bar{S}_{xy} = \int dS_{xy} = \iint dx\,dy = \int \hat{k}\cdot\hat{n}\, dS = \int \cos\varphi\, dS$$

Volume

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

In Cylindrical co-ordinates

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



$$V = \int_0^{\ell} A(z)\,dz$$

Let us compute the volume of a cylinder

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

And the volume of a cone: $r = az$ $\Rightarrow r_e = a\ell \Rightarrow a = \frac{r_e}{\ell}$

$$V = \int_0^\ell A(z)\,dz = \int_0^\ell \pi (az)^2\,dz = \pi a^2 \Big|_0^\ell \frac{1}{3} z^3 = \frac{\pi a^2 \ell^3}{3} = \frac{\pi r_e^2 \ell}{3}$$

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

$$V = \int_0^\ell A(z)\,dz = \int_0^\ell \pi (r_0 + az)^2\,dz = \pi \int_0^\ell \left(r_0^2 + 2r_0 az + a^2 z^2\right) dz$$

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

What is $r(\ell)$? $r(\ell) = r_0 + a\ell \Rightarrow a = \frac{r_e - r_0}{\ell}$

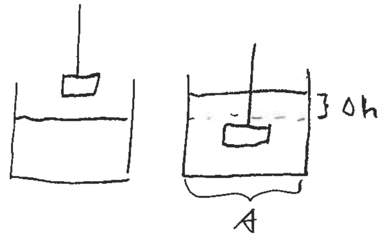
$$V = \pi \ell \left[r_0^2 + r_0(r_e - r_0) + \frac{1}{3}(r_e - r_0)^2\right]$$

$$= \frac{\pi \ell}{3}\left[r_e^2 + r_0 r_e + r_0^2\right] = \frac{\pi \ell}{12}\left[d_0^2 + d_0 d_e + d_e^2\right]$$

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

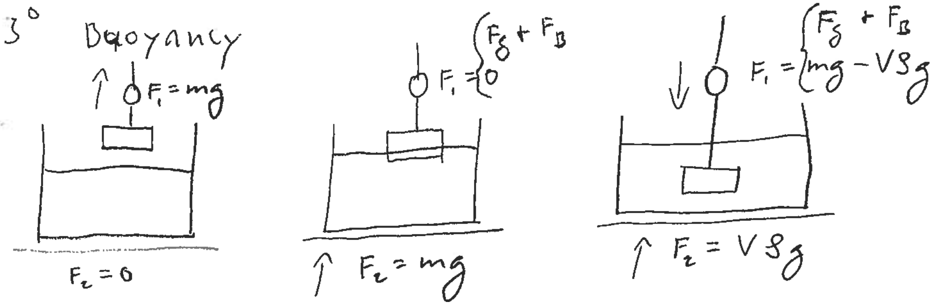
- Within any small section, shape difference will be negligible...
- The same applies even for a cylinder...

2° Fluid Replacement



$$V = A \Delta h$$

3° Buoyancy



Measurement of mass

1° Spring displacement

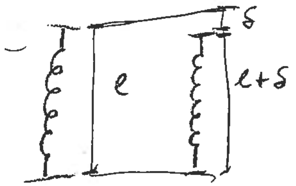
2° Balance of forces

3° Balance of torque momenta

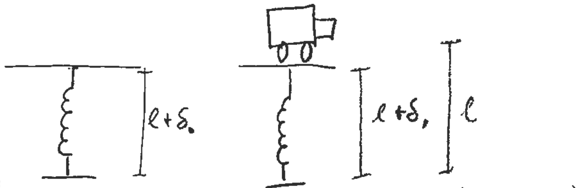
4° Buoyancy - fluid replacement

- others

1 -



Spring Equation $F = k\delta$

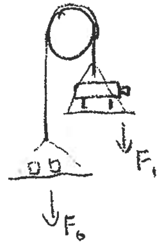


$F_0 = k\delta_0$

$F_1 = k\delta_1 = k(\delta_0 + \Delta\delta_1)$
$= F_0 + \Delta F_1$

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

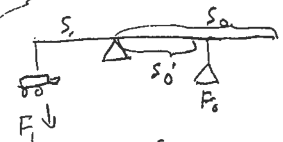
2° -



$F_1 = F_0$

$mg = m_0 g$

$m_1 = m_0$

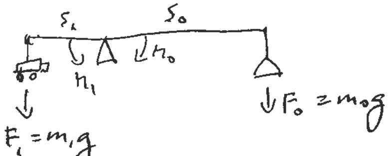


$M_1 = s_1 m g + \int_0^{s_1} \frac{dm}{ds} g\, s\, ds$

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

$$m_1 = \frac{s_0' m_0 + \int_0^{s_0} \frac{dm}{ds} s\, ds - \int_0^{s_1} \frac{dm}{ds} s\, ds}{s_1}$$

3°

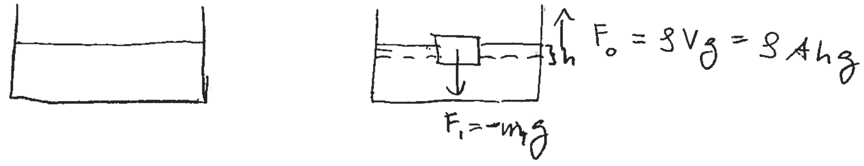


$M_1 = M_0$

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

Measurement of mass cntd

4°



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

$m_1 = \rho A h$

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

since $F_1 = -\Delta p A = -\rho g h A$

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

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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

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

Enthalpy

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

Gibb's Function

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

Phase Transition: $dp = dT = 0$

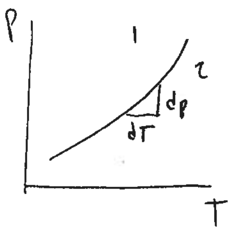
$$\Rightarrow \Delta H = T \Delta S$$

change of Heat

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

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

$$\Delta G_1 = -S_1 dT + V_1 dp$$
$$\Delta G_2 = -S_2 dT + V_2 dp$$



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

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

Clausius – Clapeyron Eq.

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Surface Energy γA

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

Stress due to surface tension

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

Balance of Forces

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

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

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

$$\mu_g = \mu_l \Rightarrow G_{mg} = G_{ml}$$

at $dT = dN = 0$

$$V_{mg} dp_g = V_{ml} dp = V_{ml} (dp(r = \infty) + d\Delta p)$$

Ideal Gas: $pV_m = RT$

$$\frac{RT}{p} dp_g = V_{ml} dp_\infty + V_{ml} d\Delta p$$

$$RT \ln p_g = V_{ml} p_\infty + V_{ml} \Delta p + C$$
$$= V_{ml} p_\infty + V_{ml} \frac{2\gamma}{r} + C$$

$$p_g = e^{\frac{V_{me} p_\infty}{RT}} e^{\frac{V_{me} 2\gamma}{rRT}} C_2$$

$$= C_3 \, e^{\frac{V_{me} 2\gamma}{rRT}}$$

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

$$= p_\infty \, e^{\frac{2\gamma M}{rRT\rho}} \qquad \text{KELVIN Eq.}$$

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

Set $p_g(r = r_s) = p_s$

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

Clausius-Clapeyron Continued

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

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

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

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

$m = n \, m_{mol}$

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

For Water:

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

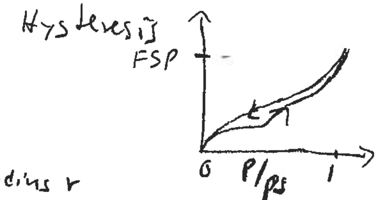
$m_{mol} = 18 \, g/mol$

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

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

$$\equiv p_s \qquad \text{SATURATION VAPOR PRESSURE}$$

$$\left.\begin{array}{l} \text{Relative Vapor Pressure} \\ \text{Water Activity} \\ \text{Relative Humidity} \end{array}\right\} \; p/p_s \; \Rightarrow \; \text{Equilibrium moisture content}$$



Why does MC Increase w. p/p_s ?

KELVIN Eq II:

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

Vapor pressure in droplet of radius r

$: p_s$

γ = surface tension

V = molar volume

For largest droplet

$$1 = \frac{\cancel{p_\infty} p}{p_s} e^{\frac{V 2\gamma}{RTr}}$$

$$p/p_s = e^{-\frac{V 2\gamma}{RTr}}$$

$$-\frac{V 2\gamma}{RTr} = \ln p/p_s$$

$$r_{max} = -\frac{V 2\gamma}{RT \ln p/p_s}$$

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

What happens to water activity as a function of Temperature?

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

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

$\approx -73\cdot 10^{-5}\frac{1}{K}$

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

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

Measuremen of RH

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

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

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 P/P_0 corresponds to Fiber Saturation Point? → Solution from Kelvin Eq

$$P/P_s = e^{-\frac{2\gamma\eta}{r_s RT\delta}}$$

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

Moisture Content and Electrical Conductivity

spring Eq.

$F = K\,\delta$

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

Hooke's Law

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

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

Potential difference Eq.

$\Delta Q = R\ I$

$[V]\ \left[\frac{V}{A}\right]\ [A]$

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

$[\Omega]$

Specific Resistance Eq.

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

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

$[\Omega m]$

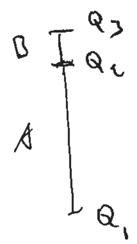
Conductivity Eq

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

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

How do we measure conductivity?

Conductors A and B in series



$I_A = I_B$

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

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

Some Specific Resistances

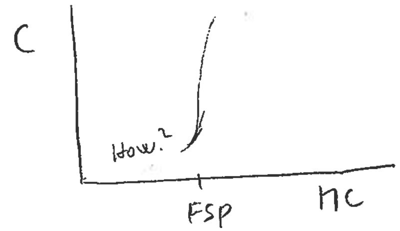
Dry Wood $10^{12}\ \Omega m$

Distilled Water $5 \cdot 10^3\ \Omega m$

$C = C(mc)$

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

$2 \cdot 10^{-4}\ \frac{1}{\Omega m}$



Signal Processing

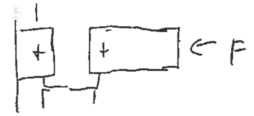
Signal generator — Displacement due to force

Input transducer — Electrical signal

Signal modifier — Conversion to linear Voltage ±5V

Output transducer — Conversion to Newtons

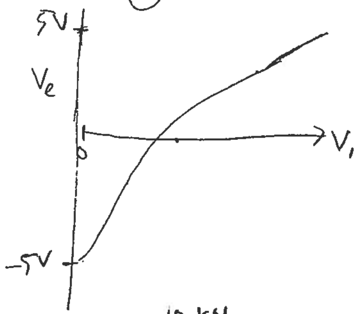
1°



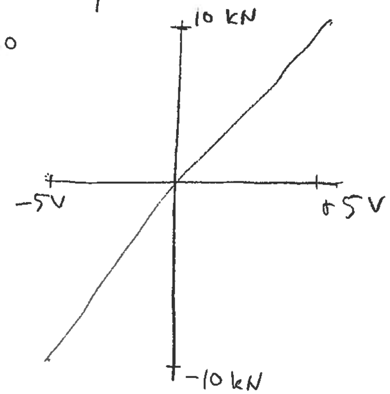
2°

$V_1 = R_1 I$

3°

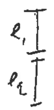


4°



Eventual problems

- Signal generator displacement
  → specimen displacement
- Finite Signal generator stiffness
- Finite mounting system stiffness
- Signal dampening
- Temperature-dependence
- Hysteresis



$\delta = \delta_1 + \delta_2$

$= \frac{F}{k_1} + \frac{F}{k_2}$

$F = k_1 \delta_1 = k_2 \delta_2$

Effective K:

$K_e = \frac{F}{\delta} = \frac{F}{\delta_1 + \delta_2}$

$= \frac{F}{\frac{F}{k_1} + \frac{F}{k_2}} = \frac{1}{\frac{1}{k_1} + \frac{1}{k_2}}$

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...

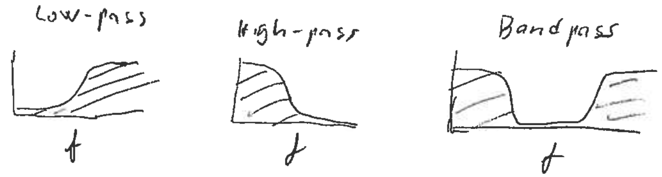
Car → Heart rate meter

{ Subway → computer screen
{ mobile phone ↗

Solutions – Actions

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

Filtering



Integration
- Boxcar
- Ensemble Averaging
- Moving-Average smoothing
- Weighed Moving-Average Smoothing

Dirac δ

$$\int \delta(x)\,dx = 1$$

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

$$\delta(t) = 0 \quad \text{for } t \neq 0$$

$$\int f(t)\,\delta(t-a)\,dt = f(a)$$

Fourier Transform

$$\mathcal{F}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(t)\, e^{-i\omega t}\, dt \;\rightarrow\; \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(u)\, e^{-i\omega u}\, du$$

Inverse Fourier Transform

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

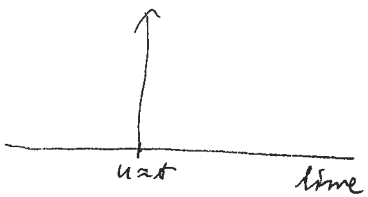
$$= \int_{-\infty}^{\infty} du\; f(u) \left\{ \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega(t-u)}\, d\omega \right\}$$

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

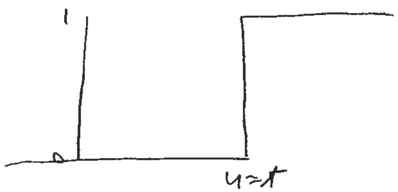
Euler Identity

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

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



Cumulative Distribution:



$$f(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \mathcal{F}(\varphi)\, e^{i\varphi t}\, d\varphi.$$

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

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

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

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

Some Fourier Transformations

21a

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

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

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

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

$$f\left[\sqrt{2\pi}\,\delta(\omega)\right] = 1 \quad \Rightarrow \quad \boxed{f\left[\delta(\omega)\right] = \frac{1}{\sqrt{2\pi}}}$$

21b

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

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

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

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

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

22

Spectroscopy

- Monitoring a spectrum of something

- Affected by interaction with matter
  - Electromagnetic radiation
  - Mechanical waves
  - Particles

$\boxed{\begin{array}{l}\text{Absorption Spectroscopy}\\ \text{Emission Spectroscopy}\\ \text{Scattering Spectroscopy}\end{array}}$

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:

$\frac{\partial}{\partial z}A = -kA_0\sin(kz-\omega t)$

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

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

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

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

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

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

23

Lognitudinal Mechanical Waves

$I = F\Delta t$

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

Fluid in a tube

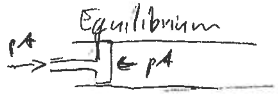
Momentum - Impulse theorem

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

$\Delta P = m\Delta v$

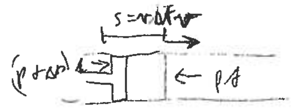
$\Delta P + I = 0$

$\Delta P = -I$



Additional pressure Δp applied for time Δt

$\Rightarrow$ Acceleration of a Fluid Element of length $s = v\Delta t$, v = velocity of the frontier of the element



$\vec{v}_z$ = 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: $\Delta P = (\rho v\Delta t A)v_z$

Fractional volume change of the Fluid element: $\frac{\Delta V}{V} = -\frac{v_z\Delta t A}{v\Delta t A} = -\frac{v_z}{v}$

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

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

$\Delta P = -I$

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

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

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

Intensity of longitudinal wave

Differential work
$$dW = \frac{\partial W}{\partial x_1}dx_1 + \frac{\partial W}{\partial x_2}dx_2 + \frac{\partial W}{\partial x_3}dx_3$$
$$= F_1\, dx_1 + F_2\, dx_2 + F_3\, dx_3$$
$$= F_i\, dx_i$$

Force in one dimension

$$\rightarrow \quad dW = F_1\, dx_1 = F\, dx$$

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

$$\frac{dW}{dt} = F v_z = \Delta p A v_z = B\frac{v_z}{v} A v_z \qquad \rightarrow F v_z$$
$$= B\frac{v_z^2}{v}A$$

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

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

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

$$\omega = 2\pi f = \frac{2\pi}{\tau}$$
$$k = \frac{\omega}{v} = \frac{2\pi}{\lambda}$$

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

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

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

Cycle Average Intensity
$$= \frac{1}{\tau}\int_0^\tau \sqrt{B\rho}\, A_\Delta^2 \omega^2 \cos^2(\omega t - kz)\,dt = \frac{1}{2}\sqrt{B\rho}\, A_\Delta^2\omega^2$$
$$= \frac{1}{2}\rho v A_\Delta^2 \omega^2$$

How to determine A_Δ ?

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

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

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

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

$\rightarrow$ Measure pressure amplitude, compute displacement amplitude!

Thermal transitions

- changes in thermal properties

First-order transition

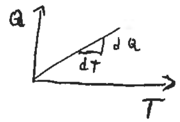
- change in heat capacity
- latent heat involved

Second-order transition

- change in heat capacity only

Heat: thermal energy [J] Q

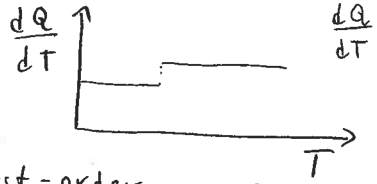
Heat Capacity: $\frac{dQ}{dT}$



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

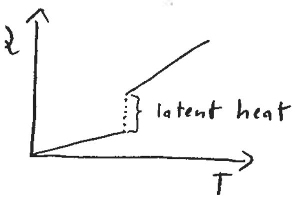
Temperature change rate $\frac{dT}{dt}$

Thermal transition

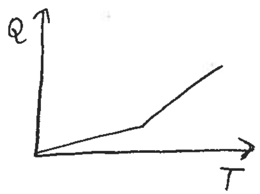


$$\frac{dQ}{dT} = \frac{dQ/dt}{dT/dt}$$

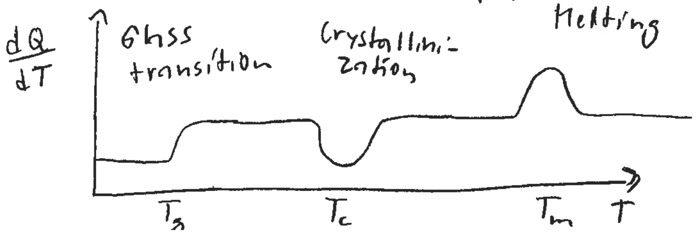
First-order



Second-order



Thermal transitions of polymers



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

Work $\int \Delta P\, I\, dt$ → 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

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

$$dG^s = dG^e$$

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

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

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

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

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

$\Delta H = T \Delta S$

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

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

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

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

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

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

Melting Temperature Spectrum

→ pore size distribution

Mass of freezing water in pores of diameter between D_1 and D_2

$$[m_{FW}]_{D_1,D_2} = \frac{1}{\Delta H_m}\int_{T_1(D_1)}^{T_2(D_2)} \frac{dQ}{dT}\,dT = \frac{1}{\Delta H_m}\int_{t_1(T_1)}^{t_2(T_2)} \frac{dQ}{dt}\,dt$$

$$\Delta H_m \approx 333\ J/g$$

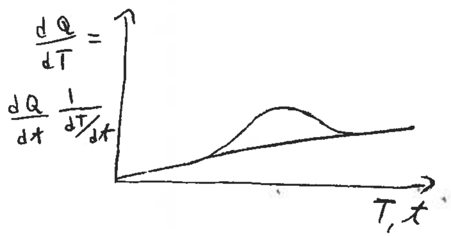
T [°C]	D [nm]
-30	1,4
-10	4,2
-5	8,6
-2,5	17
-1,2	36
-0,6	72
-0,3	144
-0,2	216
-0,1	433

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 $\qquad dE = \underset{\text{Heat}}{dQ} - \underset{\text{work}}{dW}$

$$dU = dE + \mu\,dN$$
$$= dQ - dW + \mu\,dN$$

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

Chain Rule of partial derivatives

→ Total Differential

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

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

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

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

Maxwell Relations (some)

$$dE = TdS - pdV$$

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

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

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

Gibbs Function

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

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

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

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

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

Kelvin's Thermoelastic Eq.

$$dQ = TdS$$

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

Isothermal process $\Rightarrow dT = 0$

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

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

$$\partial V = \Delta V = A\,\Delta \ell \qquad \text{Uniaxial elongation}$$

$$\frac{\partial \ell/\ell}{\partial T} = \frac{\Delta \ell/\ell}{\Delta T} = \alpha \qquad \text{Linear Thermal expansion coefficient}$$

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

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

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

$$\left.\begin{array}{l}\Delta F = \frac{\Delta \sigma}{A} \\ V = A\ell\end{array}\right\} \rightarrow \boxed{\frac{\Delta Q/V}{\Delta \sigma} = T\alpha}$$

Energy Change in Thermoelastic Uniaxial Straining

(32)

$$dE = dQ - dW$$

$$= T\alpha \ell \, dF + F \, d\delta$$

$$\frac{dF/A}{d\delta/\ell} = \frac{d\sigma}{d\varepsilon} \equiv Y$$

$$dF = YA \, d\varepsilon$$

$$F \, d\delta = F\ell \, d\varepsilon$$

$$= A\ell\sigma \, d\varepsilon$$

$$= VY\varepsilon \, d\varepsilon$$

$$dE = T\alpha VY \, d\varepsilon + VY\varepsilon \, d\varepsilon$$

$$= VY \left[T\alpha \, d\varepsilon + \varepsilon \, d\varepsilon \right] \quad \Big| \int$$

$$\Delta E = VY \Big[\underbrace{T\alpha\varepsilon}_{\text{Heat}} + \underbrace{\tfrac{1}{2}\varepsilon^2}_{\text{Work}} \Big] \quad \Big| \frac{d}{dt}$$

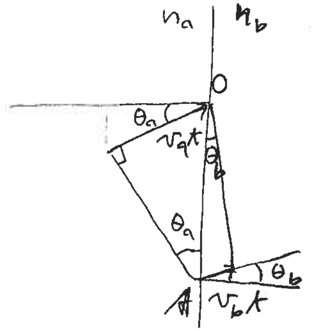
$$\dot{E} = VY \left[T\alpha\dot{\varepsilon} + \varepsilon\dot{\varepsilon} \right]$$

What if there is an Irreversible process?

(33)

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

Snell's Law of Refraction

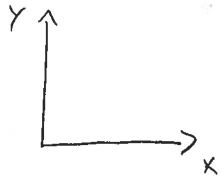


$$\sin\theta_a = \frac{v_a t}{AO} \Rightarrow AO = \frac{v_a t}{\sin\theta_a}$$

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

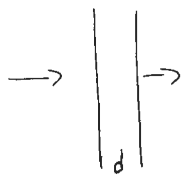
$$\frac{\sin\theta_a}{\sin\theta_b} = \frac{v_a}{v_b} = \frac{1/v_b}{1/v_a} = \frac{n_b}{n_a}$$

Birefringence: Anisotropic Index of Refraction



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

Passage through a layer d



Passage Time difference $\quad t = \frac{d}{v}$

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

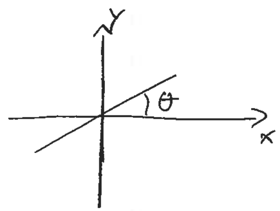
Path Difference (after crossing the layer)

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

Phase Difference

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

Apply linearly polarized light



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

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

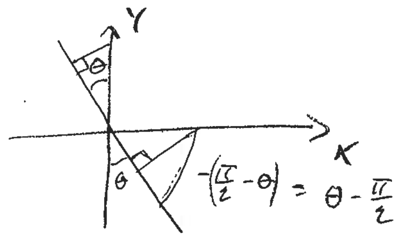
$$A_y = A\sin\theta = A_0 \sin\theta \sin(\omega t)$$

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



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

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

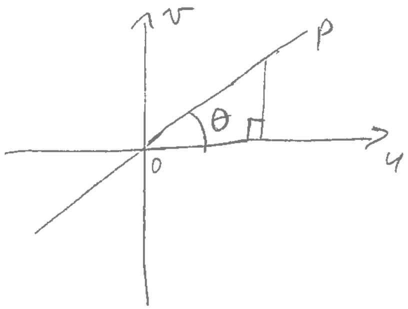
$$= \sin\theta\cos\theta \left[\sin(\omega t + \delta) - \sin(\omega t)\right] A_0$$

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

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

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

Elliptical Polarization



Apply linearly polarized light (along OP)

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

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

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

Passing through birefringent material induces phase retardation

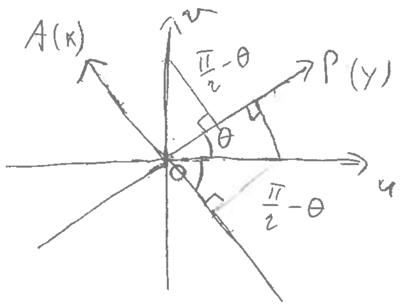
$$A'_u = A_0 \cos\theta \sin(\omega t - \delta)$$

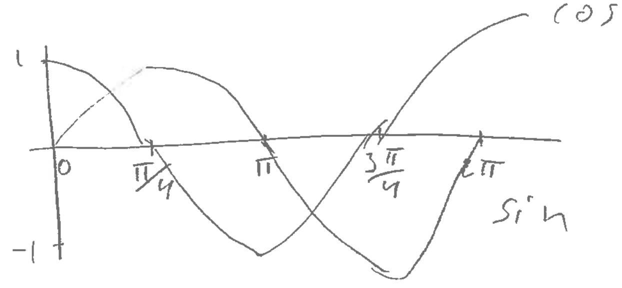
$$A'_v = A_0 \sin\theta \sin(\omega t)$$

Project into (P, A) - crd-system

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

$$A_x = -A'_u \cos\left(\frac{\pi}{2} - \theta\right) + A'_v \sin\left(\frac{\pi}{2} - \theta\right)$$





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

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

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

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

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

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

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

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

Some Trigonometry

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

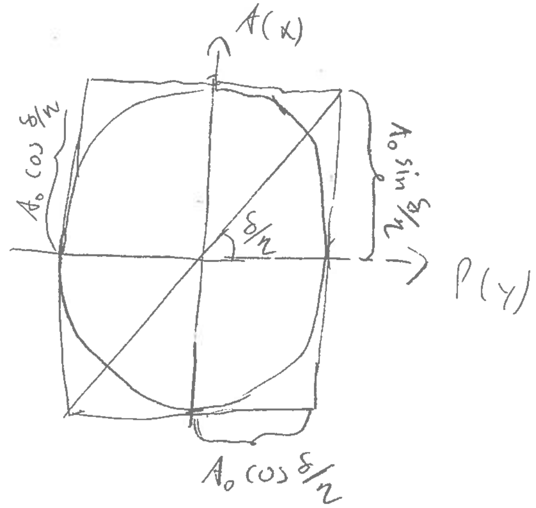
$$= A_0 \cos\left(\omega t - \frac{\delta}{2}\right)\sin\left(\frac{\delta}{2}\right)$$

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!



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 $\frac{\pi}{2}$! $\quad \left(\theta = \frac{\pi}{4}\right)$

Could we get rid of it?

If yes, we would have

a linearly polarized wave in the direction $\vartheta = \delta/2$

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

This Angle can be determined by turning the Analyzer to distinction:

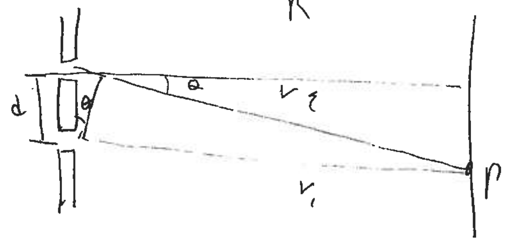
$$\delta = 2\vartheta = 2\pi \frac{p}{\lambda} = 2\pi \frac{d}{\lambda}(n_u - n_r)$$

How?

Use a Quater Wave Plate ...

→ de Sénarmont Compensator

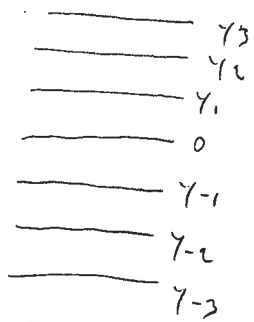
Interference → Diffraction



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

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

Interference Pattern:



$$\frac{Y_m}{R} = \tan\theta_m \approx \sin\theta_m$$

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