

Electrical Properties of Materials - esp. for beginning scatterbrains.

Ref: Moore, Feynman, internet e.g. Google "hyper physics"

The great mnemonic of E & M:

$$W = q \cdot E \cdot d = F \cdot d$$

$$E \text{ units} = \frac{\text{work}}{q \cdot d} = \frac{\text{joule}}{\text{Coul} \cdot \text{m}} = \frac{\text{volt}}{\text{m}} = \frac{\text{nt}}{\text{Coul}}$$

Note that  
 $E = -\frac{d\phi}{dx}$   
 $= -\nabla\phi$   
 $\phi = \text{potential}$

Note that  
 $W = \mu E$  where  
 $\mu = \text{dipole}$

TWO SYSTEMS

S.I

$$F = \frac{1}{4\pi\epsilon_0} \frac{q^2}{\epsilon_r r^2}$$

$\epsilon_r = \text{dielectric constant (unitless)}$

Unit breakdown

$F = \text{nt}$	}	$\frac{1}{4\pi\epsilon_0} \rightarrow \frac{\text{nt} \cdot \text{m}^2}{\text{Coul}^2}$
$\epsilon_r = \text{unitless}$		$\frac{1}{4\pi\epsilon_0} \rightarrow \frac{\text{Volt} \cdot \text{m}}{\text{Coul}}$
$q = \text{Coul}$ $r = \text{m}$		$\frac{1}{4\pi\epsilon_0} \rightarrow \frac{\text{joule} \cdot \text{m}}{\text{Coul}^2}$

$\epsilon_0$  has units  $\frac{\text{Coul}^2}{\text{nt} \cdot \text{m}^2}$   
 Vacuum permittivity

"esu"

$$F = \frac{q^2}{\epsilon_r r^2}$$

Unit breakdown

$F$ in dynes	}	$q$ has units of $\text{dyne} \cdot \text{cm}^2$
$r$ in cm		
$\epsilon_r$ unitless		

No Coulombs!  
 charge itself is given units related to the forces it produces.

$$1 \text{ esu} = (\text{dyne} \cdot \text{cm}^2)^{1/2} = \left(\frac{\text{g} \cdot \text{cm}}{\text{s}^2} \cdot \text{cm}^2\right)^{1/2}$$

$$1 \text{ esu} = \left(\frac{\text{g} \cdot \text{cm}^3}{\text{s}^2}\right)^{1/2}$$

Note that one electron =  $1.6 \times 10^{-19}$  Coul  
=  $4.8 \times 10^{-10}$  esu

EM2

Note that  $\frac{1}{4\pi\epsilon_0} = c^2 \times 10^{-7}$  by definition of  $\epsilon_0$   
 $\left\{ \begin{array}{l} 3 \times 10^8 \text{ m/s} \\ \text{mf} \end{array} \right.$

$$= (9 \times 10^{16}) \times 10^{-7} = 9 \times 10^9$$

The units of  $\frac{1}{4\pi\epsilon_0}$  are  $\frac{\text{nt} \cdot \text{m}^2}{\text{Coul}^2}$

in c.g.s.  $\frac{1}{4\pi\epsilon_0} = 9 \times 10^9 \frac{\text{nt} \cdot \text{m}^2}{\text{Coul}^2} = 9 \times 10^9 \frac{\text{kgm}^2}{\text{sec}^2} = 9 \times 10^9 \times 10^{3+6} \frac{\text{gcm}^2}{\text{sec}^2} = 9 \times 10^{18} \frac{\text{gcm}^2}{\text{sec}^2}$

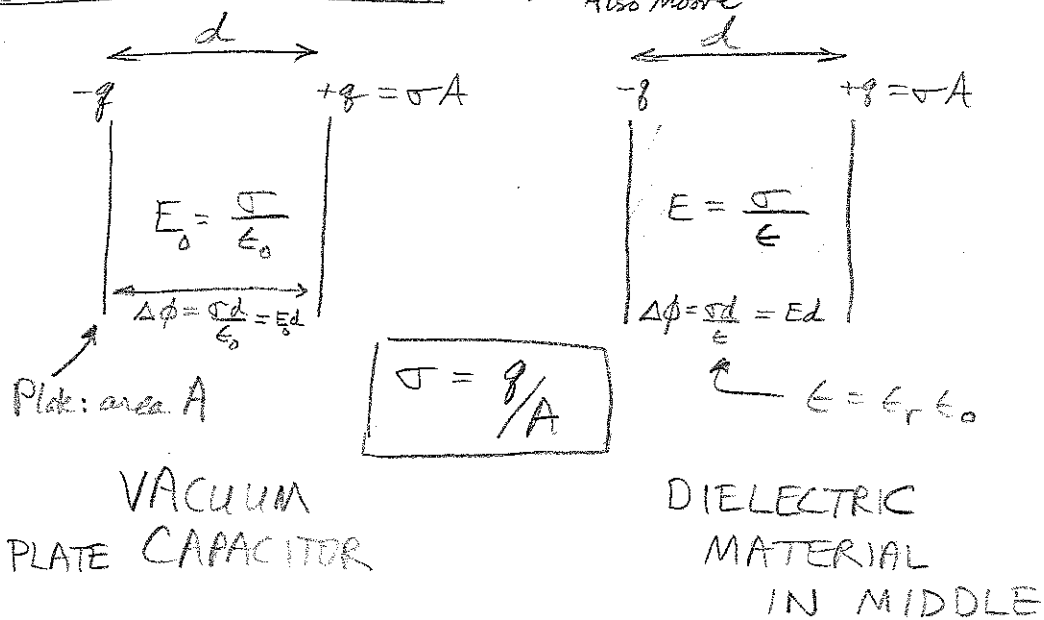
We will also require units of  $E$  in the esu system

$$E = \frac{F}{q} = \frac{\text{force on a test charge}}{\text{charge of test charge}}$$

$$E \Rightarrow \frac{(\text{esu})^2/\text{r}^2}{\text{esu}} = \boxed{\frac{\text{esu}}{\text{cm}^2}} = \text{areal charge density!}$$

These units make it clear how to generate a field: spread some charge over an area, as in a capacitor.  $E \propto$  charge density

# Dielectric media (Ref: Atkins Also Moore)



Define Capacitance  $C = \frac{q}{\Delta\phi}$

$\Delta\phi =$  The potential difference between the plates

$\Delta\phi = E d$  where  $d =$  separation

Thus  $C_0 = \frac{q}{E_0 d} = \frac{\sigma A}{E_0 d} = \frac{\sigma A}{(\sigma/\epsilon_0) d} = \frac{A \epsilon_0}{d}$

$C = \frac{q}{E d} = \frac{\sigma A}{E d} = \frac{\sigma A}{(\sigma/\epsilon) d} = \frac{A \epsilon}{d}$

Thus,  $\frac{C}{C_0} = \frac{\epsilon}{\epsilon_0} = \epsilon_r = \text{dielectric Constant}$

Thus, The dielectric constant of a material is easily determined - e.g. measure  $\Delta\phi$  with a voltmeter, then drain the charge on the plates through a current meter & integrate the total current. Insert the dielectric material & repeat.

What's the point?

As chemists, we want to relate  $\epsilon_r$  to molecular properties.

And it turns out  $\epsilon$  is related to optical properties required for light scattering.

The molecular-dielectric-optical connection is an essential development, but it takes some effort.

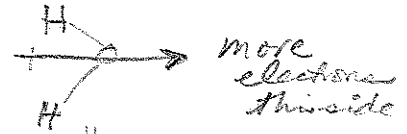
In the first place, it really does matter:

$$\epsilon_r, \text{H}_2\text{O} \approx 78$$

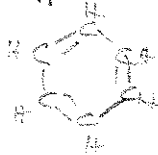
$$\epsilon_r, \text{Benzene} \approx 2.3$$

other "~~70~~ or 80"  
numbers for H<sub>2</sub>O  
 $\Delta H_f = 80 \text{ cal/g}$   
 $\gamma = 72 \text{ dynes/cm}$

Water: permanent dipoles



Benzene: no permanent dipoles



Why isn't  $\epsilon_r, \text{benzene} = 0$ ?

Because it is polarisable. In an electric field, its electrons are distorted.



Benzene: induced dipoles (weak but fast)

Water: induced dipoles plus permanent dipoles  
(weak but fast) (strong but slow)



Dipole:  $\mu = q \cdot d$

permanent : strong; change no faster than molecule rotates  
 induced : weak; can change as fast as electrons move.

Unit: 1 Debye =  $3.336 \times 10^{-30} \text{ C}\cdot\text{m}$

Typical values: (electron  $\times$  1 Å)  $\Rightarrow \approx 5 \text{ D}$

## Polarization in a dielectric

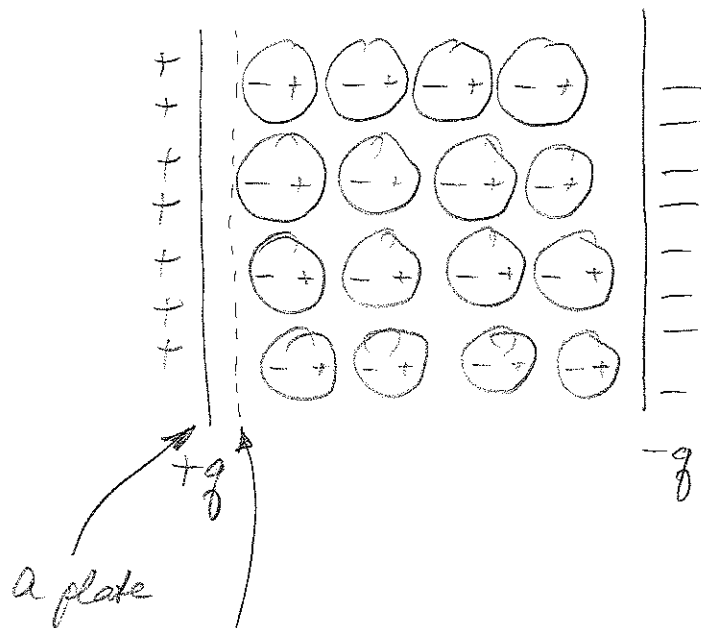
Preface: we learn  $\epsilon_r$  first through Coulomb's Law

e.g.  $F = \frac{q^2}{4\pi\epsilon_0\epsilon_r r^2}$        $E = \frac{-q}{4\pi\epsilon_0\epsilon_r r}$

★ { forces are reduced ; field is reduced  
 The effect is by division

The polarization concept also involves reduction of field, but by subtraction.

Define: Polarization = average dipole moment  
per unit volume



the surface of the material (not the plates)

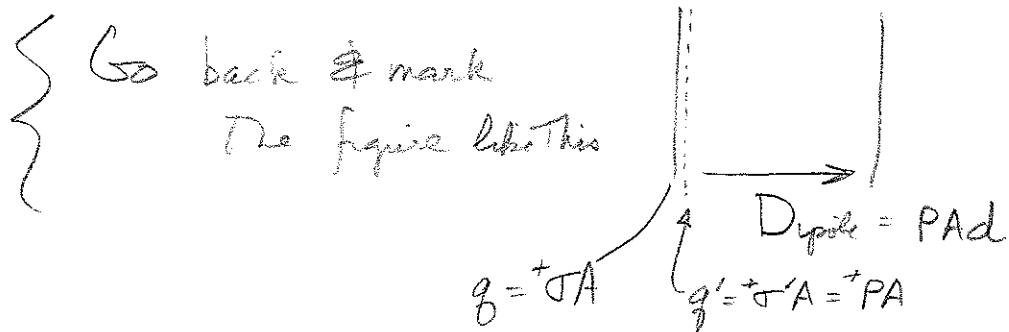
Most of the charges in the bulk cancel out.

Let  $\sigma' =$  charge density of surface  
of material.

The total dipole is  $\sigma'(Ad)$

$$P = \frac{\text{Total dipole}}{\text{Volume}} = \frac{\sigma'(Ad)}{Ad} = \sigma'$$

$P$  can be defined as dipole per unit volume  
or surface charge density of the material



P can be related to  $\epsilon_r$

- 1) Write field  $E$  as reduced by  $\epsilon_r$  by division

$$E = \frac{\sigma}{\epsilon_r \epsilon_0} \Rightarrow \sigma = E \epsilon_r \epsilon_0$$

- 2) Write field  $E$  as if formed in a vacuum using the net charge (plate - surface)

$$E = \frac{\sigma - \sigma'}{\epsilon_0} = \frac{\sigma - P}{\epsilon_0}$$

$$\Rightarrow \sigma = E \epsilon_0 + P$$

The 2 expressions for  $\sigma$  are equal:

$$\Rightarrow E \epsilon_r \epsilon_0 = E \epsilon_0 + P$$

$$\Rightarrow \boxed{P = \epsilon_0 E (\epsilon_r - 1)}$$

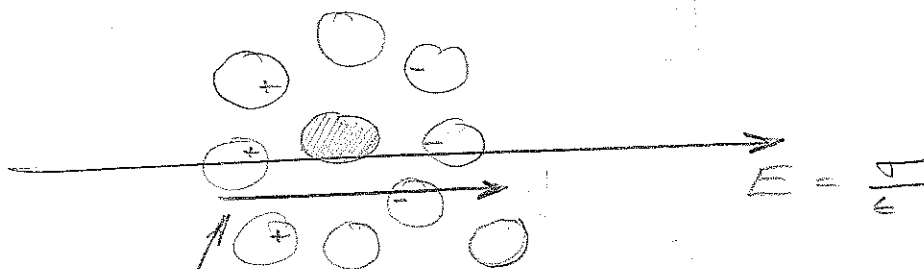


Define:  $\chi_e = \epsilon_r - 1 =$  electric susceptibility

$$P = \chi_e \epsilon_0 E$$

(how much electrons  
can cancel each other  
in the field)

So far we have looked at many molecules; now  
look at just one to make it "more molecular"



extra field due to local charges

Lorentz showed extra is  $\frac{P}{3\epsilon_0}$

$$E^* = \text{local field} = E + \frac{P}{3\epsilon_0}$$

$$\text{But } E = \frac{P}{\epsilon_0(\epsilon_r - 1)}$$

$$\text{So } E^* = P \left( \frac{1}{\epsilon_0(\epsilon_r - 1)} + \frac{1}{3\epsilon_0} \right)$$

$$\frac{P}{\epsilon_0} \left( \frac{3 + (\epsilon_r - 1)}{3(\epsilon_r - 1)} \right)$$

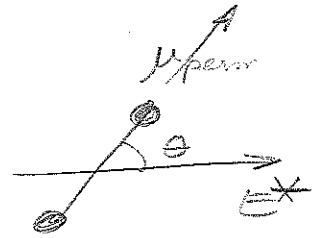
$$E^* = \frac{P}{3\epsilon_0} \left( \frac{\epsilon_r + 2}{\epsilon_r - 1} \right)$$

The polarization arises out of the response of the individual molecules to this local field.

There are 2 kinds of response

- 1) molecules align if they possess a permanent moment
- 2) molecules distort - i.e. get polarized.

Effect 1: permanent dipoles  $\mu_{perm}$



$$\text{Energy} \propto \mu_{perm} E^* \cos \theta$$

$$\mu_{avg} = \int_{\theta=0}^{2\pi} \mu(\theta) P(\theta) d\theta$$

$\mu_{perm} \cos \theta$   $\xrightarrow{\text{exp}}$   $\frac{-\text{Energy}/kT}{\text{Boltzmann weighting}}$

If  $\frac{\text{Energy}}{kT} \ll 1$  (as in most fluids.) then

See Moore,  $\approx$  p. 522

$$\mu_{avg} \Rightarrow \frac{\mu_{perm}^2 E^*}{3kT}$$

See Boltzmann

~~approx. 1/3 and  
"approx. 1/3"  
and Energy  $\ll$   
kT~~

Let  $V$  = number density of molecules

$$P_{perm} = V \mu_{avg} = \frac{V \mu_{perm}^2 E^*}{3kT}$$

$$\text{Thus } \mu_{perm}^2 = \frac{3kT P_{perm}}{V E^*}$$

$$\text{But } E^* = \frac{P(\epsilon_r + 2)}{3\epsilon_0(\epsilon_r - 1)} \text{ from Lorentz}$$

$$\text{So } \frac{\mu_{\text{perm}}}{E^*} = \frac{3\epsilon_0(\epsilon_r - 1)}{(\epsilon_r + 2)}$$

$$\mu_{\text{perm}}^2 = \frac{3kT}{V} \left( \frac{3\epsilon_0(\epsilon_r - 1)}{\epsilon_r + 2} \right)$$

$$= \left( \frac{9\epsilon_0 kT}{V} \right) \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right)$$

★ note: Atkins  
3rd ed 9

IF IT WERE NOT FOR POLARIZABILITY,  
THIS EQUATION COULD BE USED TO  
MEASURE  $\mu_{\text{perm}}$  from dielectric constants.

## Effect 2: Polarizability

$$\mu_{\text{induced}} = \alpha \cdot E^*$$

↑  
polarizability

Dimension: Units of polarizability

mks  
S.I.  
System

$$\text{Coul-m} = (\alpha \text{ units}) \left( \frac{\text{Volt}}{\text{m}} \right)$$

$$\Rightarrow \alpha_{\text{units}} = \frac{\text{Coul-m}}{\frac{\text{Volt}}{\text{m}}} = \frac{\text{Coul-m}}{\frac{\text{Joul}}{\text{Coul-m}}}$$

$$\alpha_{\text{units}} = \frac{\text{Coul}^2 \text{-m}^2}{\text{Joul}} \quad \text{Yuck}$$

cgsesu  
System

$$\text{esu-cm} = (\alpha \text{ units}) \left( \frac{\text{esu}}{\text{cm}^2} \right)$$

$\alpha \text{ units are cm}^3$

OK!

$\alpha$  increases like volume i.e. Mol.

Define:

$\chi_{\text{old}} = \text{volume polarizability} = \frac{\alpha}{4\pi \epsilon_0}$

↑ units here would be  $\text{m}^3$ . Multiply by  $10^6$  for c

The contribution of induced moments to polarization will be:

$$P_{\text{ind}} = N \mu_{\text{ind}} = V \alpha E^*$$

$$P = P_{\text{total}} = P_{\text{perm}} + P_{\text{ind}} = V \left( \alpha + \frac{\mu_{\text{perm}}^2}{3kT} \right) E^*$$

But recall  $E^* = \frac{P(\epsilon_r + 2)}{3\epsilon_0(\epsilon_r - 1)}$

and  $P$  in this eqn. means  $P_{\text{total}}$

Then 
$$P = \frac{3\epsilon_0(\epsilon_r - 1)E^*}{\epsilon_r + 2} = V \left( \alpha + \frac{\mu_{\text{perm}}^2}{3kT} \right) E^*$$

\* if you leave out the  $\mu_{\text{perm}}$  term it is called the Clausius Mossotti Eqn

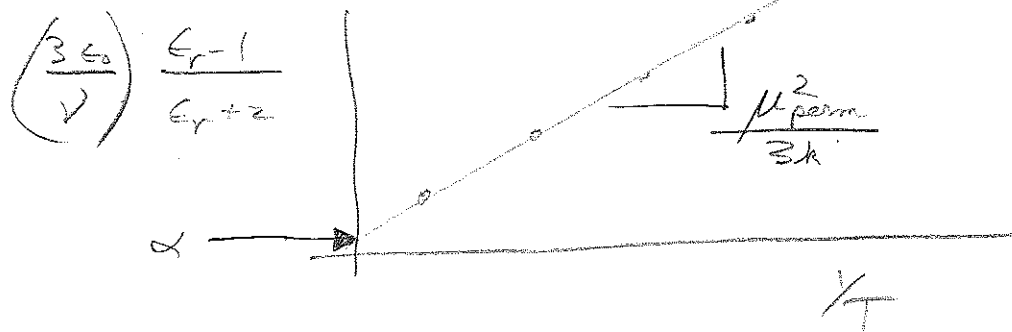
$$\Rightarrow \frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{V}{3\epsilon_0} \left( \alpha + \frac{\mu_{\text{perm}}^2}{3kT} \right)$$

Debye Eqn.

Thus, dielectric constant cannot give  $\mu_{\text{perm}}$  but only  $\alpha + \frac{\mu_{\text{perm}}^2}{3kT}$

What to do?

Answers: measure vs. temp



## Results

	$\mu_{perm}/D$	$\Delta\epsilon_{gas} / 10^{-24} \text{ cm}^3$
$\text{H}_2$	0	0.82
$\text{HCl}$	1	2.6
$\text{H}_2\text{O}$	1.9	1.5
$\text{CCl}_4$	0	10.5

Since molecules can't respond to light frequencies, the contribution of permanent dipoles to  $\epsilon_r$  at high  $\omega$  is nil.

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{V}{3\epsilon_0} \left( \alpha + \frac{\mu_{\text{perm}}^2}{kT} \right) \quad \text{Debye}$$

high frequency  $\Downarrow$

$$\lim_{\omega \rightarrow \infty} \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \frac{V}{3\epsilon_0} \alpha$$

$$\lim_{\omega \rightarrow \infty} \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \frac{N}{V} \left( \frac{\alpha}{3\epsilon_0} \right) \quad \begin{array}{l} N = \text{Avogadro's \#} \\ V = \text{molar volume} \end{array}$$

Clausius-Mosotti Eqn

\* It turns out that  $\lim_{\omega \rightarrow \infty} \epsilon_r = n^2$

d.e. for water  $\epsilon_r(\omega=0) \approx 78$

$$\epsilon_r(\omega=\infty) = n^2 = 1.33^2 = 1.8$$

The induced dipole effect is way smaller than perm. dipole effect for water, since water has such a big permanent dipole.

\* May be complicated - see Feynman

See also McQuarrie Appendices I, J, K.



Water at optical frequencies is about as effective at reducing electric fields as benzene is at low (or high) frequencies. In fact, benzene is a bit better!

$$\text{Thus } \frac{n^2 - 1}{n^2 + 2} V = \frac{N\alpha}{3\epsilon_0}$$

Allows  $\alpha$  to be connected to optical properties

for gases,  $n \approx 1$ , so:

$$(n^2 - 1)V \approx \frac{N\alpha}{\epsilon_0}$$

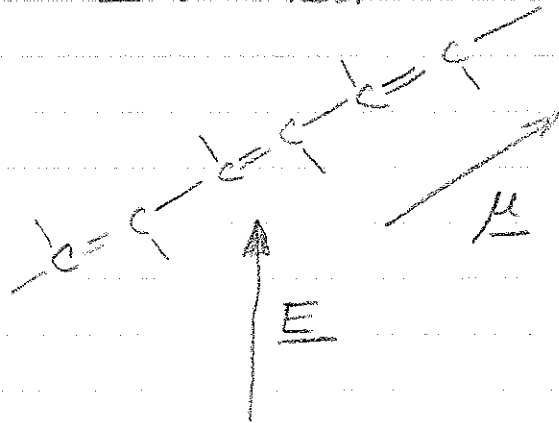
or

$$n^2 - 1 = \frac{\alpha V}{\epsilon_0} \quad \text{S.I.}$$

$$n^2 - 1 = 4\pi\alpha V \quad \text{ESU}$$

Actually,  $\underline{\mu}$  is a vector quantity:  $\underline{\mu} = \underline{\alpha} \underline{E}$

and  $\underline{\alpha}$  is a tensor



The function of  $\underline{\alpha}$  is to produce displacements in a direction not necessarily parallel to the driving force field.

$$\underline{\mu} = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz} \end{pmatrix} \begin{pmatrix} E_x \\ E_y \\ E_z \end{pmatrix}$$

$$\text{i.e. } \underline{\mu}_x = \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z$$

$$\underline{\mu}_y = \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z$$

$$\underline{\mu}_z = \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z$$

$\underline{\alpha}$  is a rank two tensor

$\underline{\mu}$  is a rank one tensor (a vector)

Now, Symmetry demands that  $\alpha_{xy} = \alpha_{yx}$  EM19  
 $\alpha_{xz} = \alpha_{zx}$   
 $\alpha_{yz} = \alpha_{zy}$

Thus, only six of the nine elements are independent.

As a result, the tensor can be "diagonalized"

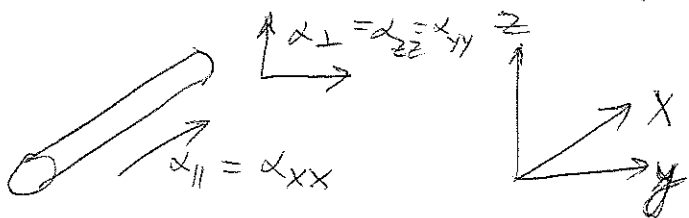
(means that there is some set of  $x, y, z$  axes where

$$\underline{\underline{\alpha}} = \begin{pmatrix} \alpha_{xx} & & 0 \\ & \alpha_{yy} & \\ 0 & & \alpha_{zz} \end{pmatrix}$$

The average polarizability is independent of frame:

$$\text{Trace } \underline{\underline{\alpha}} = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

Some molecules have cylindrical symmetry



Recap

- ⇒ Perm dipoles may exist; induced dipoles always exist
- ⇒  $\epsilon_r$  is related to structures through both types of dipole
- ⇒  $\underline{\mu}_{ind}$  not always  $\parallel$  to  $\underline{E}$

$$\Rightarrow n^2 = \lim_{\omega \rightarrow \infty} \epsilon_r$$

$$n^2 - 1 = 4\pi \alpha V \quad (\text{cgs})$$

## Electrical Properties of Polymers (and how it affects applications).

From Seymour "Modern Plastics Technology" p. 123, 124

Arc resistance (obvious - There is an ASTM test for it)

Dielectric constant (Another ASTM test)

$\epsilon_r$  is measured just as we described (parallel plate)

Dissipation factor

Ratio of in-phase to out of phase power.

Dielectric Strength: max voltage a (in thick piece) of the plastic can withstand w/o failure (arcing, I guess) for 1 minute

Power Factor: energy lost compared to total energy passing through the circuit.

Use: polymers with high power factor like PVC can be softened by application of AC current - it generates that much heat!

polymers with power factors that are low (eg. polyethylene) are useful as electrical insulators, esp. LDPE

Volume resistivity: The electrical resistance between opposing faces of a 1-inch cube of the material.

A little bit about low- $\kappa$  materials.

Fun stuff: nylon has v. high elec. resistance  $\Rightarrow$   
builds up surface charges  $\Rightarrow$  static electricity  $\Rightarrow$  ZAP !!