

$$\langle \vec{J} \rangle = \vec{\sigma} \cdot \vec{E} + \quad \Bigg| \Rightarrow \text{steady (DC) conductance}$$

↑ conductivity ↑ field

more general, allowing for time dependence

$$\langle J(t) \rangle = \int_0^t dt' \underbrace{\vec{\Phi}(t-t')} \cdot \vec{E}(t)$$

after effect (lag)

Fourier-Laplace transform

$$\langle \vec{J}_\omega \rangle = \vec{\sigma}(\omega) \cdot \vec{E}_\omega$$

$$\langle \vec{J}_\omega \rangle = \int_0^\infty e^{-i\omega t} \langle \vec{J}(t) \rangle dt$$

$$\vec{E}_\omega = \int_0^\infty e^{-i\omega t} \vec{E}(t) dt$$

$$\vec{\sigma}(\omega) = \int_0^\infty dt e^{-i\omega t} \Phi(t)$$

The above results are general
(i.e., not limited to the example
of electrical conductivity)

B depends on ext. field, F

$$\langle B(t) \rangle = \int_0^\infty \phi(t-t') F(t') dt'$$

$$\langle B_\omega \rangle = \chi(\omega) F_\omega$$

↖ freq.-dep.
susceptibility

Dielectric relaxation of a gas of non-interacting dipoles

$$\vec{P} = \chi(\omega) \vec{E} \quad \text{total polarization of a gas} \\ \text{(dipole/unit vol)}$$

$$\vec{D} = \vec{E} + 4\pi\vec{P}$$

$$\vec{D} = \epsilon \vec{E}$$

$\phi(t)$ real \rightarrow

$\chi(\omega)$, $\epsilon(\omega)$ complex

$$\epsilon(\omega) = 1 + 4\pi\chi(\omega) = \text{dielectric constant}$$

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \quad \left| \quad \varepsilon'' = \frac{nC\alpha(\omega)}{\omega} = \text{dielectric loss} \right.$$

$n = \text{index of refraction}$
 $\alpha = \text{absorption coeff.}$

$$I = I_0 e^{-\alpha x}$$

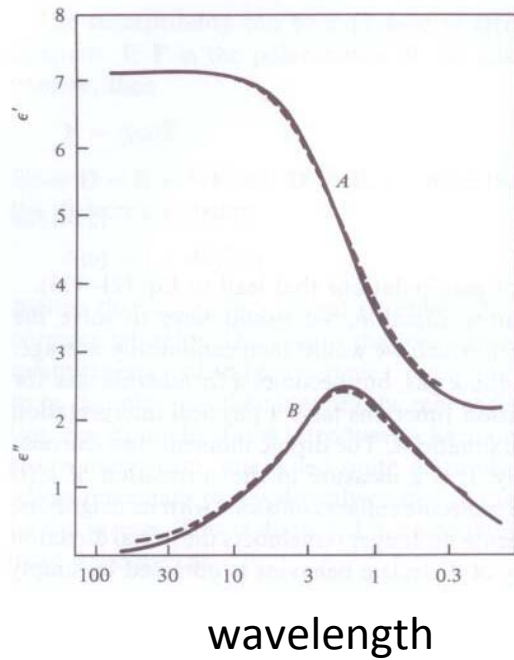
Debye: $\langle u_z(0)u_z(t) \rangle = u_{z0}^2 e^{-|t|/\tau}$

$$\rightarrow \chi(\omega) = \beta\mu_0^2 \left[\frac{1}{1 + \omega^2\tau^2} - \frac{i\omega\tau}{1 + \omega^2\tau^2} \right]$$

$$\varepsilon' - 1 = 4\pi\beta\mu_0^2 \left(\frac{1}{1 + \omega^2\tau^2} \right)$$

$$\varepsilon'' = 4\pi\beta\mu_0^2 \left(\frac{\omega\tau}{1 + \omega^2\tau^2} \right)$$

Debye
equations



molecules begin to absorb radiation as they lag behind the field

eventually freq so high, molecules cannot respond

(from McQuarrie)

Kramers-Kronig relations

$$\left\{ \begin{aligned} \chi'(\omega) &= \frac{2}{\pi} \int_0^{\infty} \chi''(\omega') \frac{\omega' d\omega'}{\omega^2 - \omega'^2} d\omega' \\ \chi''(\omega) &= \int_0^{\infty} \chi'(\omega') \frac{\omega d\omega'}{\omega^2 - \omega'^2} d\omega' \end{aligned} \right.$$

More generally

$$I(\omega) = \frac{\hbar \varepsilon'' \omega}{4\pi^2 (1 - e^{-\beta \hbar \omega})} = \frac{1}{2\pi} \int_{-\infty}^{\infty} \langle \mu_z \mu_z(t) \rangle e^{-i\omega t} dt$$

$$C(t) = \langle \mu_z \mu_z(t) \rangle$$

Real part $C \rightarrow$ even function of t

Imag part $C \rightarrow$ odd function of t vanishes in classical system

Note: we can express time dependence *via* taylor series

$$\langle A(0)A(t) \rangle = \langle A(0)A(0) \rangle + \underbrace{\langle A(0)\dot{A}(0) \rangle}_0 t + \langle A(0)\ddot{A}(0) \rangle \frac{t^2}{2} + \dots$$

0 \leftarrow for equil. system

$$\langle A(0)A(t) \rangle \approx \langle A(0)A(0) \rangle - \langle \dot{A}(0)\dot{A}(0) \rangle \frac{t^2}{2} + \dots$$

$$\begin{aligned}\langle u_z u_z(t) \rangle &= \int_{-\infty}^{\infty} e^{i\omega t} I(\omega) d\omega \\ &= \sum_{n=0}^{\infty} \frac{(it)^n}{n!} \underbrace{\int \omega^n I(\omega) d\omega}_{\text{moments}}\end{aligned}$$

moments

moments give information on the lineshape