IMI-NFG's MITT Course on
Relaxation Processes in Glass

Electrical Relaxation

Topic 1: Quasi-free ion transport

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Outline: Electrical relaxation

1. Introduction – what is electrical about it?
2. Basics of electrical and dielectric relaxation
3. Data representations
4. BNN relation
5. Universal dielectric response
6. Nearly constant loss – second universality

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Resources

- Universal Relaxation Law, A.K. Jonscher, Chelsea Dielectric Press, London, 1996
- Impedance Spectroscopy – Theory, Experiment and Applications, E. Barsouvkov and J.R. Macdonald, Wiley 2005.
- 'Dielectric Characteristics of Glass', M. Tomozawa in Treatise on Materials Science and Technology: Vol. 12, M. Tomozawa and R. H. Doremus, Eds. Wiley, 1977
- 'Measurement of Electrical Conductivity of Glasses', H. Jain in Experimental Techniques of Glass Science, C.J. Simmons and O.H. El-Bayoumi, eds., American Ceramic Society, 433-461 (1993).
- Previous MITT lectures:

  https://connect.clemson.edu/p12937309/

  https://connect.clemson.edu/p41792127/

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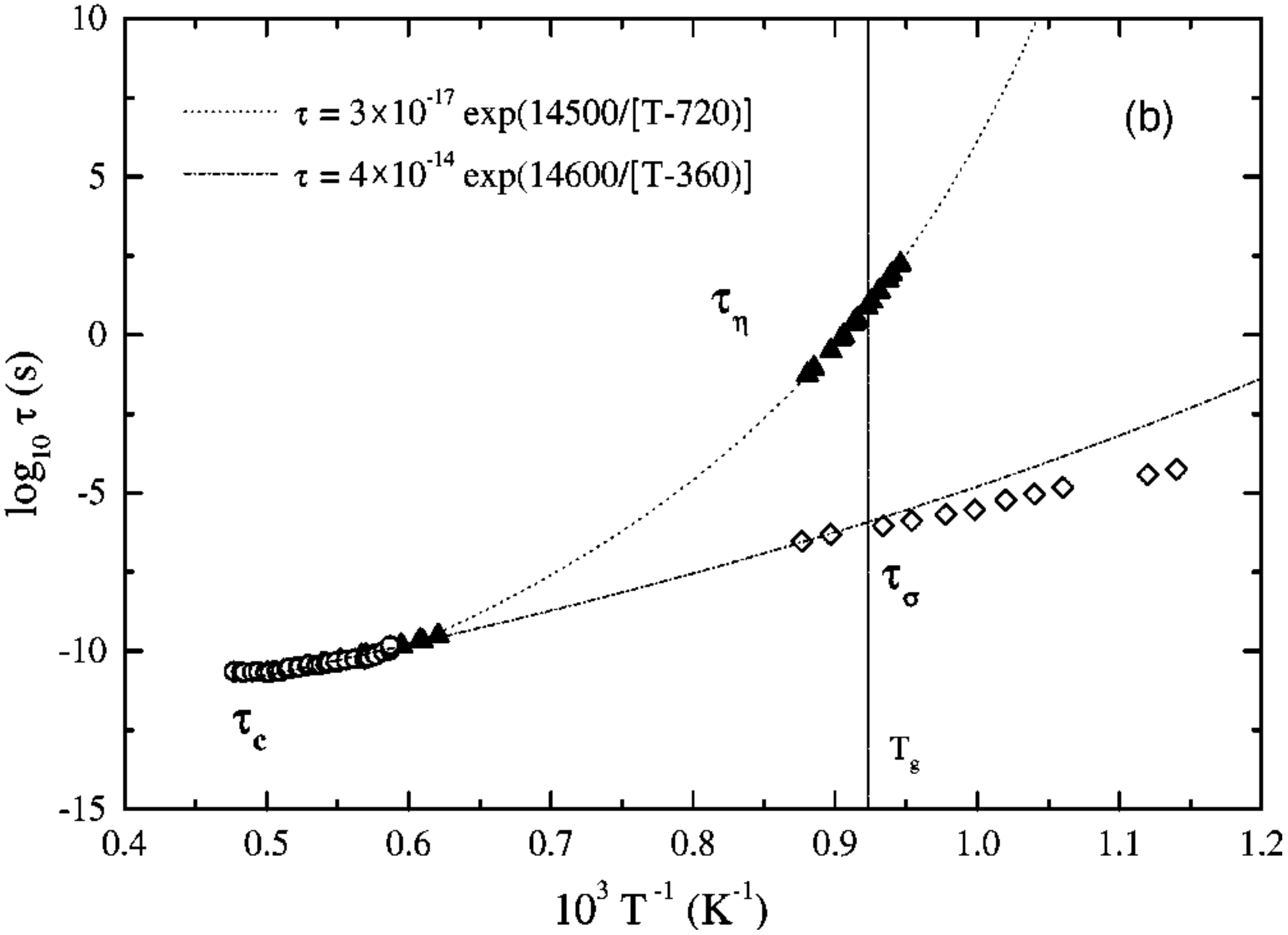
Comparison of viscosity, conductivity and NMR

SiO_2 - 44.0
Al_2O_3 - 12.5
CaO - 43.5
Tg(K) - 1083



Relaxation map from NMR (τ_C), *viscosity (τ_η), and conductivity (τ_σ) measurements.*

Gruener et al. PRB (2001)

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Viscosity relaxation

$$\tau_\eta = \frac{\eta}{G_\infty},$$

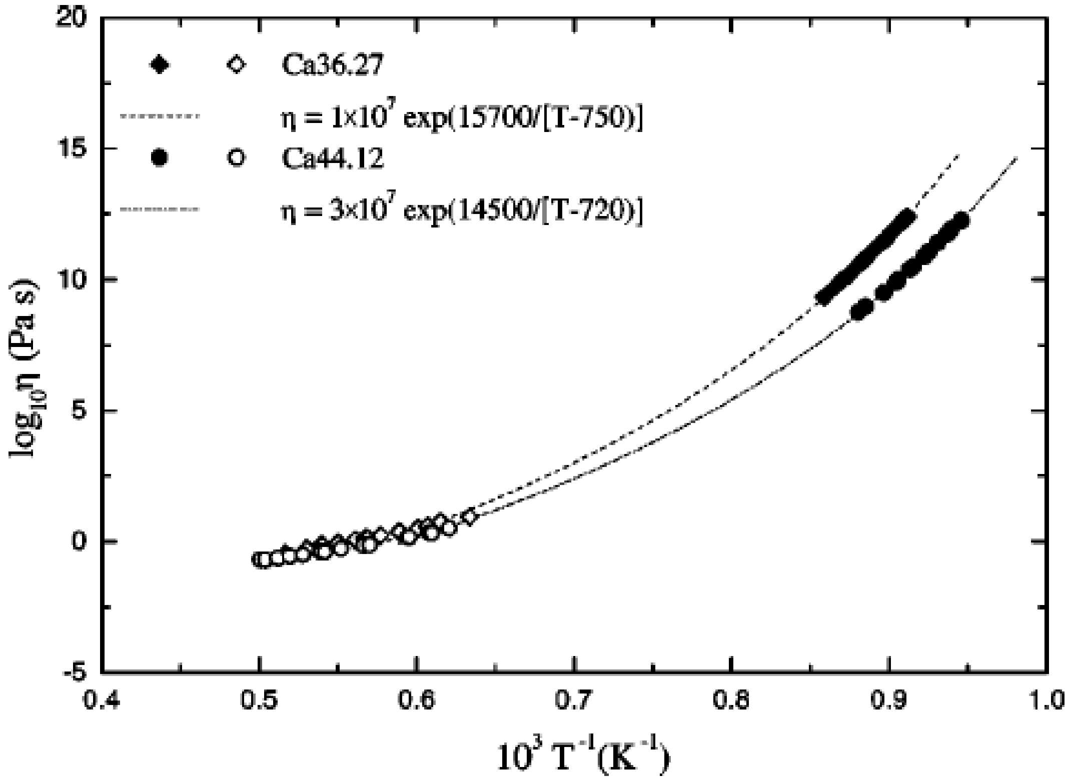

FIG. 2. Viscosity against reciprocal temperature for Ca44.12 and Ca36.27 liquids. Data are from Table III near the glass transition range and from Ref. 11 at superliquids temperatures.

AC conductivity vs. frequency

$$\sigma(\omega)=\sigma(0)+a\omega^{\alpha},$$

$\tau_{\sigma} \approx 1/\omega$ where $\sigma(\omega)=2\sigma_{dc}$

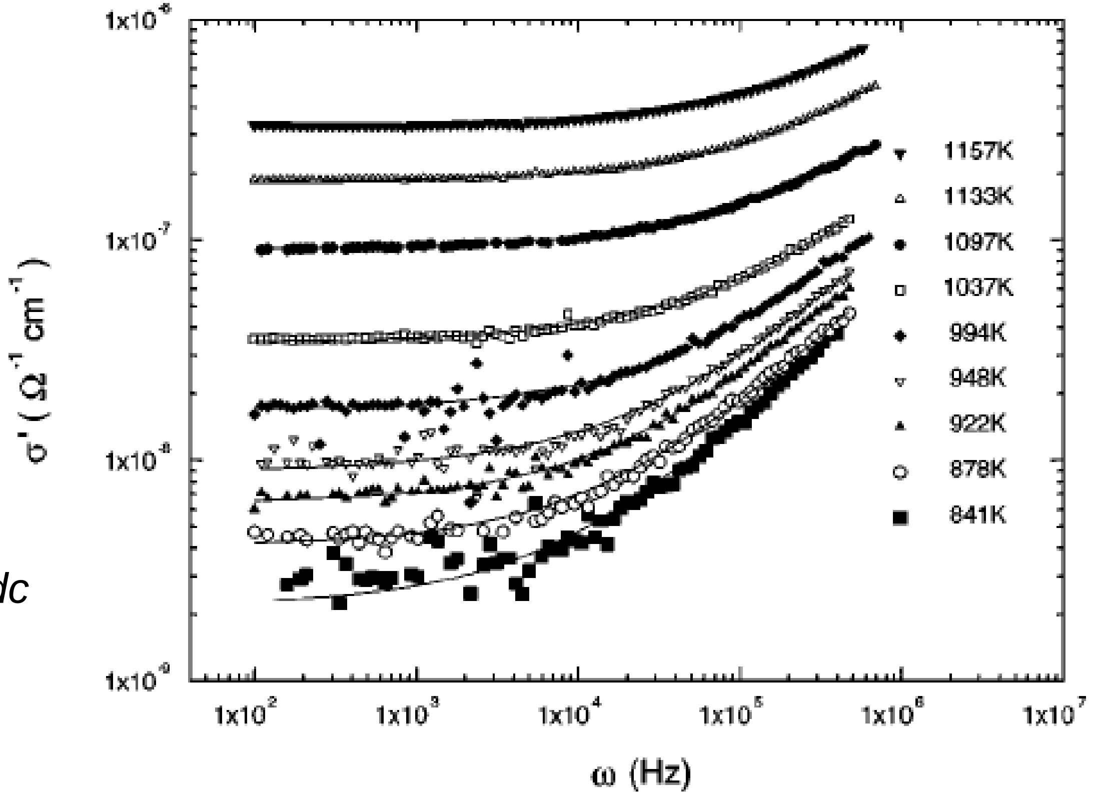

FIG. 4. Real part of the conductivity against the frequency at various temperatures for the Ca36.27 glass sample: experimental data and fitting by UDR law (solid lines).

NMR relaxation time

T_1: Nuclear spin relaxation time
T_2: Spin-spin relaxation time

$$T_1 = T_2^* = \frac{1}{\pi \nu_{1/2}}$$

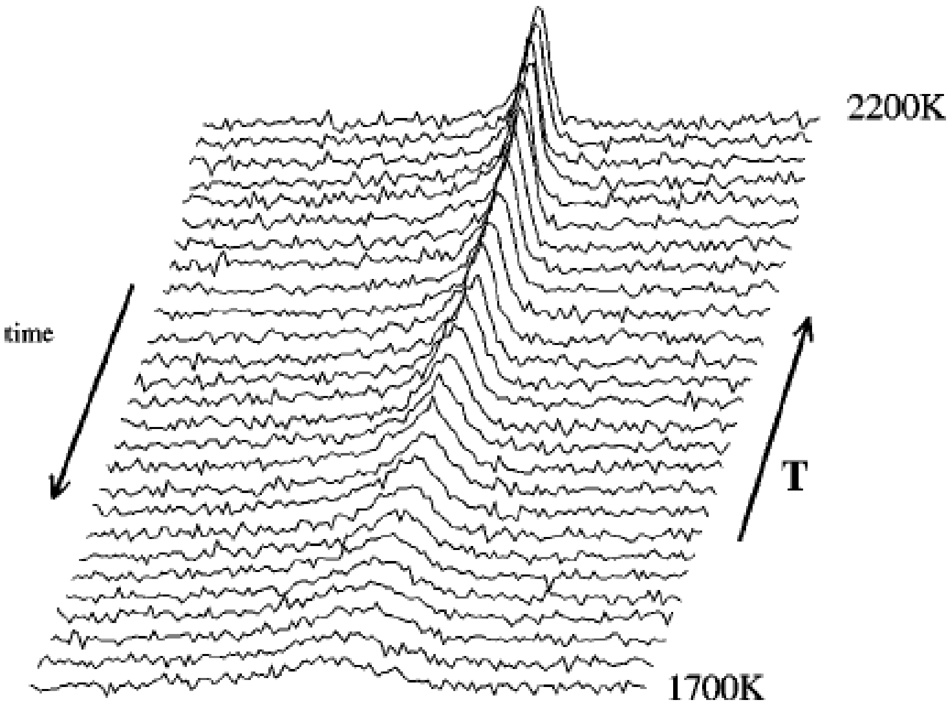

FIG. 5. Variation with temperature of the ^{27}Al static NMR spectra of Ca36.27 liquid on cooling from 2000 K.

Frequency domain ↔ Time domain

Apply brief (delta function) electric field pulse E for time Δt. The resulting polarization is given by response function, f(t).

$$P(t) = \varepsilon_0 (E\Delta t) f(t)$$

Fourier transform of f(t) describes the relaxation phenomena in the frequency domain. Dielectric susceptibility χ is given by:

$$\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = \int_0^\infty f(t)\exp(-i\omega t)\,dt$$

$$\chi'(\omega) = \int_0^\infty f(t)\cos(\omega t)\,dt$$

$$\chi''(\omega) = \int_0^\infty f(t)\sin(\omega t)\,dt$$

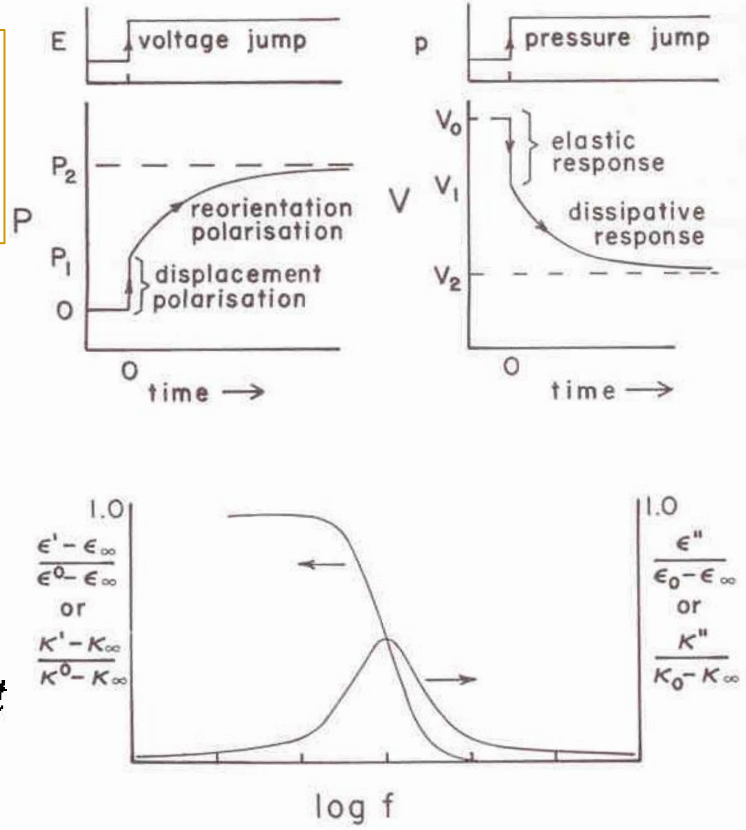

FIG. 1. (a) Polarization response P to a sudden increase in electric field E on a polar liquid. (b) Volume response V to a sudden increase in pressure p on a compressible liquid. (c) Frequency domain equivalent of response functions (a) and (b): real and imaginary parts of complex dielectric susceptibility or compressibility.

Structure in the response functions at very short times (and in the ε' and ε" at very high frequencies) due to details of the vibrational motions has not been included.

Angell and Wong, p. 714

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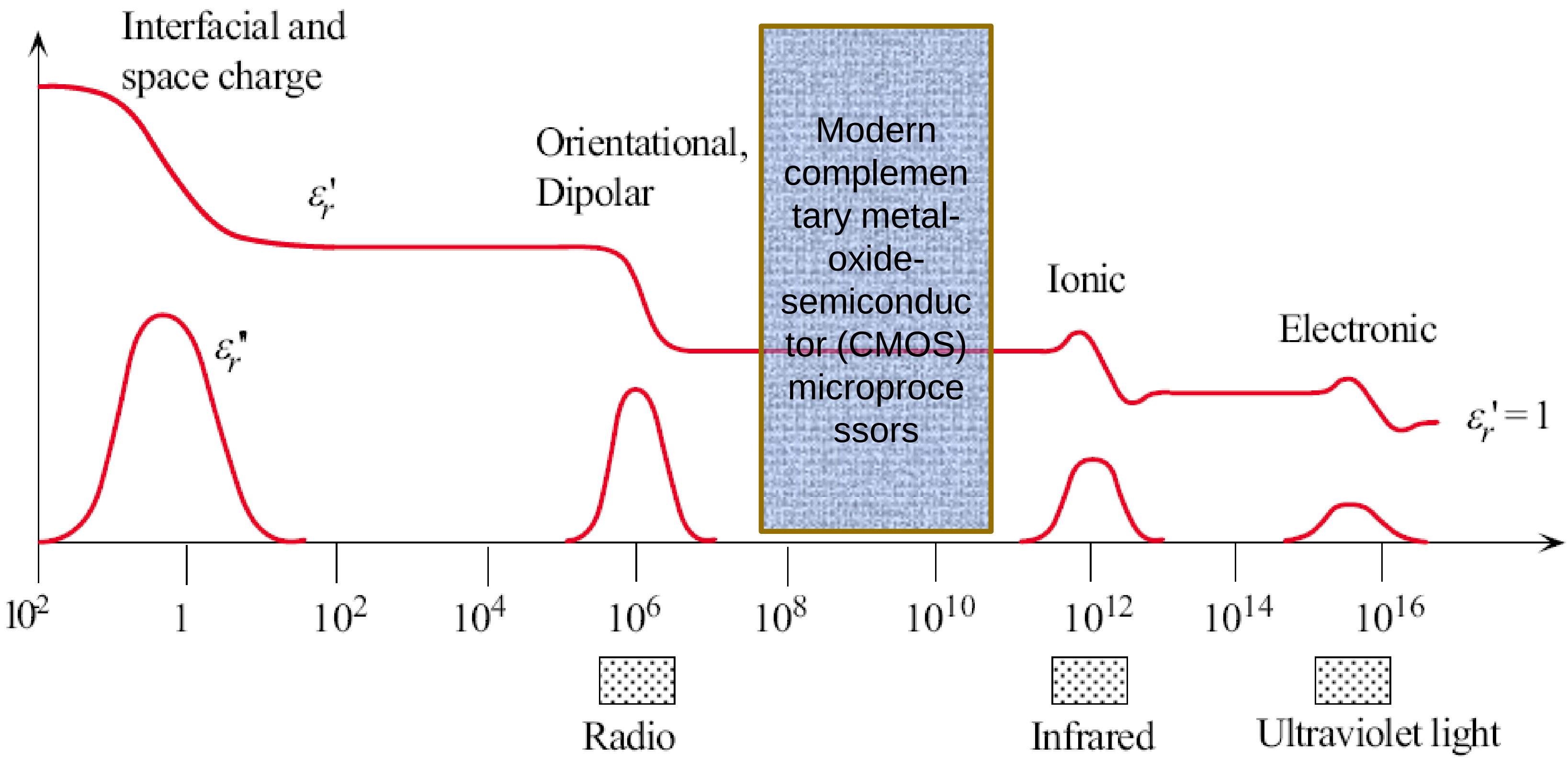
Application: e.g. glass in microelectronics

(a) Gate dielectrics, (b) Tunneling oxides in memory devices, (SiO_xN_y)

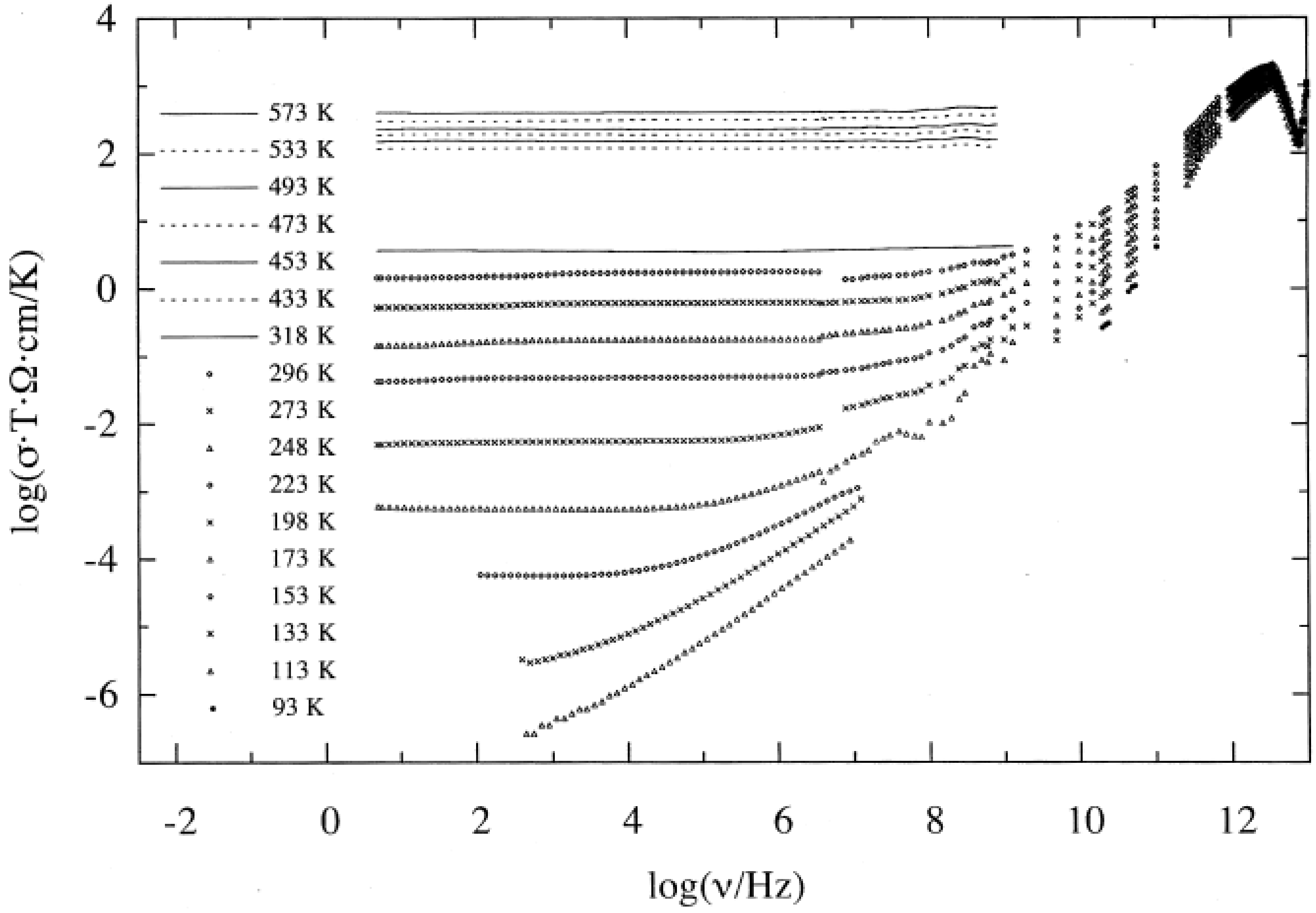
(c) Capacitors, (d) Interconnect dielectrics, (e) Isolation dielectrics



Modern complementary metal-oxide-semiconductor (CMOS) microprocessors

Electronic and Ionic polarizations are most important.

Broad conductivity spectrum



Complete experimental conductivity spectra of 0.48$(AgI)_2$-0.52 Ag_2SeO_4 at various temperatures. Kramer and Buscher, Solid State Ionics (1998)

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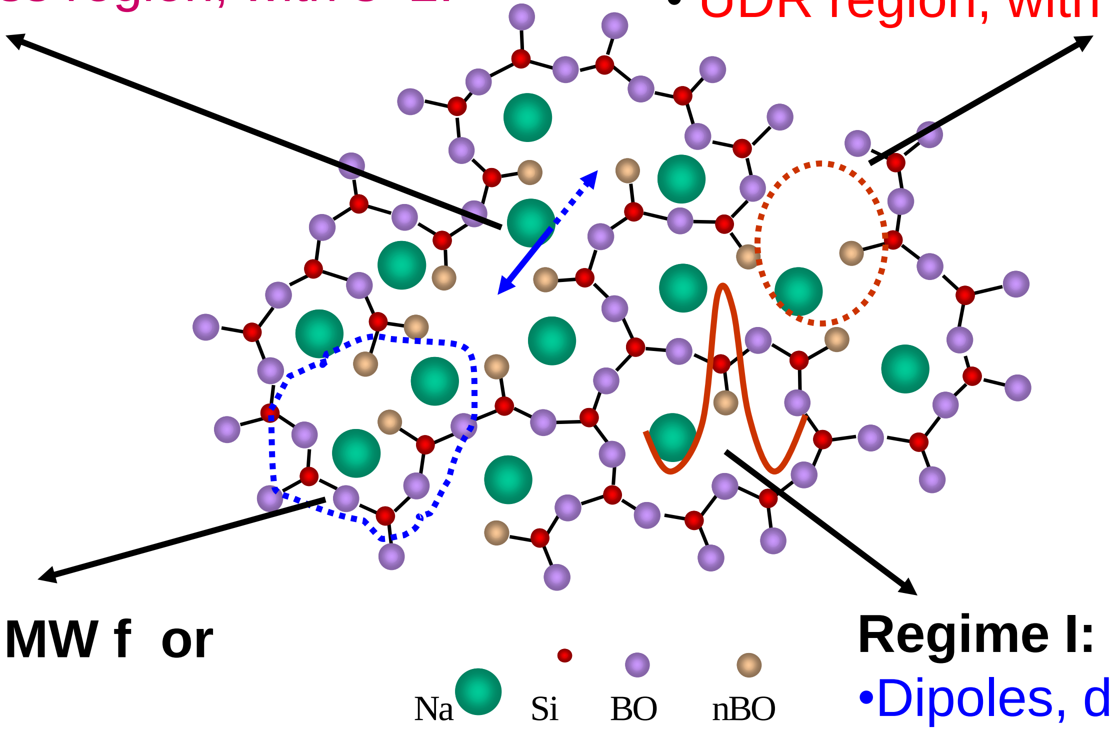
Broad view of the structural origin of conductivity



Regime IV: Very high f

- Vibrational loss region, with s≈2.

Regime II: High T - Intermediate f

- UDR region, with s≈0.6.

Regime III: MW f or Low T

- Jellyfish region, with s ~ 1.0.

Regime I: High T - low f

- Dipoles, dc conductivity region, with s=0.

Random network structure of a sodium silicate glass in two-dimension **(after Warren and Biscoe)**

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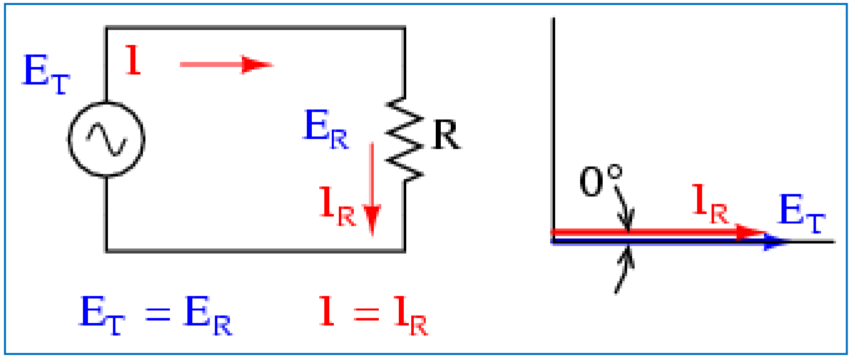
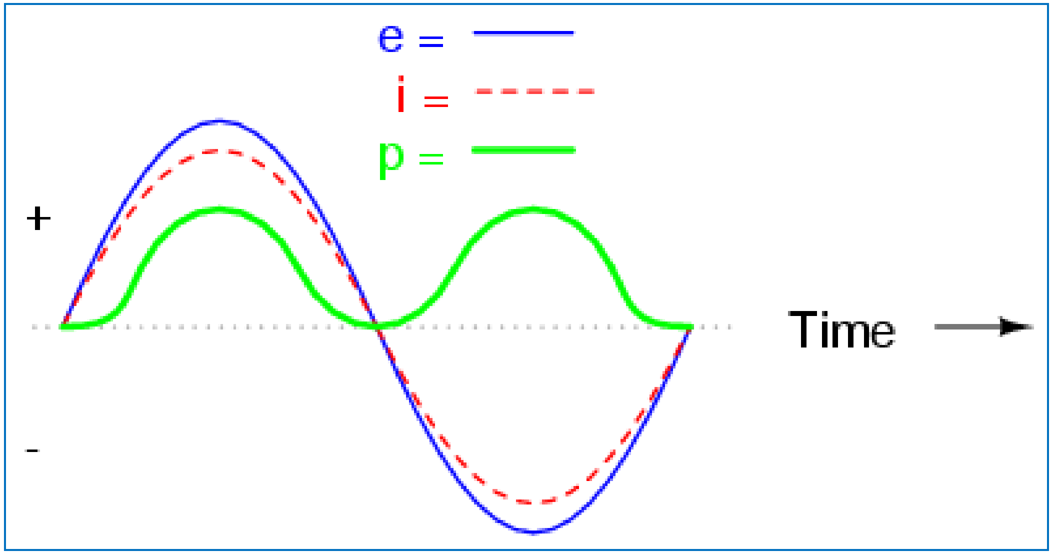
Dielectric in AC Field: **Macroview i.e. a bit of EE**

$E=E_0 \sin \omega t$

$i=i_0 \sin \omega t$



R is frequency independent.



Voltage and current are "in phase" for resistive circuit. Power or energy loss, p, $\propto Ri^2$ which is always positive and ω independent.

http://www.ibiblio.org/kuphaldt/electricCircuits/AC/AC_6.html

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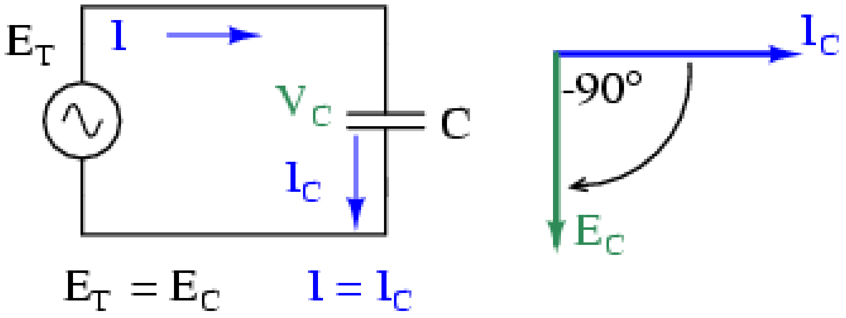
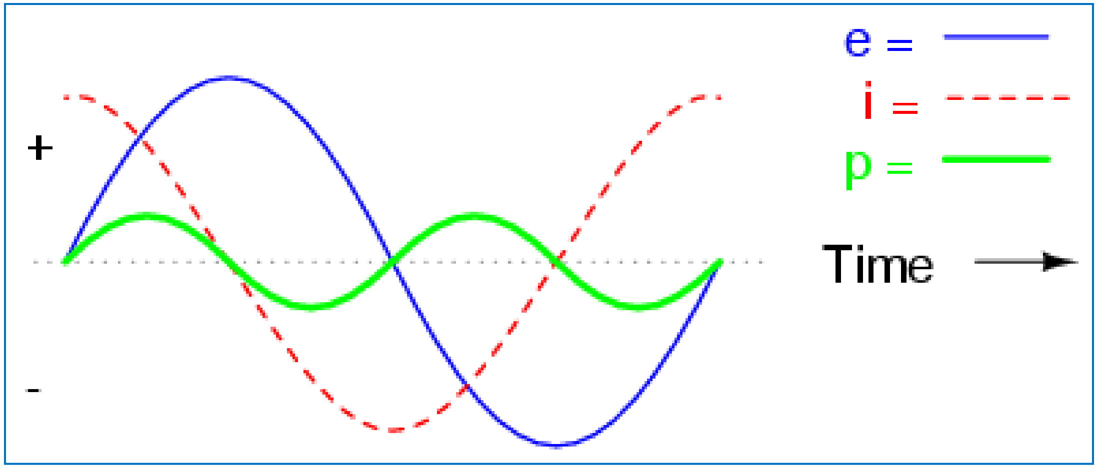
Ideal vs. Real Dielectric

$E=E_0 \sin \omega t$

$i=i_0 \cos \omega t$



C is frequency independent

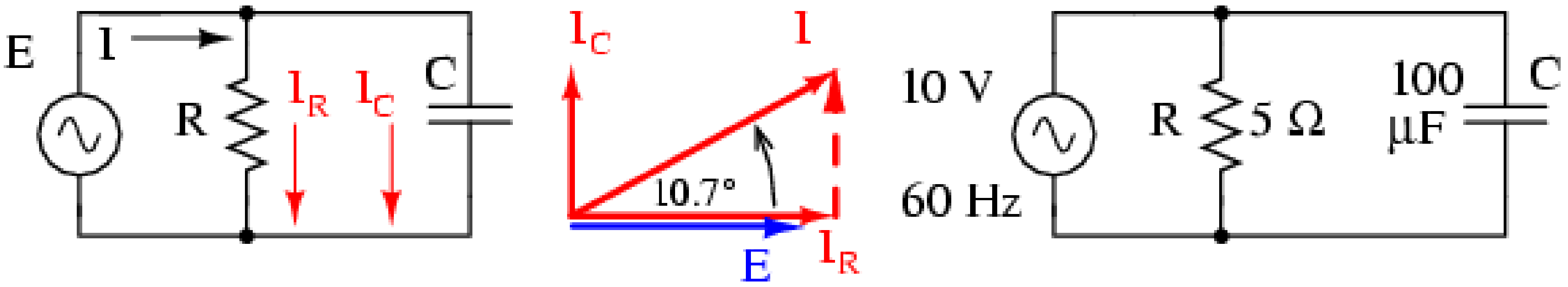


In an ideal dielectric, current is ahead of voltage (or voltage lags behind the current) by 90°.

The power (p) is positive or negative, average being zero i.e. there is no energy loss in a perfect dielectric.

http://www.web-books.com/eLibrary/Engineering/Circuits/AC/AC_4P2.htm

Real dielectric: A parallel circuit of R and C



$$I = I_R + I_L$$

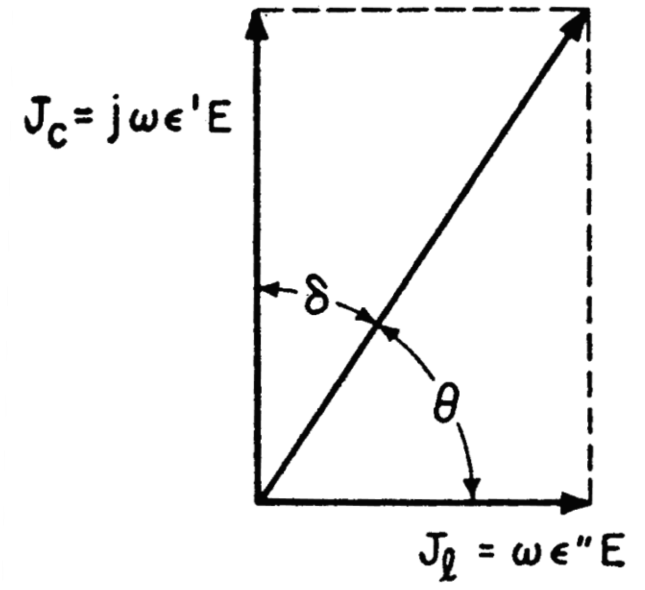
$$E = E_R = E_C$$

The total current can be considered as made of a lossy resistive component, I_L (or I_R) that is in-phase with voltage, and a capacitive current, I_C, that is 90^o out-of-phase.

Unlike ideal dielectric, real dielectric has finite conductivity that causes loss of energy per cycle.
In this case, the current is ahead of voltage by <90^o.

Complex Relative Permittivity

$$\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$$



Charging and loss current density.

ε_r = dielectric constant

ε'_r = real part of the complex dielectric constant

ε''_r = imaginary part of the complex dielectric constant

j = imaginary constant $\sqrt{(-1)}$

There are many parameters to represent the dielectric response (permittivity (ε*), susceptibility (χ*), conductivity (σ*),modulus (M*), impedance (Z*), admittance (Y*), etc.) emphasizing different aspects of the response. However, they are all interrelated mathematically. One needs to know only the real and imaginary parts of any one parameter.

$$\boxed{\varepsilon^*(\omega,T) = \varepsilon' - j[\sigma(\omega,T)/\omega]}$$

$$\boxed{\varepsilon_0\varepsilon_r''(\omega,T) = \sigma'(\omega,T)/\omega}$$

Energy loss in a dielectric

Loss tangent or loss factor $\tan\delta = \frac{\varepsilon_r''}{\varepsilon_r'}$

Describes the losses in relation to dielectric's ability to store charge.

Energy absorbed or loss/volume-sec

$$W_{\mathrm{vol}} = \omega E^2 \varepsilon_o \varepsilon''_r = \omega E^2 \varepsilon_o \varepsilon_r' \tan\delta$$

Loss tangent of silica is $1\mathrm{x}10^{-4}$ at 1 GHz, but can be orders of magnitude higher for silicate glass (Corning 7059) = 0.0036 @ 10 GHz.
Depends on ω and T.

For most applications, loss tangent or loss factor should be as small as possible.

Interconnected formalisms

the complex admittance, $Y^* = (R_p)^{-1} + j\omega C_p$ (1)

the complex impedance, $Z^* = (Y^*)^{-1} = R_s - j/\omega C_s$ (2)

the complex permittivity, $\epsilon^* = \epsilon' - j\epsilon''$ (3)

the complex modulus, $M^* = (\epsilon^*)^{-1} = M' + jM''$ (4)

where the subscripts p and s refer to the equivalent parallel and series circuit

$$Y^* = j\omega C_0 \epsilon^* \quad (5)$$

Similarly the series or "impedance" functions are related:

$$M^* = j\omega C_0 Z^* \quad (6)$$

where C_0 is the vacuum capacitance of the cell.

I. Hodge, M. Ingram, A. West, *J. Electroanal. Chem.* 74 (1976) 125.

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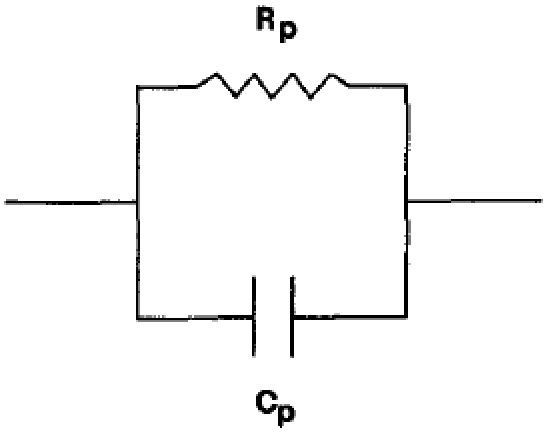
Simplest dielectric element



The equivalent circuit of the "ideal solid electrolyte".

$R_p = l0^{-6}\Omega$
$C_p = 10^{-12}$F
Geometric factor, k = 1

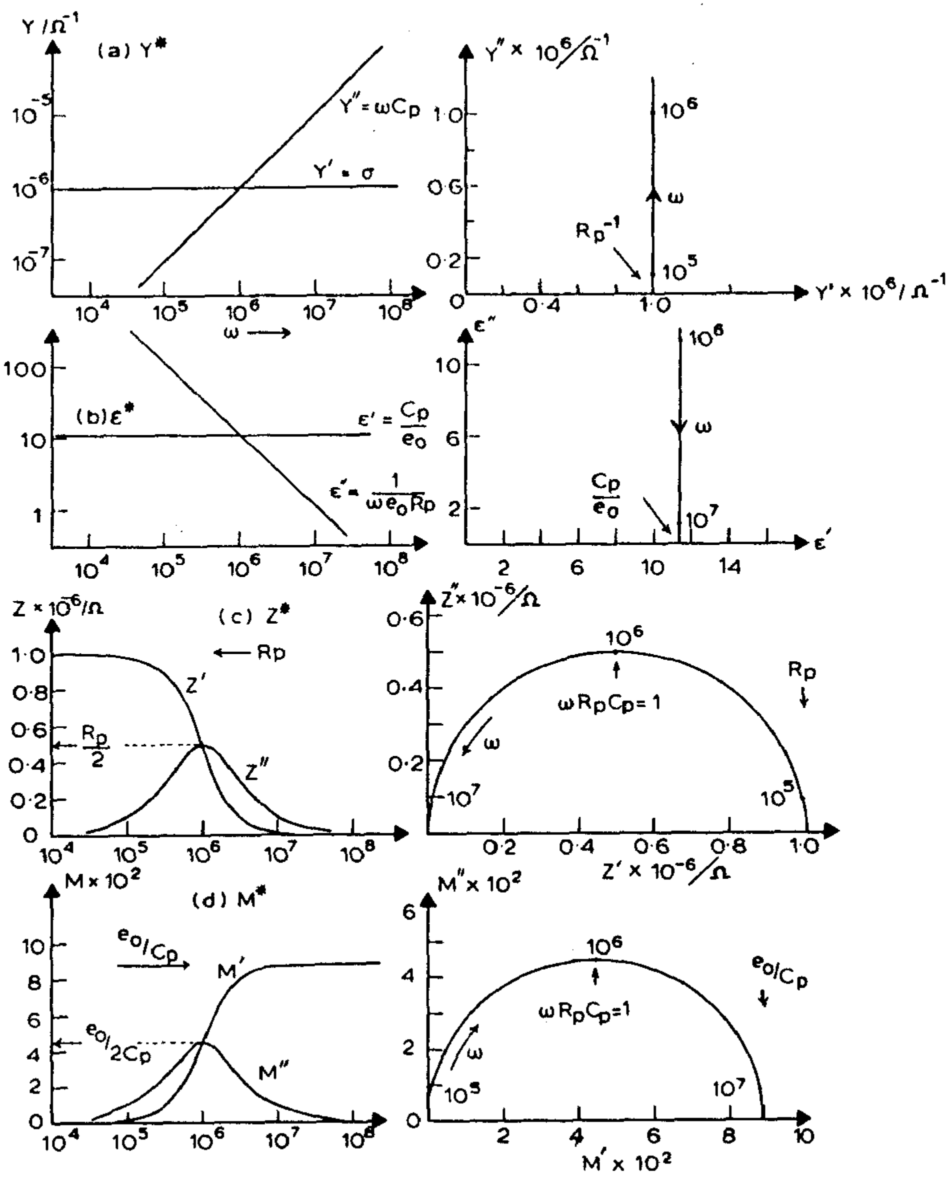


Fig. 2. Simulated "spectra" and complex plane diagrams for the ideal solid electrolyte, where $R_p = 10^6\ \Omega$, $C_p = 10^{-12}$F, and the cell constant $k = 1$. (a) Y^*; (b) ϵ^*; (c) Z^*; (d) M^*.

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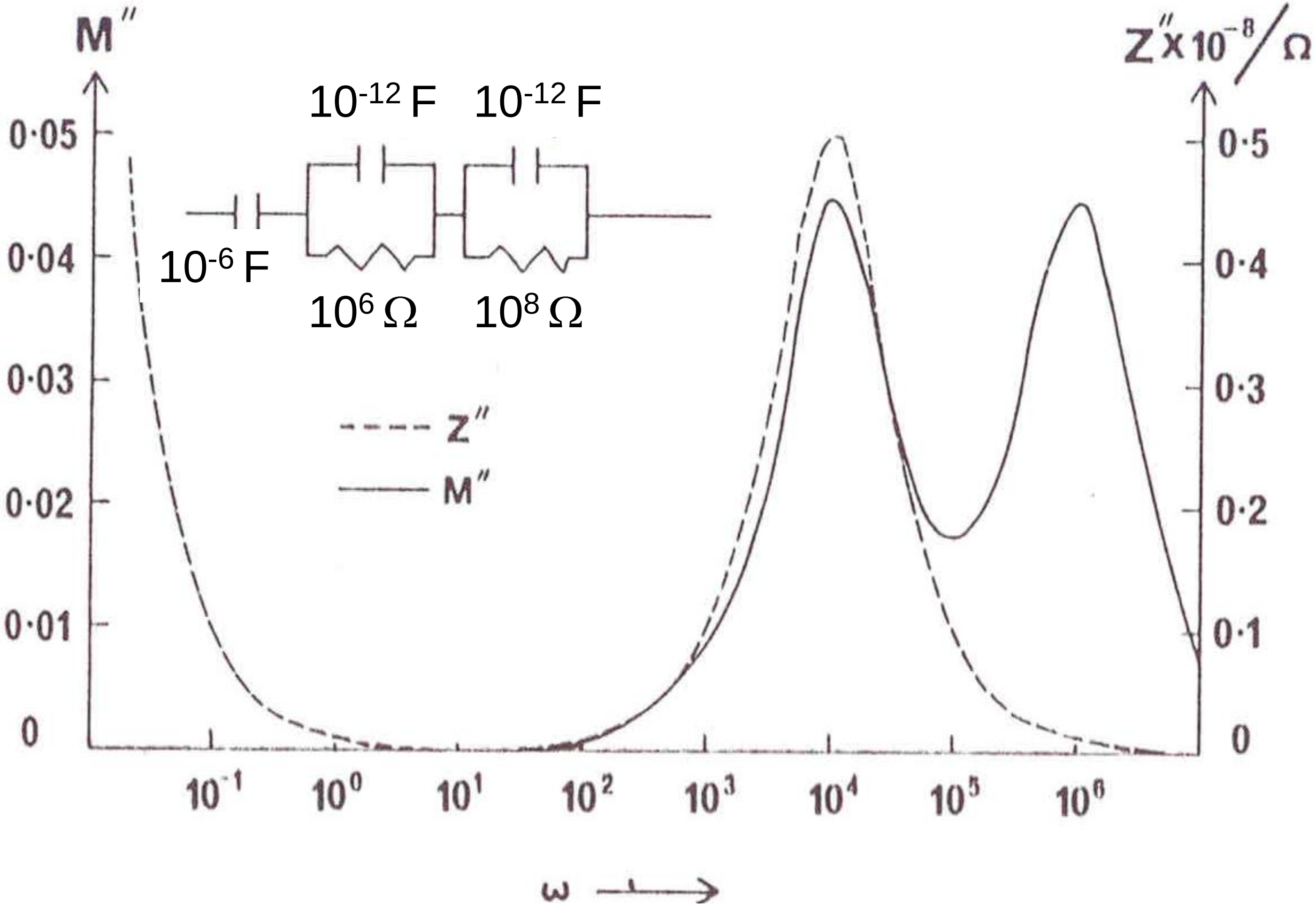
Two bulk phases + electrodes



Simulated impedance and modulus spectra for a "real" electrolyte containing two different crystalline phases ⇒ **M'' spectrum is preferred for studies of the bulk**

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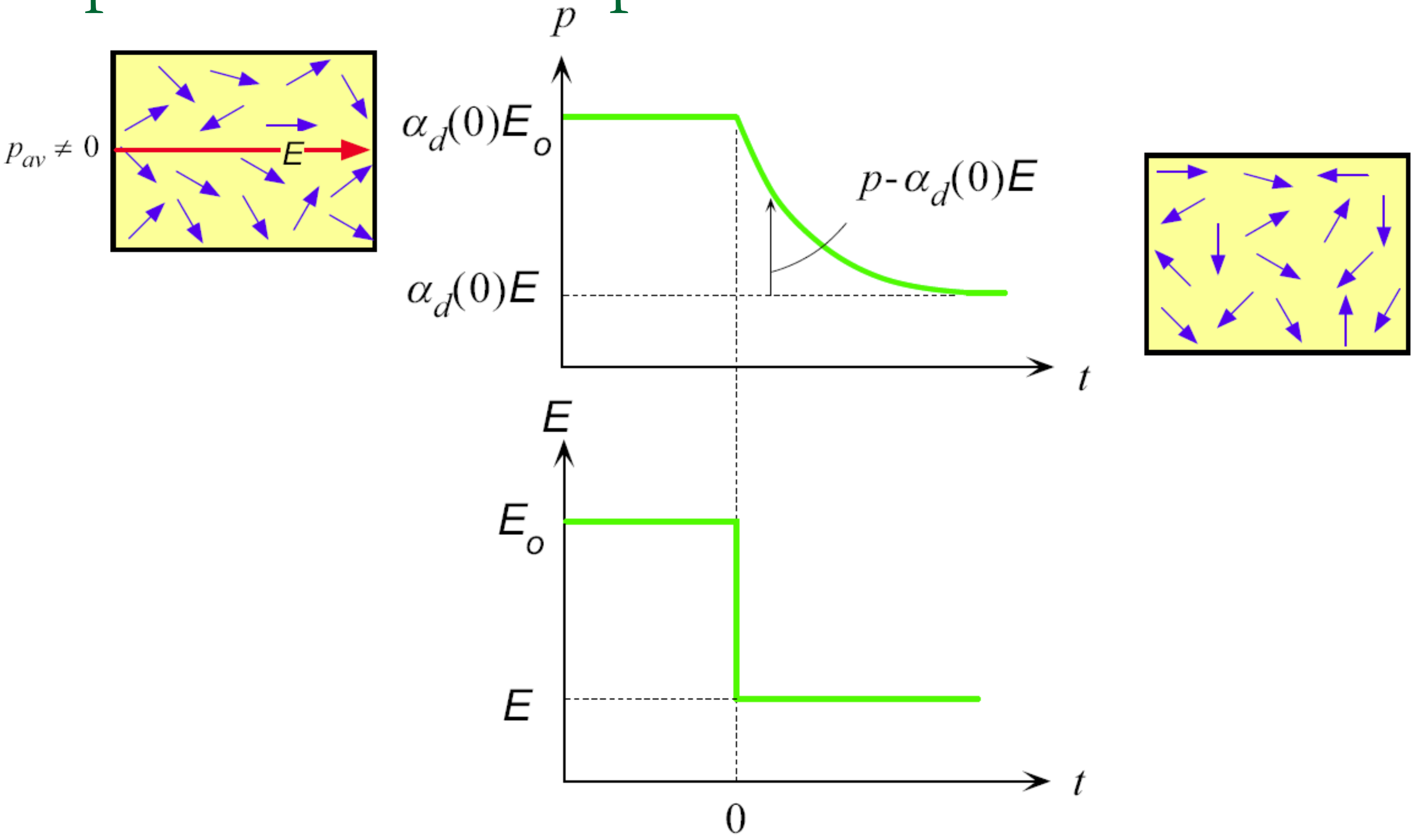
Depolarization of dipolar dielectric



The dc field is suddenly changed from $\mathcal{E}_o$ to $\mathcal{E}$ at time $t = 0$. The induced dipole moment p has to decrease from $\alpha_d(0)\mathcal{E}_o$ to a final value of $\alpha_d(0)\mathcal{E}$. The decrease is achieved by random collisions of molecules in the gas.

Dipolar Relaxation Equation

$$\frac{dp}{dt} = -\frac{p - \alpha_d(0)\mathcal{E}}{\tau}$$

p = instantaneous dipole moment = α_d ***E***,

dp/dt = rate at which p changes, α_d = dipolar orientational polarizability,

$\mathcal{E}$ = electric field, τ = relaxation time

When AC field ***E***=***E*₀** exp (jωt), the solution for p or α_d vs. ω:

$$\varepsilon_r = \varepsilon_r' - j\varepsilon_r'' \qquad \alpha_d(\omega) = \frac{\alpha_d(0)}{1 + j\omega\tau}$$

ω = angular frequency of the applied field, j is √(–1).

Debye Equations

$$\varepsilon_r' = 1 + \frac{[\varepsilon_r(0) - 1]}{1 + (\omega\tau)^2} \qquad \varepsilon_r'' = \frac{[\varepsilon_r(0) - 1]\omega\tau}{1 + (\omega\tau)^2}$$

ε_r = dielectric constant (complex)

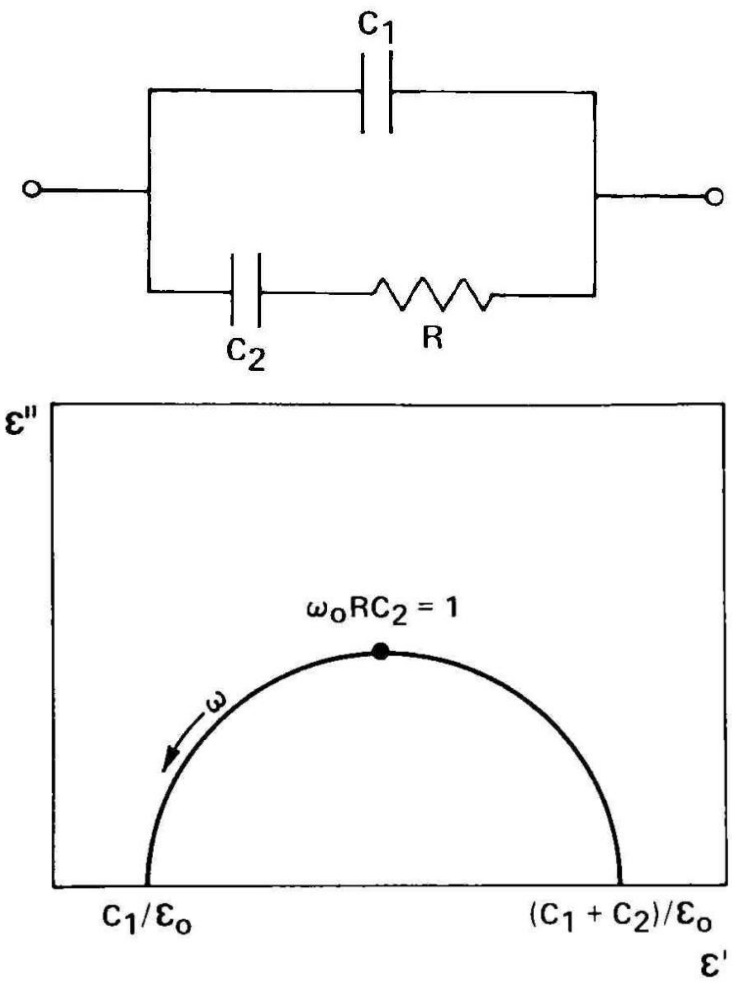
ε'_r = real part of the complex dielectric constant

ε''_r = imaginary part of the complex dielectric constant

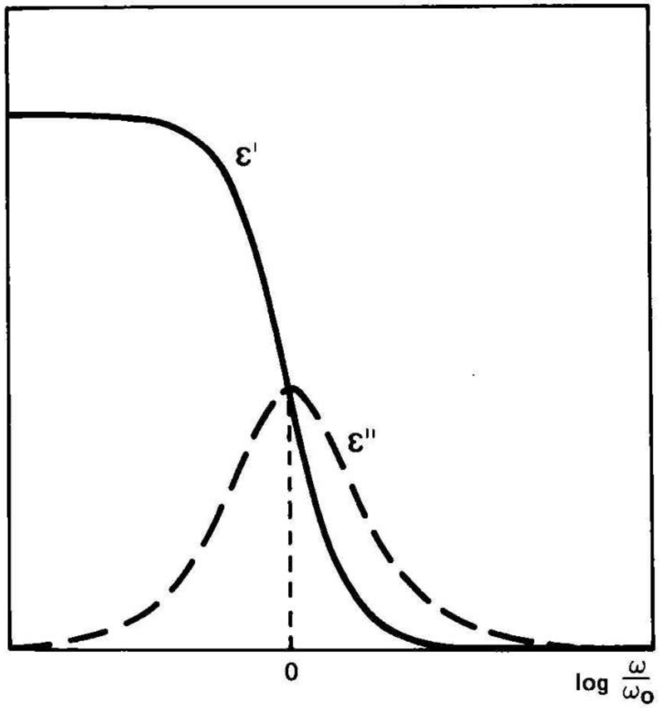
ω = angular frequency of the applied field

τ = relaxation time

Equivalent Debye dielectric element

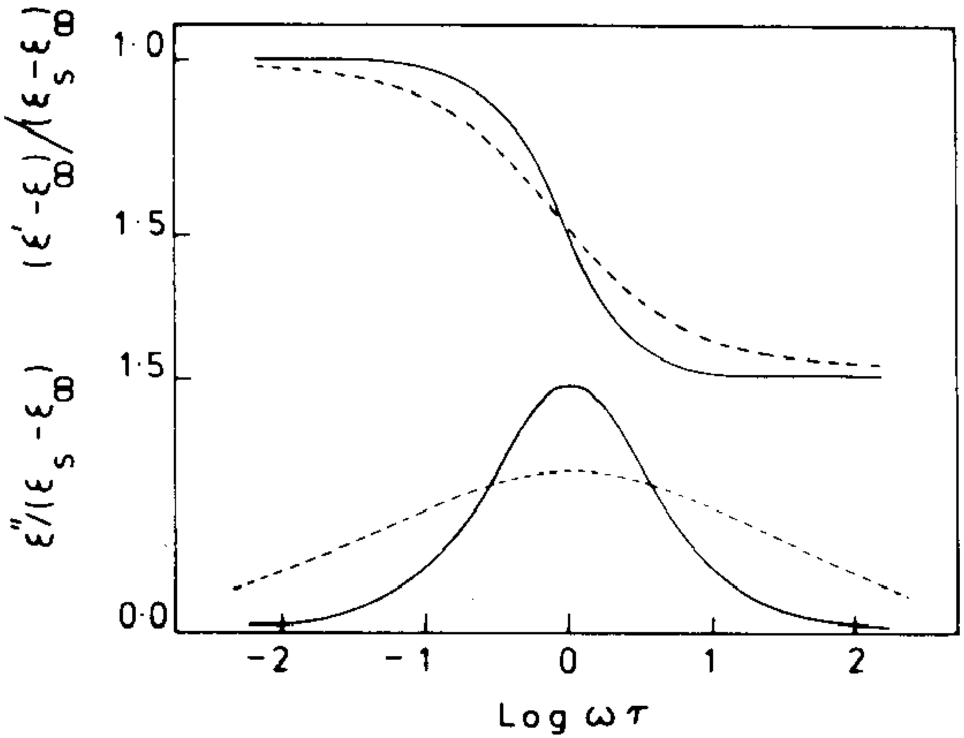


$$\varepsilon - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{1+\omega^2\tau^2} - j\frac{\omega\tau(\varepsilon_s - \varepsilon_\infty)}{1+\omega^2\tau^2}$$



The same equivalent circuit may describe dipolar loss and electrode polarization ⇒ A peak in dielectric loss could be for either reason, but with different parameters.

Dipolar dielectric loss in complex systems



$\tau = \tau_0 \exp(Q/RT)$
where Q is activation energy for the reorientation of a dipole.

How would the loss peak change with increasing T?

It will shift to higher temperature with the same activation energy.

Debye Eqs are valid when the dipole (ion) conc is small i.e. non-interacting dipoles, andε” vs log ω shows symmetric Debye peak at ωτ = 1

For high x, the dipoles interact causing distribution of τ ⇒ the loss peak is smeared.

$$\epsilon^* = \epsilon_\infty + (\epsilon_s - \epsilon_\infty) \int_0^\infty \frac{G(\tau)\, d\tau}{1 + i\omega\tau}$$

where G(t) is an appropriate distribution function.

An example:$18Na_2O$-$10CaO$-$72SiO_2$ glass

Typical oxide glasses show a broad loss peak, suggesting dipoles in the glass.

Invariably, the activation energy for the loss peak frequency is the same as of dc conductivity.

Is the loss peak due to intrinsic dipoles, or interfacial polarization?

Intro to Ceramics
Kingery et al.

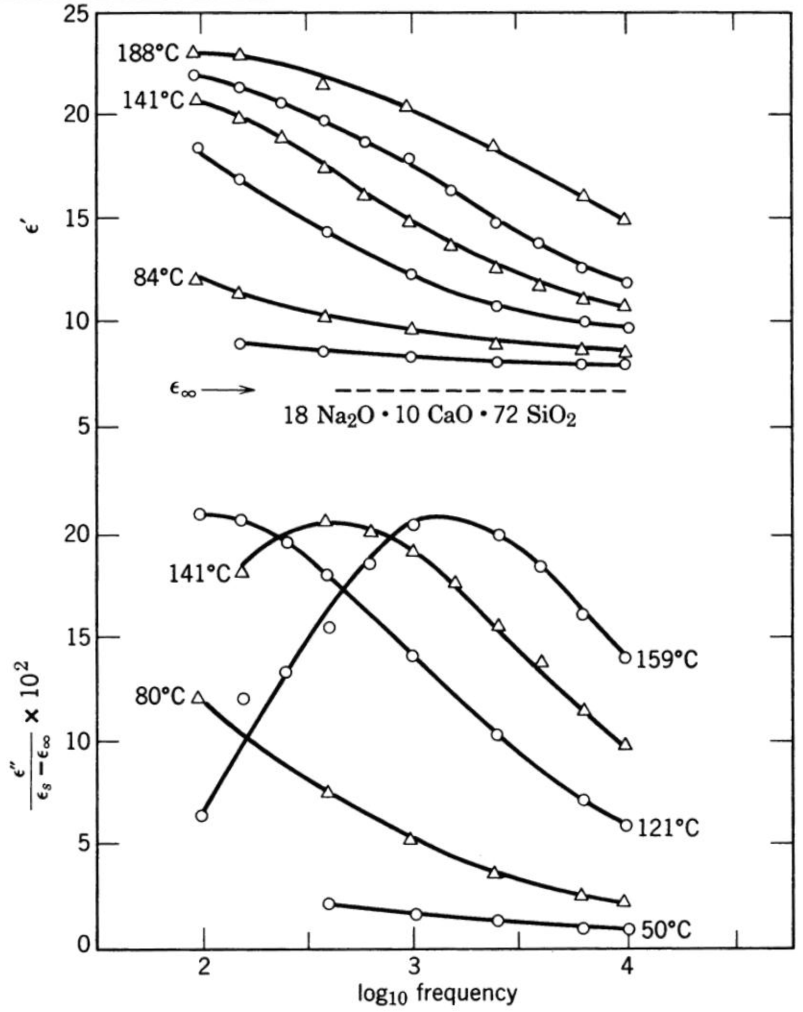


Fig. 18.18. Dielectric dispersion and absorption curves, corrected for dc conductivity, for a typical soda-lime-silicate glass. From H. E. Taylor, *J. Soc. Glass Technol.*, **43**, 124 (1959).

Electrode polarization vs. dipolar relaxation

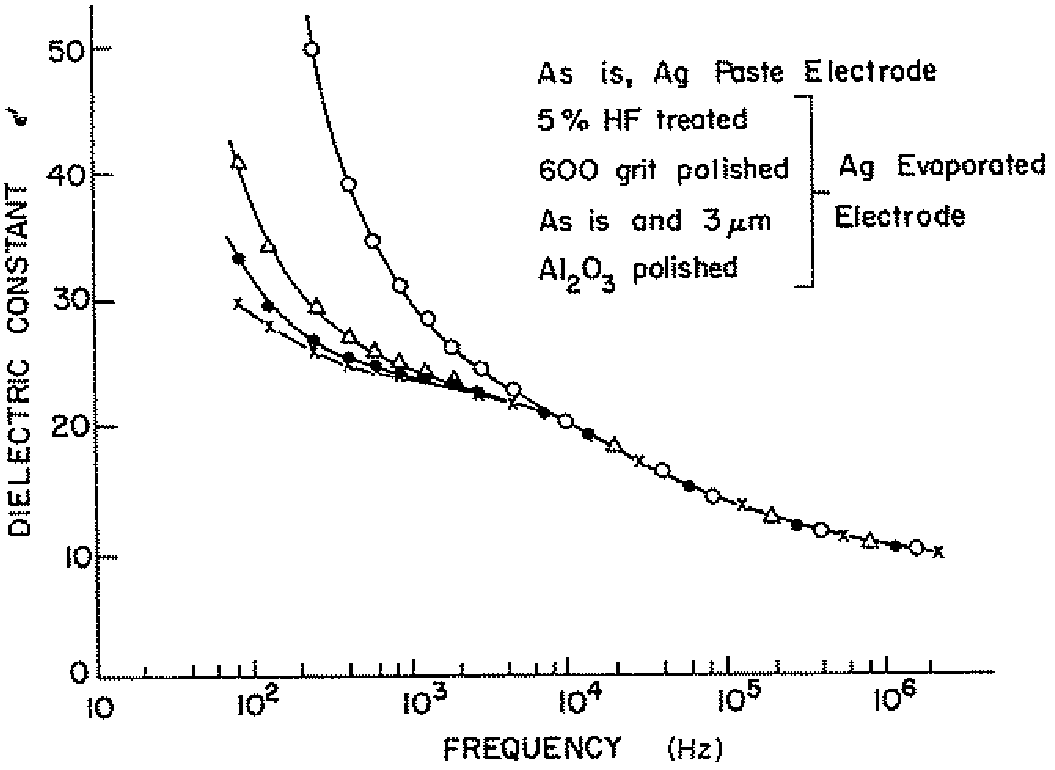


Fig. 9. Dielectric constant of soda–lime glass with various surface conditions; Ag electrodes at 247 ± 1°C. (After Kim and Tomozawa, 1976a.)

The step in ε' persists even with reversible electrodes. Its small magnitude indicates another bulk relaxation process, not interfacial polarization.

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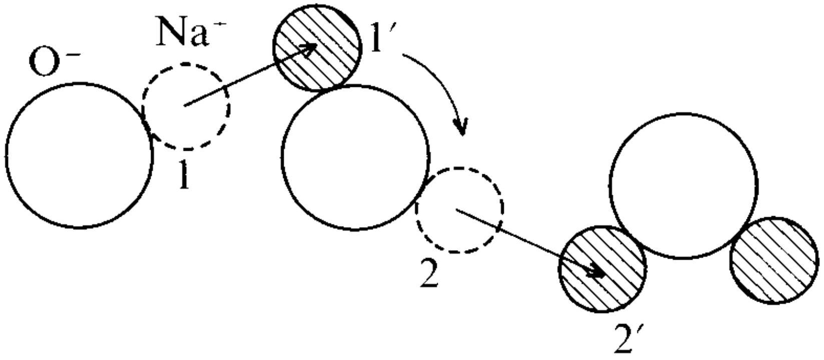
Barton-Nakajima-Namikawa (BNN) relation

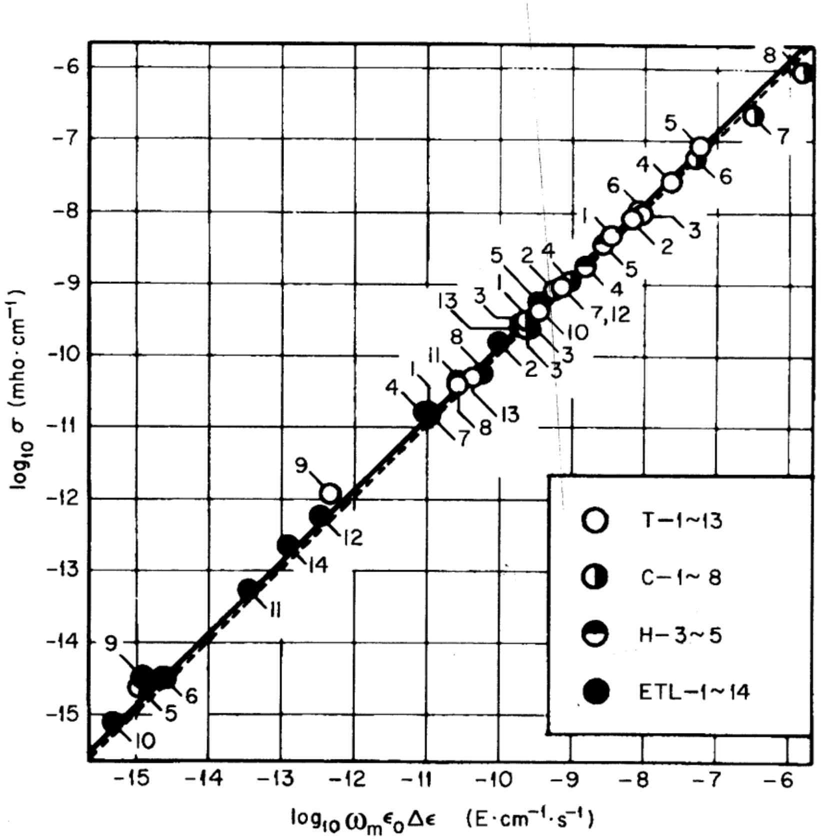
$$\sigma_{dc} = p\varepsilon_0\Delta\varepsilon\omega_m$$

where p is a constant ~ 1. $\Delta\varepsilon$ is the step in ε' across the peak, ω_m is freq of ε" maximum.

$$\omega_m = 1/\tau = \tau_0^{-1}\exp[-\Delta E_m/RT]$$

Dc conductivity and ε" maximum have same activation energy⇒ common origin.





Correlation between conductivity and dielectric relaxation. ○ = Taylor (1957,
9); ◑ = Charles (1962; 1963); ◒ Heroux (1958); ● = measured at Electrotechnical Labo-
ory, MITI, Japan. (After Nakajima, 1972.)

re 15-8. Confirmation of the BNN relationship. The symbols T, C, H,
ETL correspond to measurements at four different laboratories cited by Tomozawa[11].

Summary, thus far …

Ion conducting glasses show evidence of dipolar relaxation, which is closely related to alkali diffusion.

Its presence suggests ‘quasi-free’ ion hopping that produces low frequency electrical relaxation in glass

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