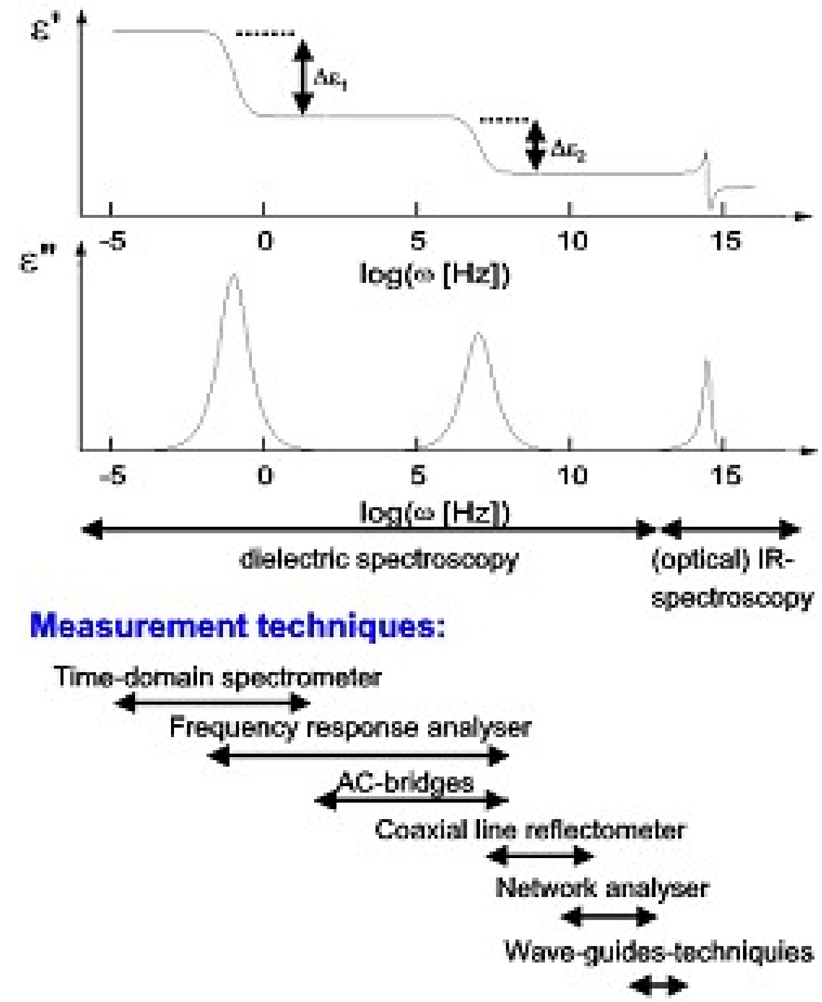
Introduction to Broadband Dielectric Spectroscopy BDS



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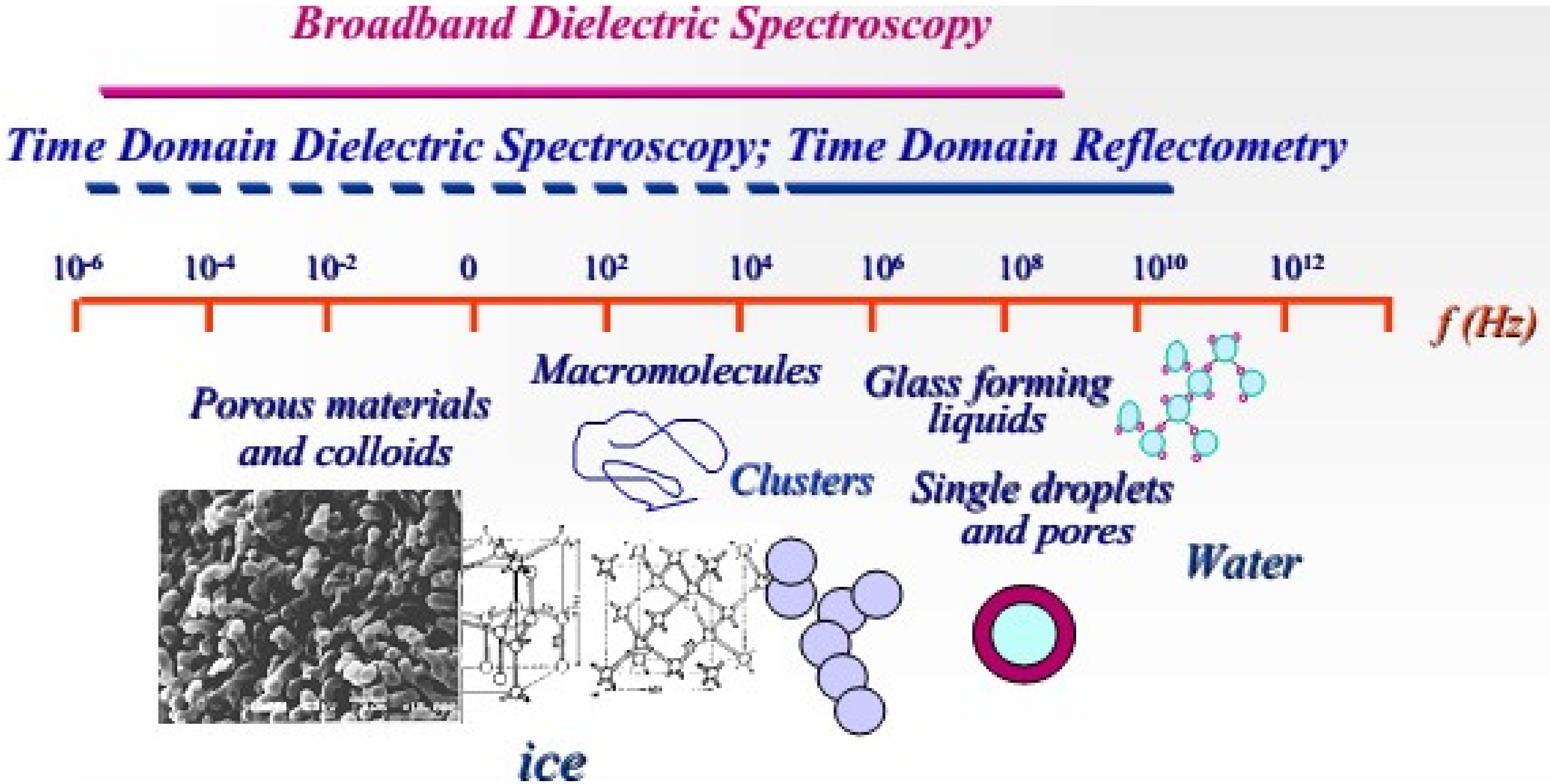
(http://http://scholar.uoa.gr/antpapa/home


Broadband Dielectric Spectroscopy
Time Domain Dielectric Spectroscopy; Time Domain Reflectometry
10-6
10-4
10-2
0
10²
10⁴
10⁶
10⁸
10¹⁰
10¹²
f (Hz)
Porous materials and colloids
Macromolecules
Clusters
Glass forming liquids
Single droplets and pores
Water
ice

THE MATTER IN STATIC ELECTRIC FIELDS

Polarization $\vec{P} = \frac{1}{V}\sum \vec{p}_i = \int_V \vec{r}\rho(\vec{r})dV$

If ρ_{FREE} *polarize the dipoles:* Displacement $\vec{D} \equiv \varepsilon_0 \vec{E} + \vec{P}$

(related with electric flux (Gauss law))

$\vec{E} = -\text{grad}U$ related with force on charges

Linear response: $\vec{P} = \varepsilon_0 \chi \vec{E}$ → $D = \varepsilon_0 (1+\chi)\vec{E} = \varepsilon_s \vec{E}$

Susceptibility

Dielectric constant (tensor)

$$\varepsilon_s = \varepsilon_0 (1+\chi)$$

Correlation of macroscopic to molecular properties

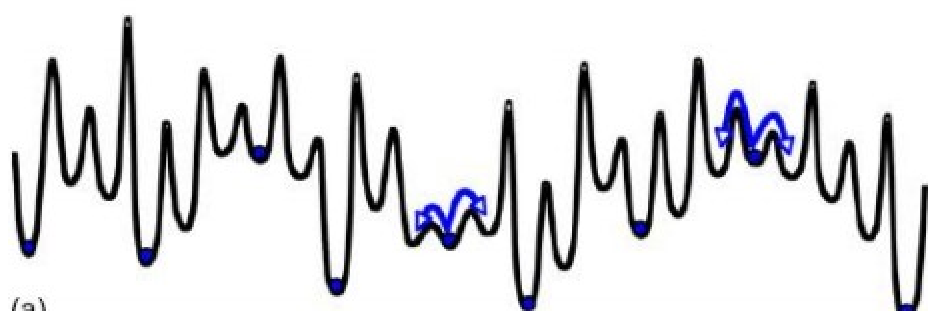
Induced polarization:

$$\left.\begin{array}{r}\vec{P} = N\vec{p} = N\alpha\vec{E}_{LOCAL} \\ \vec{P} = \varepsilon_0\chi\vec{E} \\ \varepsilon_s = \varepsilon_0(1+\chi)\end{array}\right\} \quad \varepsilon_s - 1 = \frac{N\alpha E_{LOCAL}}{\varepsilon_0 E}$$

Polarizabilities

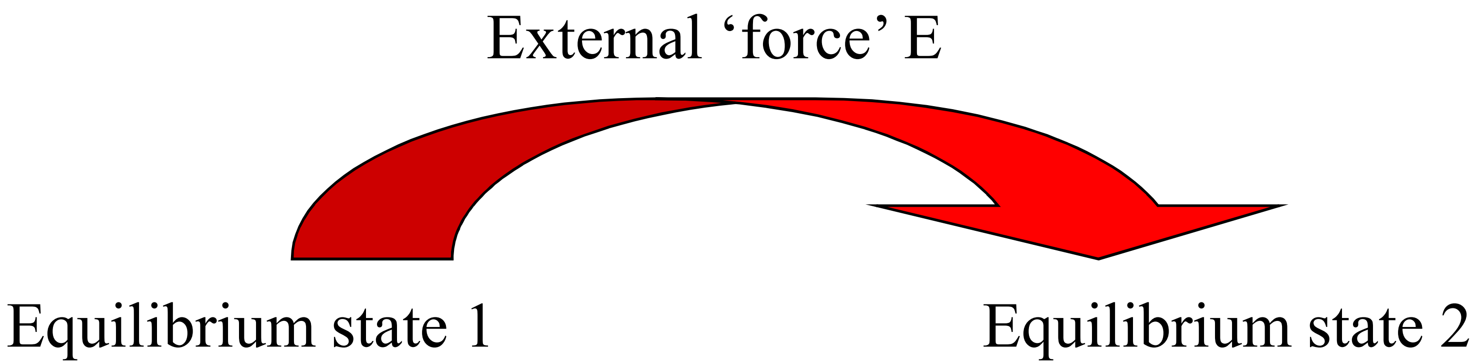
Electronic
Atomic
Permanent electric dipole rotation
Spatial localization of 'free' charges {*Space charge*, *Interfacial*, *Disorder induced localization*}

Electrode polarization:
Experimental and Computational suppression



(a)

Dielectric relaxation

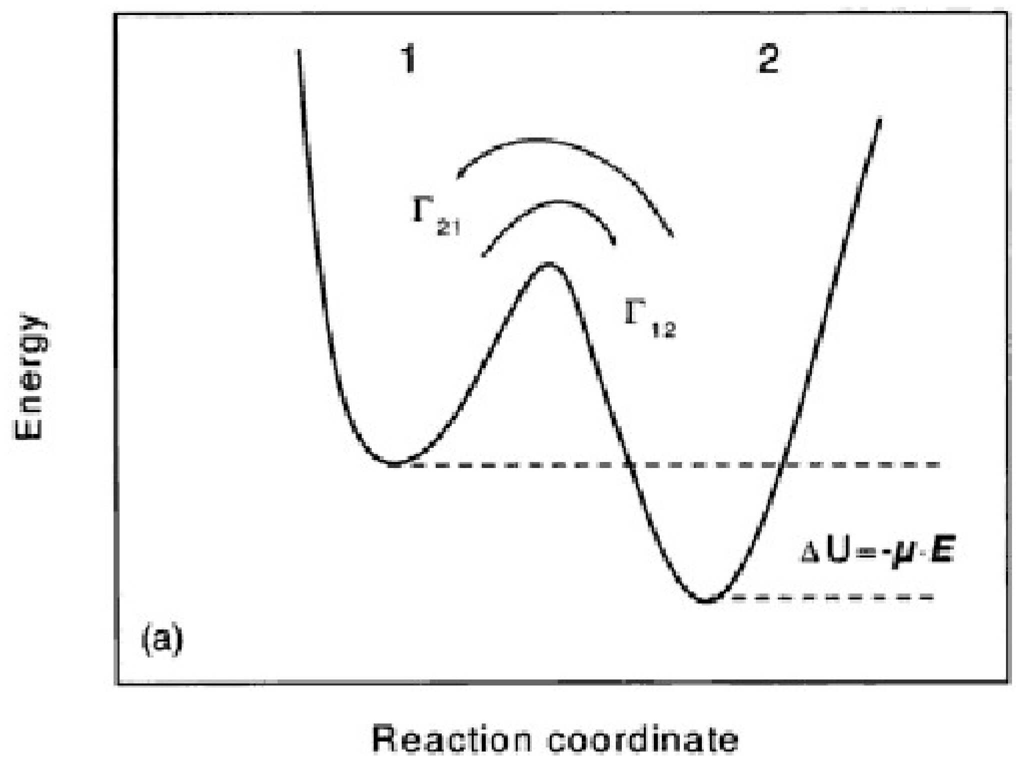


Correlation between spatial and temporal scales

$$f \propto 1/\tau \qquad\qquad L \approx \langle \upsilon \rangle \tau$$

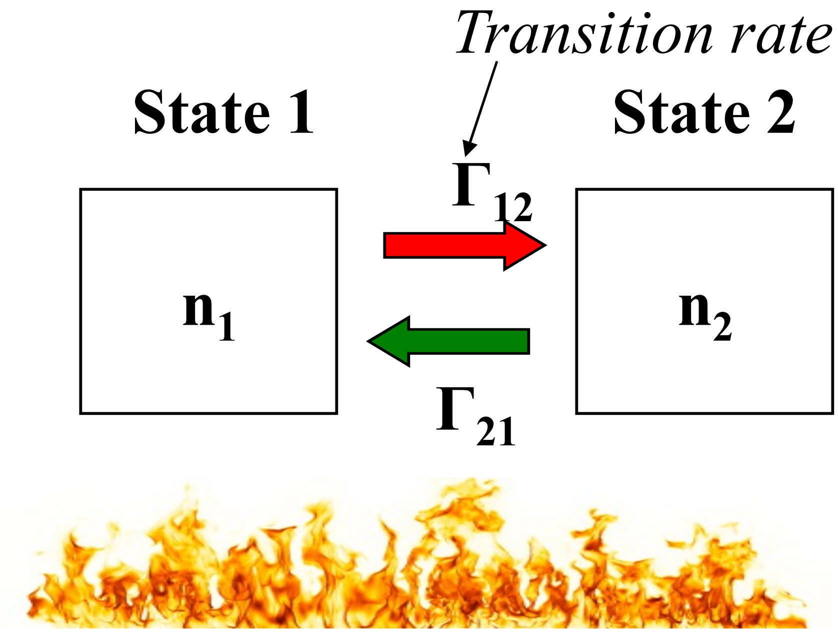
Linear Response Theory (LRT):
Response proportional to perturbation

Extraction of Debye equations from microscopic principles

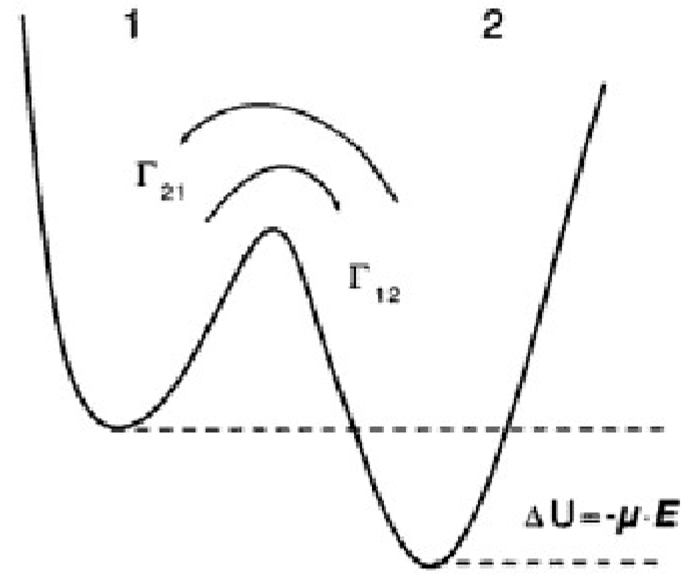


$Work = bF\cos\theta$
$= beE\cos\theta$

Electric field modifies the potential, **but** too weak to push charges
$\Delta G \gg kT$
Fluctuations / thermal vibrations are needed.



Thermal fluctuatioons



Perturbation

symmetrical potential ($\Gamma_{12} = \Gamma_{21} = \Gamma$, $n_1 = n_2 = 1/2$)

$\Gamma_{12} \neq \Gamma_{21}$ and $n_1 \neq n_2$

Work=bFcosθ=beEcosθ

$$n_2 = n_1 \exp\left[-\frac{2\Delta U}{k_B T}\right]$$

$$\boldsymbol{P} = \boldsymbol{\mu}(n_1 - n_2)$$

$n_1 \sim \exp\{(-\Delta G - \Delta U)/kT\}$

$n_2 \sim \exp\{(-\Delta G + \Delta U)/kT\}$

Switch off E, at t=0

Γ

$$dn_1/dt = -n_1\Gamma + n_2\Gamma$$

$$P = \mu(n_1 - n_2)$$

$$\frac{dP}{dt} = \mu\left[\frac{dn_1}{dt} - \frac{dn_2}{dt}\right] = -2\mu\,\Gamma[n_1 - n_2] = -2\Gamma P(t)$$

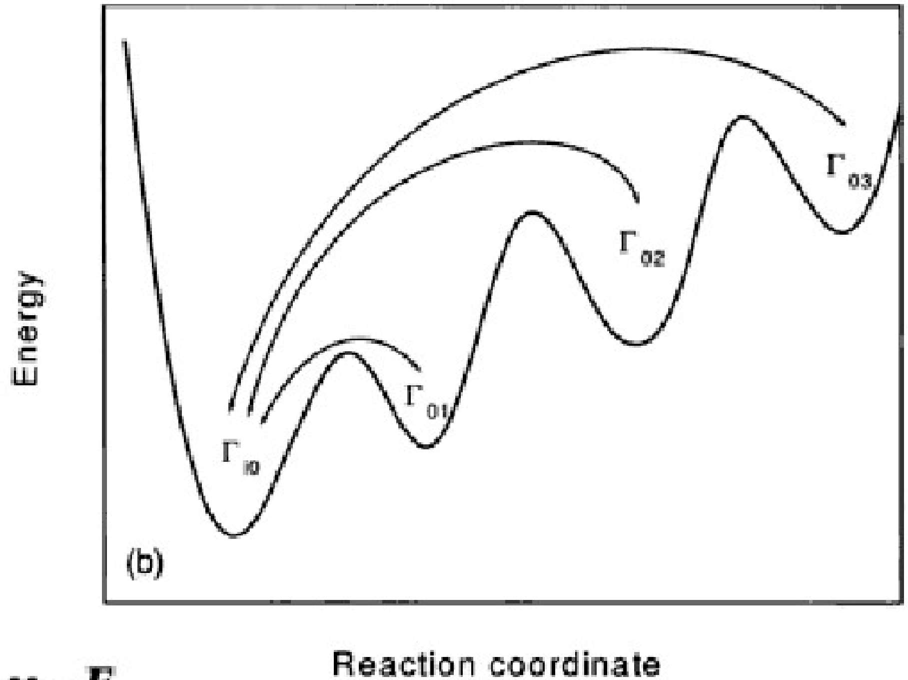
$$dn_1/dt = -\,dn_2/dt$$

(Debye equation)

$$\dot{P}(t) = -\frac{P_{\infty} - P(t)}{\tau_{\varepsilon}}$$

$$\tau_{\varepsilon} = 1/2\Gamma$$

Assymetric potential minima



$$w_i = \frac{\exp\left(-\frac{U_i}{k_B T}\right)}{\sum_{i=k}^{3} \exp\left(-\frac{U_k}{k_B T}\right)} \quad i = 0, 1, 2, 3$$

$$\boldsymbol{\mu}_{i0} = \boldsymbol{\mu}_i - \boldsymbol{\mu}_0$$

$$w_{iE} = \frac{\exp\left(-\left[\frac{U_i - \boldsymbol{\mu}_{i0} \boldsymbol{E}}{k_B T}\right]\right)}{\sum_{i=k}^{3} \exp\left(-\left[\frac{U_k - \boldsymbol{\mu}_{k0} \boldsymbol{E}}{k_B T}\right]\right)} = w_i \frac{1 + \frac{\boldsymbol{\mu}_{i0} \boldsymbol{E}}{k_B T}}{1 + \sum_{k=0}^{3} w_k \frac{\boldsymbol{\mu}_{k0} \boldsymbol{E}}{k_B T}}$$

$$\boldsymbol{\mu}_{i0} \boldsymbol{E} / k_B T \ll 1$$

$$\mathrm{d}n_0/\mathrm{d}t + n_0(\Gamma_{01} + \Gamma_{02} + \Gamma_{03}) - n_1 \Gamma_{10} - n_2 \Gamma_{20} - n_3 \Gamma_{30} = 0$$

$$-n_0 \Gamma_{0j} + \mathrm{d}n_j/\mathrm{d}t + n_j \Gamma_{j0} = 0 \quad j = 1, 2, 3$$

$$\Gamma_{i,0} = \Gamma_{i,\infty} \exp\left(-\frac{\Delta U_i}{k_B T}\right), \; \Gamma_{0,i} = \Gamma_{i,\infty} \exp\left(-\frac{\Delta U_i + U_i}{k_B T}\right)$$

Distributed relaxation time model

$$\int_0^\infty g(\tau)d\tau = 1$$

$$\varepsilon^*(\omega) = \int_0^\infty \varepsilon^*_{DEBYE}(\omega)g(\tau)d\tau$$

Correlations: The stretched exponential KWW model

Relaxation: $P(t)=F(t)E_o$

Debye system; $\dot{P}(t) = -\frac{P_\infty - P(t)}{\tau_\varepsilon}$

Single relax. time model: $dF(t)/dt= - wF(t)$

Identical, with $\tau_\varepsilon=w^{-1}$

$$F(t) = \exp\left[-\left(\frac{t}{\tau_\varepsilon}\right)\right]$$

Real system;

$$F(t) = \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{NWW}}\right] \quad 0 < \beta_{KWW} \le 1$$

Kohlrausch-Williams-Watts (KWW)

$$\varepsilon(t) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \times \left[1 - \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right]\right]$$

$$\tau_M \approx \tau_\varepsilon \times \left(\frac{\varepsilon_\infty}{\varepsilon_s}\right)^{\frac{1}{\beta}}$$

Cole-Cole (CC)

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{1}{1 + (i\omega\tau)^\alpha}$$

$$\tau_M = \tau_\varepsilon \times \left(\frac{\varepsilon_\infty}{\varepsilon_s}\right)^{\frac{1}{\alpha}}$$

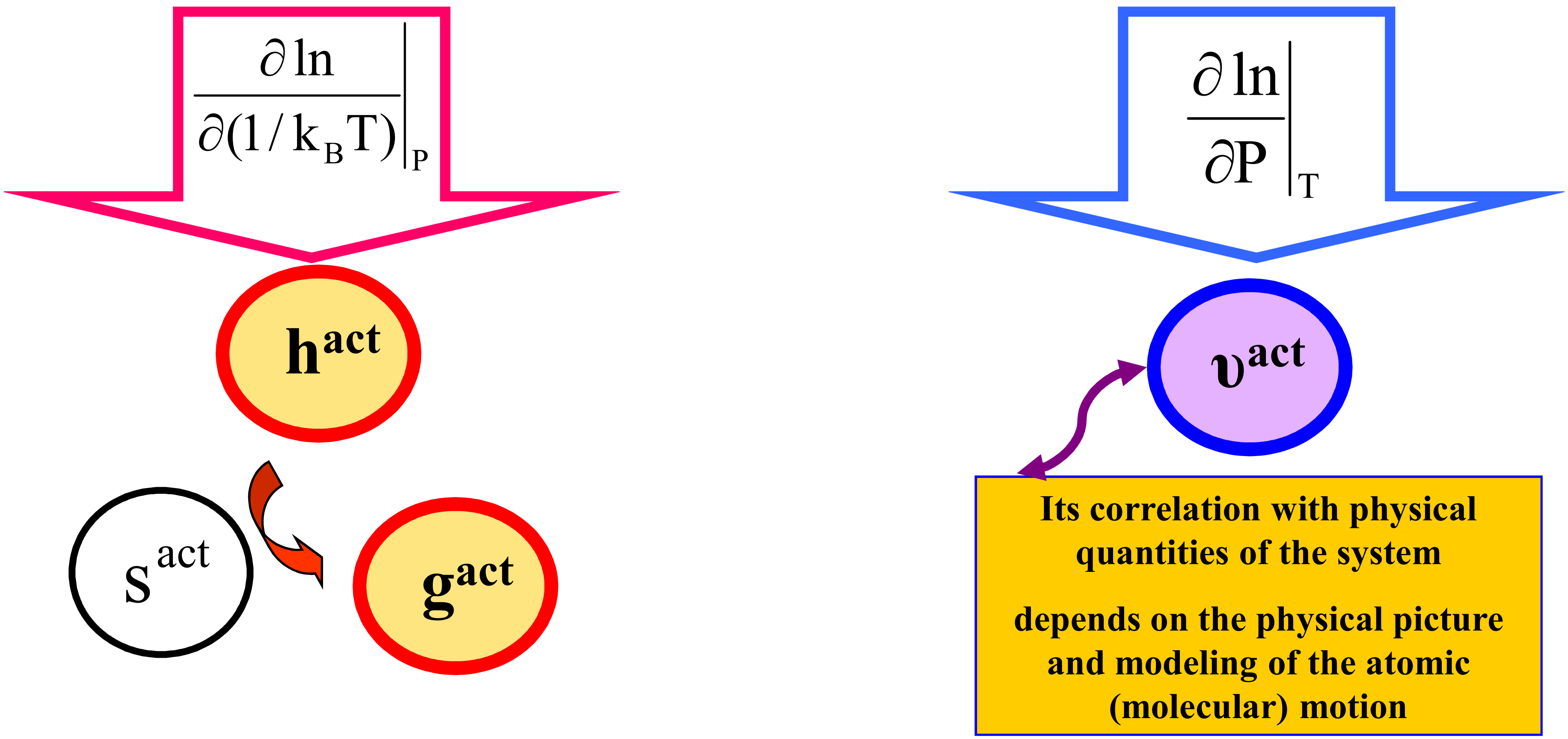
Cole-Davidson (CD)

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{1}{[1 + i\omega\tau]^\gamma}$$

$$\tau_M \approx \tau_\varepsilon \times \left(\frac{\varepsilon_\infty}{\varepsilon_s}\right)^{\frac{1}{\gamma}}$$

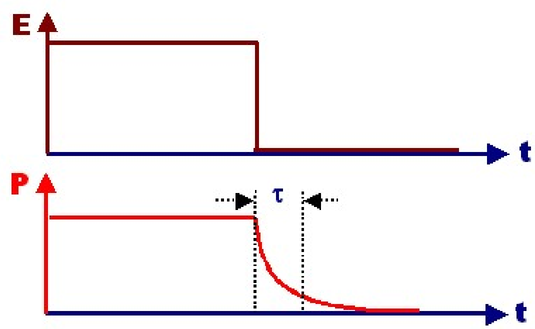
Dielectric relaxation time

Time-scale for molecular motion (molecular dynamics) or spatially localized electric charge flow.



Dielectric Functions

Relaxation function F(t) | Response function f(t) | Susceptibility $\chi^*(\omega)$



δ-function 'force'

$$\vec{P}(\omega) = \chi^*(\omega)\ \vec{E}(\omega)$$

Time-domain experiments | *Frequency domain*

$$f(t) = -\frac{dF(t)}{dt} \propto J(t)$$

$$\chi^*(\omega) = \int_0^\infty e^{-i\omega t} f(t)\, dt = L_{i\omega}\left[f(t)\right]$$

$$\vec{E}^* = E_o \exp(i\omega t)$$

$$\vec{D}^* = D_o \exp[i(\omega t - \delta_\varepsilon)]$$

$$\vec{D}^*(t) = \varepsilon^*(\omega)\ \vec{E}^*(t)$$

$\omega = 2\pi f$

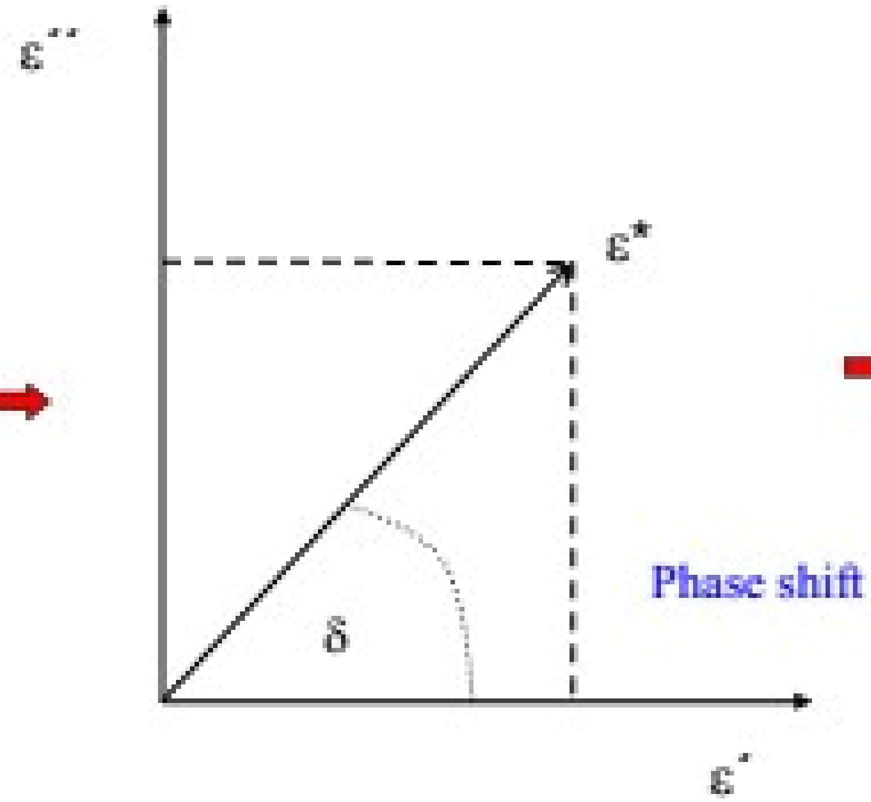
A Special Case of Linear Response Theory

Complex Compliance $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\,\varepsilon''(\omega)$

Real Part — Related to the energy stored reversibly during one cycle

Imaginary or Loss Part — Related to the energy dissipated during one cycle

Complex Plane



$$\tan\delta = \frac{\varepsilon''}{\varepsilon'}$$

Real Part → Related to the energy stored reversibly during one cycle

Loss Part → Related to the energy dissipated during one cycle

→ Law of energy conservation

↓

Relationship between both quantities

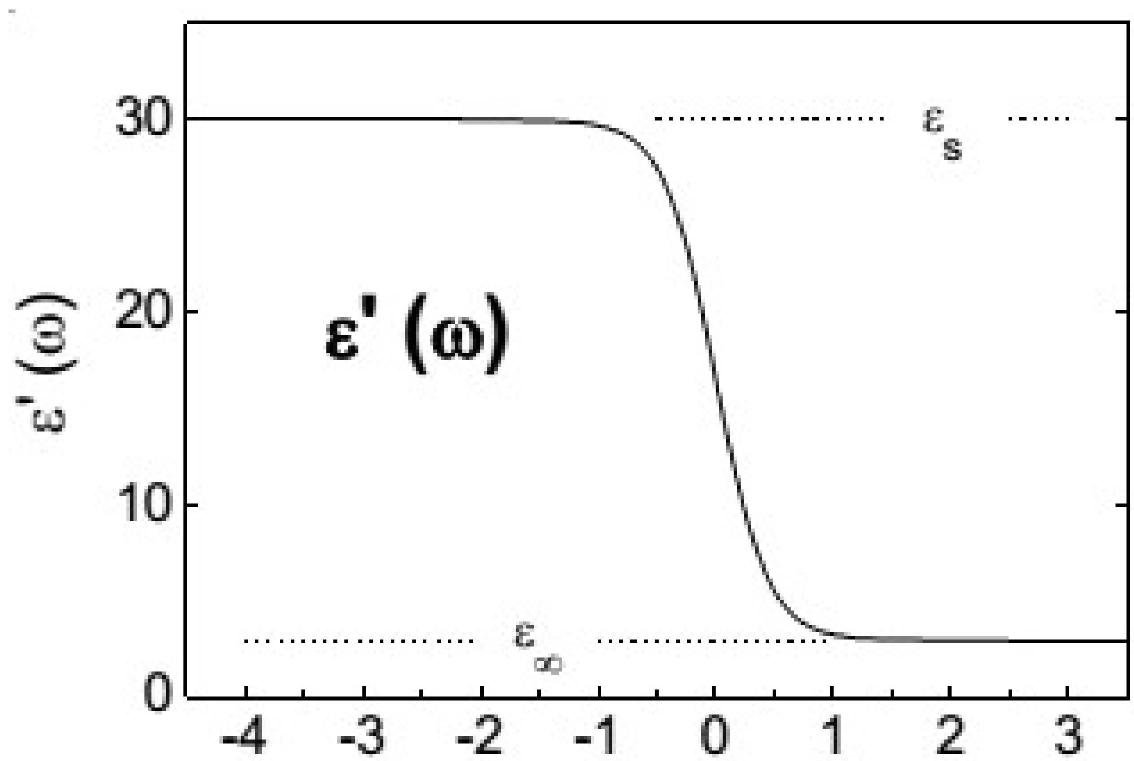
Kramers – Kronig Relationships

$$\varepsilon'(\omega) - \varepsilon_{\infty} = \frac{1}{\pi} \oint \frac{\varepsilon''(\xi)}{\xi - \omega} d\xi$$

$$\varepsilon''(\omega) = \frac{1}{\pi} \oint \frac{\varepsilon'(\xi) - \varepsilon_{\infty}}{\xi - \omega} d\xi$$

$$\varepsilon_r = \varepsilon(\omega \to 0) \approx \varepsilon_s$$

$$\varepsilon_u = \varepsilon(\omega \to \infty) \approx \varepsilon_\infty$$



Phenomenological Theory

$$\varepsilon_r = \varepsilon(\omega \to 0) \approx \varepsilon_s$$

$$\varepsilon_u = \varepsilon(\omega \to \infty) \approx \varepsilon_\infty$$

Polarization term

$$D(t) = \varepsilon_u E_o + \underbrace{(\varepsilon_r - \varepsilon_u)\,\Psi(t)\ \ E_o}_{\text{Polarization term}}$$

Superposition principle:

$$D(t) = \varepsilon_u E(t) + (\varepsilon_r - \varepsilon_u) \int_{-\infty}^{t} E(s) \boxed{\dot{\Psi}(t-s)}\, ds$$

Dielectric decay function

$$\dot{\Psi}(t) = (1/\tau\varepsilon)\ \exp\,(-\,t\,/\tau\varepsilon)$$

$\Psi\Psi(t) = ?$

$(t) = ?$

Single relaxation time model (Debye)

$P_\infty = (\varepsilon_r - \varepsilon_u)\, E_o$

$$\dot{P}(t) = -\frac{P_\infty - P(t)}{\tau_\varepsilon}$$

Assumption: Single τ_ε

$\Psi(t) = 1 - \exp(-t/\tau_\varepsilon) \Rightarrow \dot{\Psi}(t) = (1/\tau_\varepsilon)\exp(-t/\tau_\varepsilon)$

Previous slide:

$$D(t) = \varepsilon_u E(t) + (\varepsilon_r - \varepsilon_u)\int_{-\infty}^{t} E(s)\,\dot{\Psi}(t-s)\,ds$$

d/dt

$$\tau_\varepsilon \frac{dD(t)}{dt} + D(t) = \tau_\varepsilon\, \varepsilon_u \frac{dE(t)}{dt} + \varepsilon_r E(t)$$

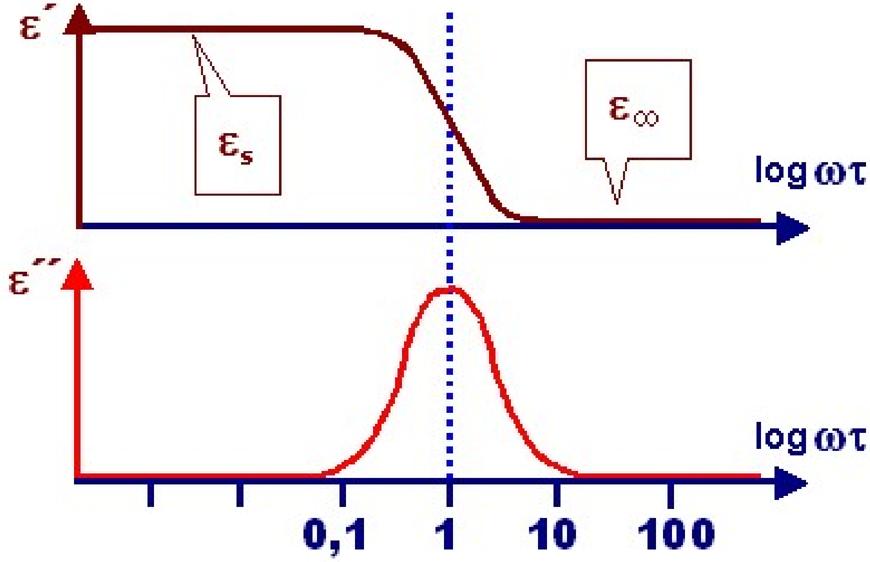
AC harmonic voltage:

$\vec{E}^* = E_o \exp(i\omega t)$

$\bar{D}^* = D_o \exp[i(\omega t - \delta_\varepsilon)]$

$$\varepsilon^*(\omega) = \varepsilon_u + \frac{(\varepsilon_r - \varepsilon_u)}{1 + i\omega\tau_\varepsilon} \Longleftrightarrow \frac{\varepsilon^*(\omega) - \varepsilon_u}{(\varepsilon_r - \varepsilon_u)} = \frac{1}{1 + i\omega\tau_\varepsilon}$$

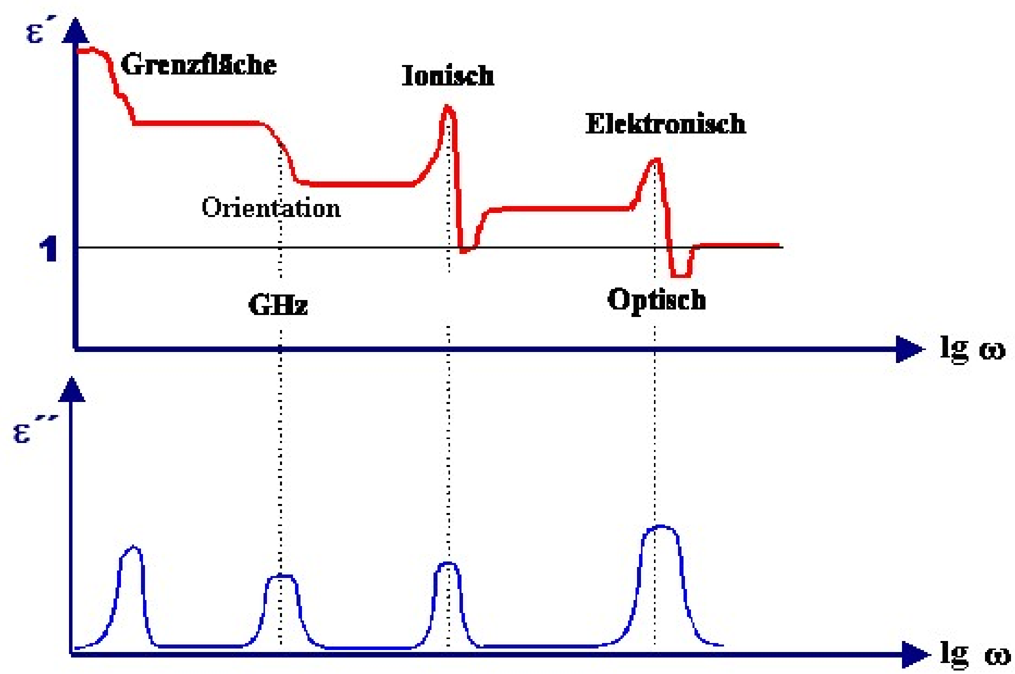
$$\begin{cases} \varepsilon'(\omega) = \varepsilon_u + \dfrac{(\varepsilon_r - \varepsilon_u)}{1 + \omega^2\tau_\varepsilon^2} \\ \varepsilon''(\omega) = (\varepsilon_r - \varepsilon_u)\dfrac{\omega\tau_\varepsilon}{1 + \omega^2\tau_\varepsilon^2} \end{cases}$$



$$\tau_\varepsilon = \frac{1}{\omega_{max}}$$

$$\varepsilon''(\omega_{max}) = \frac{\varepsilon_r - \varepsilon_u}{2}$$

$$\varepsilon'(\omega_{max}) = \frac{\varepsilon_r + \varepsilon_u}{2}$$



DC conductivity traced by BDS

Empty (parallel) capacitor $Q = C_0 V = C_0 V_0 \exp(j\omega t)$ (Q, V in phase)

⇒ $I = \frac{dQ}{dt} = j\omega C V$ out of phase to V(ω) (no losses)

Capacitor with material of DC conductivity σ_{DC}

I=GV in phase with V

Conductance $G=\sigma_{DC} A/L$

$I = (j\omega C + G)V$

$C=\varepsilon_o\, \varepsilon\, A/L$

$J = (j\omega\varepsilon_0\varepsilon + \sigma_{DC})E$

⇕

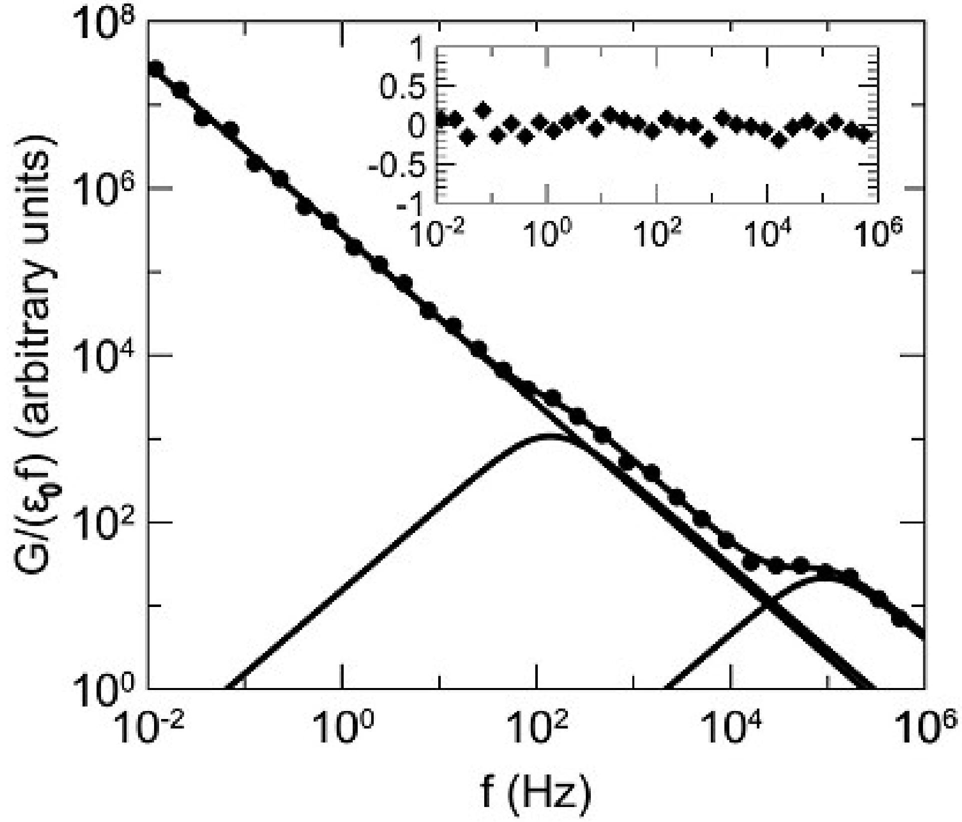
$J = (j\omega\varepsilon_0\varepsilon^*)E$

$\varepsilon^*(\omega)=\varepsilon' - j\varepsilon''$

$$\varepsilon''(\omega) = \frac{\sigma_{DC}}{\varepsilon_0\omega}$$

Straight line with slope –1 in a log-log plot

$$\varepsilon''(\omega) = \left(\varepsilon_r - \varepsilon_u\right)\frac{\omega\tau}{1+\omega^2\tau^2} + \frac{\sigma_{DC}}{\varepsilon_0\omega}$$



A.N.Papathanassiou et al APL (2013)

$$\sigma^*(\omega) = \sigma_0 + j\varepsilon_0\varepsilon^*(\omega)$$

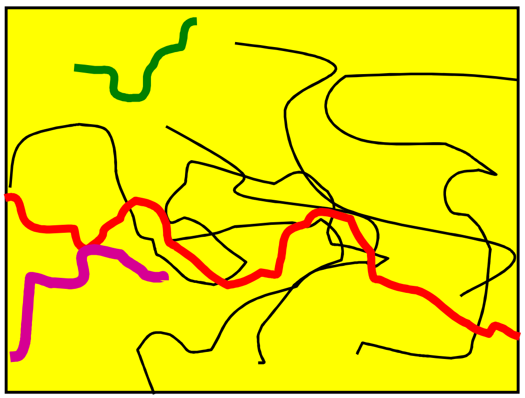
$$\sigma^*(\omega) = \sigma'(\omega) - j\sigma''(\omega)$$

$$\sigma'(\omega) = \sigma_0 + j\varepsilon_0\omega\chi''(\omega)$$

$$\sigma''(\omega) = \varepsilon_0\omega[1 + x'(\omega)]$$

Localizec electric charge flow in disordered material: 'free' charges in non-polar dielectrics

A.N. Papathanassiou, I. Sakellis and J. Grammatikakis
Universal frequency-dependent ac conductivity of conducting polymer networks
Appl. Phys. Lett. 91, 122911 (2007)



$$G(\omega) = G_{dc} + \sum_{L_k \geq L_c} G_k (L_k)$$

$$L_c = \upsilon/\omega_c$$

$$G_k \propto L_k^{-1}$$

Distribution in lengths f(logL)

$$G(\omega) = G_{dc} + \alpha \int_{L_{min}}^{L} L^{-1} f(\log L) dL = G_{dc} + \alpha \int_{\log L_{min}}^{\log L} \log f(\log L) d(\log L)$$

Generalization:

Chains → Pathways of various lengths accesible to transporting charges

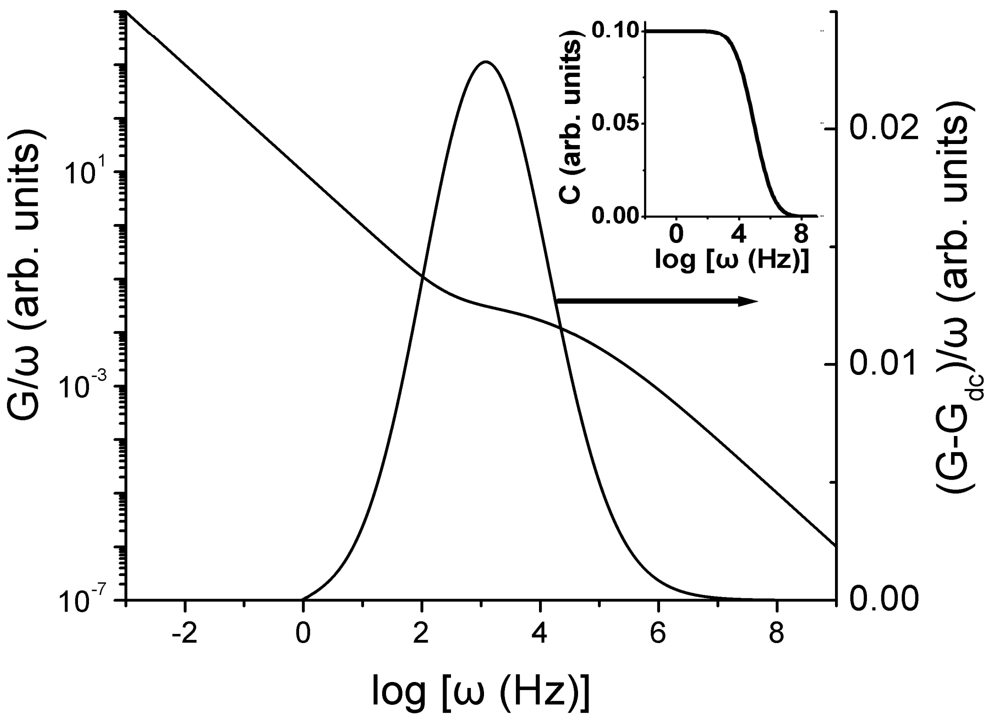
Normal distribution of log-L's

$$f(\log L) = \frac{1}{\sqrt{2\pi}\sigma}\exp\left(-(\log L - \log L_0)^2/(2\sigma^2)\right)$$

$\upsilon = L\omega$

$$G(\omega) = G_{dc} + A\int_0^{\omega}\frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(\log\omega - \log\omega_0)^2}{2\sigma^2}\right)d\omega$$

$$C(\omega) = C_0\int_{\omega}^{\infty}\frac{1}{\sqrt{2\pi}\sigma}\exp\left(-\frac{(\log\omega - \log\omega_0)^2}{2\sigma^2}\right)d\omega$$



ELECTRIC (or DIELECTRIC MODULUS M*(ω)

$$M^*(\omega) = 1/\varepsilon^*(\omega)$$

$$M'(\omega) = \frac{\varepsilon'(\omega)}{[\varepsilon'(\omega)]^2 + [\varepsilon''(\omega)]^2}$$

$$M''(\omega) = \frac{\varepsilon''(\omega)}{[\varepsilon'(\omega)]^2 + [\varepsilon''(\omega)]^2}$$

$$M^*(\omega) = M_s \frac{i\omega\tau_\sigma}{1 + i\omega\tau_\sigma} = M_s \frac{(\omega\tau_\sigma)^2}{1 + (\omega\tau_\sigma)^2} + iM_s \frac{\omega\tau_\sigma}{1 + (\omega\tau_\sigma)^2}$$

$$M_s = 1/\varepsilon_s \qquad \tau_\sigma = \varepsilon_\infty / \sigma_0$$

$$M'(\omega) = M_s \frac{(\omega\tau_\sigma)^2}{1 + (\omega\tau_\sigma)^2}$$

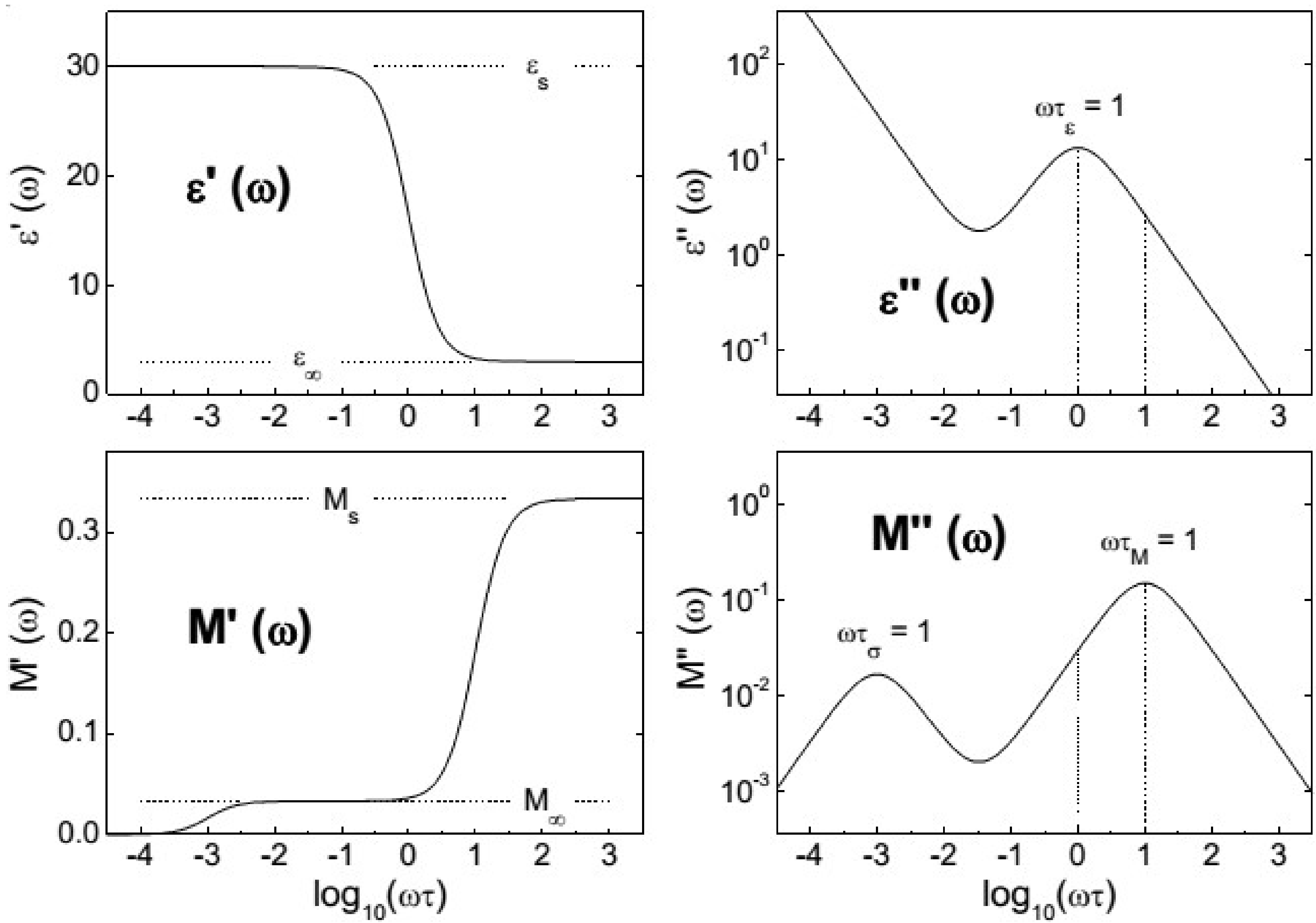
$$f_{0,\sigma} = \sigma_0 / (2\pi\varepsilon_\infty)$$

$$M''(\omega) = M_s \frac{\omega\tau_\sigma}{1 + (\omega\tau_\sigma)^2}$$

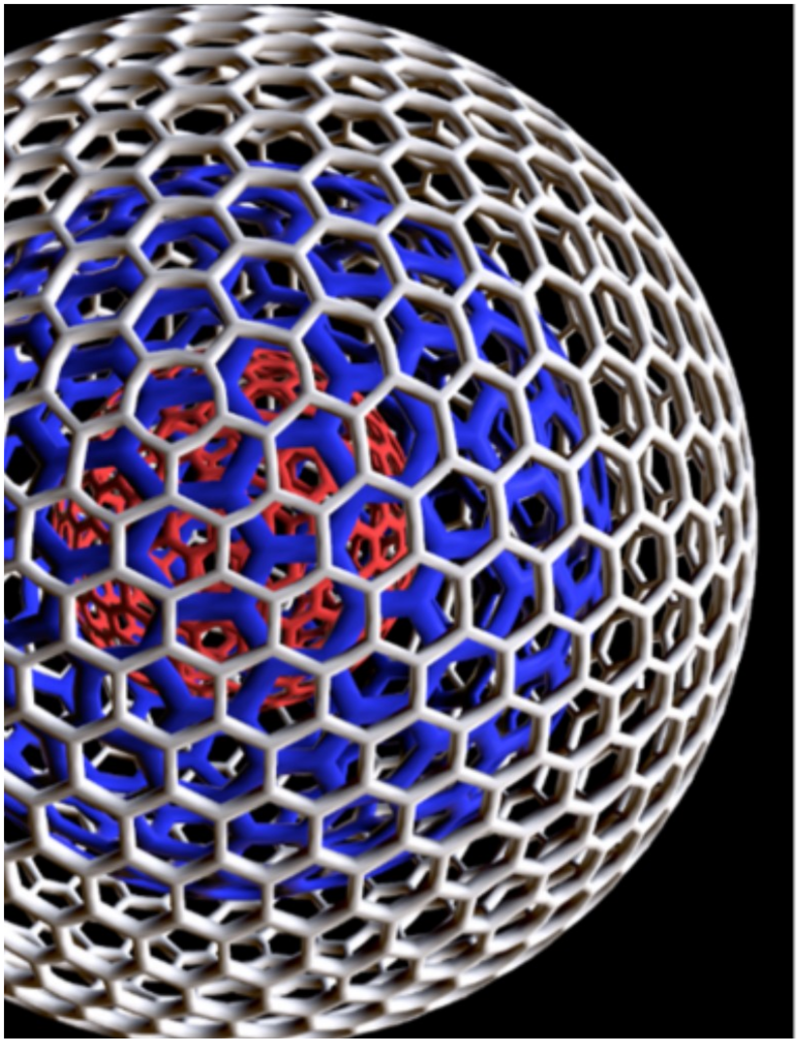
If the dc conductivity mechanism co-exists with a dielectric relaxation mechanism

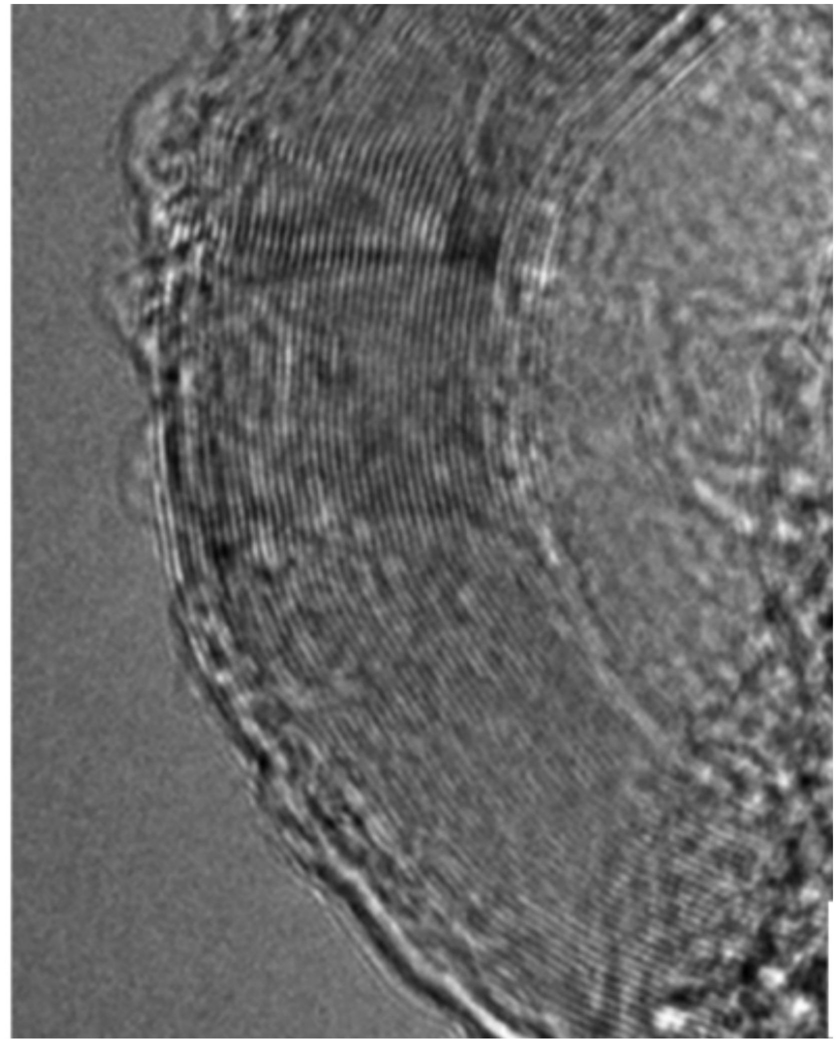
$$M^*(\omega) = M_s \frac{i\omega\tau_\sigma}{1+i\omega\tau_\sigma} + \left(M_\infty - M_s\right)\frac{i\omega\tau_d}{1+i\omega\tau_d}$$

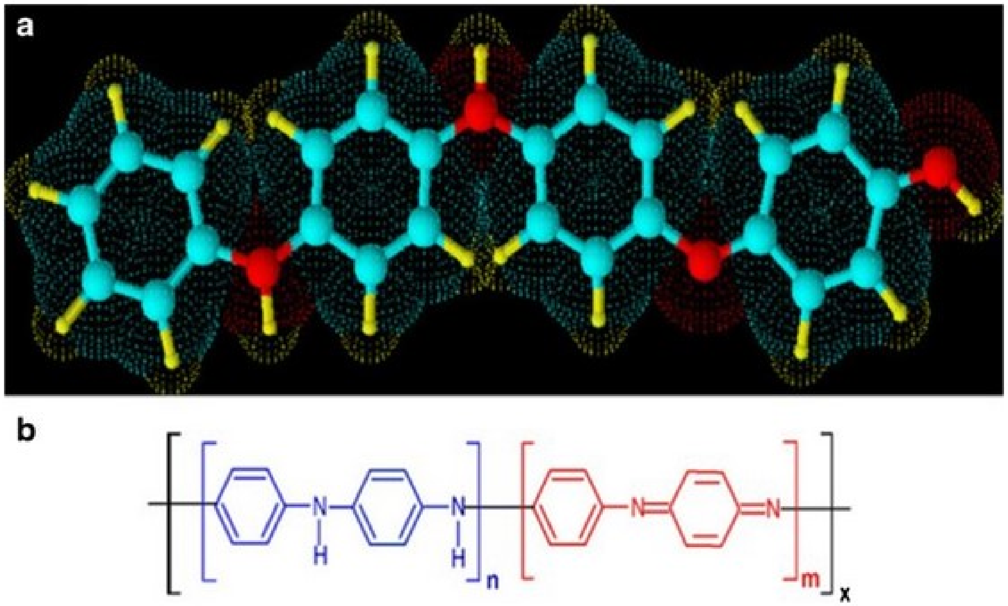
$$\tau_d=(M_s/M_\infty)\tau_\varepsilon.$$



Application:
Polynanile: Carbon Nano-Onions (PANI/CNO composites)







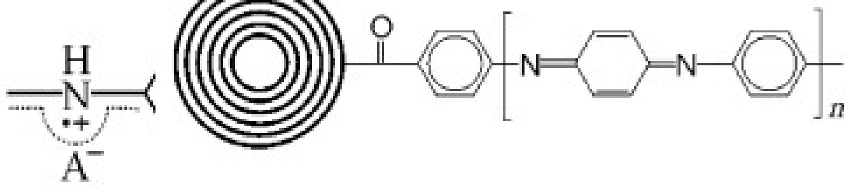
Figure

Caption

a 3D structure of polyaniline. The carbon atoms (cyan balls), nitrogen atoms (red balls), hydrogen atoms (small yellow balls), and clouds (molecular orbitals). (b) Polyaniline 2D structure. Reprinted with the permission from Dhand et al. 2011 [18]

Reversible dopping:

Oxidatuion by HCL → H+ (polarons)



CNOs/4-ABAc/PANI (5)

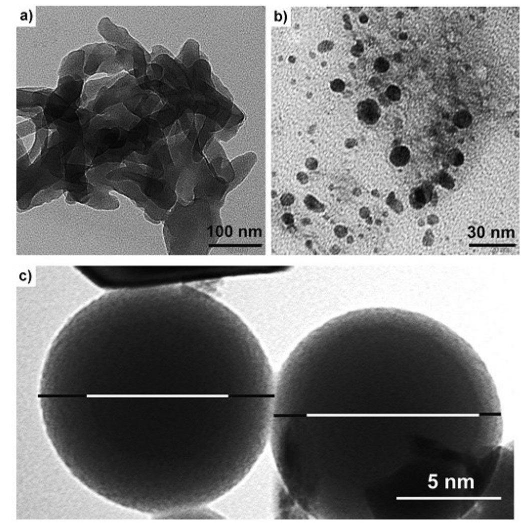


Figure 1. TEM images of a) ox-CNOs/poly-*p*-PDA/PANI and b,c) CNOs/4-ABAc/PANI.

Dielectric relaxation peak:
α=inverse localization length (1/radius of H^+ wave-function)
R=typical dimension of the regieon wherein trapped H^+ relax

Transition Rate Theory: $\tau = \nu_{ph}^{-1} \exp(2\alpha R)\ \exp(E/kT)$

Linear fit to $lnf_o(1/kT)$ data points: $f_0 = C \exp(-E/kT)$

$$\tau \equiv f_0^{-1}$$

$$R = (2\alpha)^{-1} \ln(\nu_{ph}/C)$$

$$\alpha^{-1} = 6.9\,\overset{o}{A}$$

$$\nu_{ph} \sim 10 - 40\,THz$$