The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

SMR/1856-10

2007 Summer College on Plasma Physics

30 July - 24 August, 2007

Dielectric relaxation and ac universality in materials with disordered structure.

J. Juul Rasmussen

Risø National Laboratory
Technical University of Denmark
Roskilde, Denmark.

New Trends in Nonlinear Physics, ASICTP, August 19 2007.

Dielectric relaxation and ac universality in materials with disordered structure

J. Juul Rasmussen[1], A.V. Milovanov[2], and K. Rypdal[2]

1. Risø National Laboratory, Technical University of Denmark, OPL-128, DK-4000 Roskilde, Denmark.
2. Department of Physics and Technology, University of Tromsø, N-9037 Tromsø, Norway

A rich variety of materials with structural disorder reveal a dielectric relaxation that is not described by the standard exponential (i.e., Debye like) decay with a specific decay time. Rather the dielectric properties are described by a stretched exponential decay, $\varphi(t) = \exp\{-(t/\tau)^{\beta}\}$, the so-called Kohlrausch-Williams-Watts (KWW) relaxation function, with the exponent $0 < \beta \leq 1$. These materials additionally reveal universality in the dependence of the ac (alternating current) conductivity on frequency, expressed through $\sigma(\omega) \approx \omega^{\eta}$, where $0 < \eta \leq 1$. These results are mainly empirically; based on observations in various amorphous materials as polymers and glass like materials near the glass transition temperature. The physical origin and the statistical-mechanical foundation of these behaviors have been a matter of active research for the last decades; however, detailed understanding is still lacking.

Here we will discuss the properties of dielectric relaxation in disordered materials and the connection to the ac conduction properties. We demonstrate that the exponents β and η are connected through the relation: $\eta = 1-\beta$. The key issues are, the stretched exponential character of dielectric relaxation, a power-law power spectral density, and the anomalous dependence of ac conduction coefficient on frequency. We describe the KWW relaxation kinetically by applying the formulation in terms of fractional calculus, and we propose a systematic derivation of the fractional relaxation and fractional diffusion equations from the basic properties of the materials.

References:

A. V. Milovanov, K. Rypdal, and J. J. Rasmussen, Phys. Rev. B (2007) submitted for publication.

Dielectric relaxation and ac universality in materials with disordered structure

J. Juul Rasmussen,

Risø National Laboratory, Technical University of Denmark, OPL-128
DK-4000 Roskilde, Denmark

A.V. Milovanov and K. Rypdal

Department of Physics and Technology, University of Tromsø,
N-9037 Tromsø, Norway

jens.juul.rasmussen@risoe.dk

New Trends in Nonlinear Physics, August 19, 2007
Abdus Salam ICTP, Trieste, Italy

Outline

- Relaxation and ac conduction in materials with molecular or structural disorder
- Examples: amorphous materials, polymers, glass-like near the glass transition temperature
- Connection between the dielectric relaxation and the ac conduction properties
- Self-consistent dynamical relaxation model
- Derivation of fractional relaxation equation
- Conclusions

Milovanov *et al., Submitted for publ. 2007;* arXiv:0705.4417v1 [cond-mat.dis-nn]

Milovanov *et al., Submitted for publ. 2007;* arXiv:0707.3957v1 [physics.gen-ph]

Common dynamical properties

Many materials with a disordered structure have two important properties in common...

1. Non-exponential, non-Debye character of dielectric relaxation, often described by a stretched exponential Kohlrausch-Williams-Watts (KWW) decay function

$$\phi_\beta(t) = \exp[-(t/\tau)^\beta];\ 0 < \beta \leq 1;\ \tau = const.$$

2. Universality of ac (alternating-current) conduction, which, for a range of relatively high frequencies, is expressible in terms of a power-law dependence of the real part of conductivity on frequency

$$\sigma'(\omega) \propto \omega^\eta \qquad 0 \leq \eta < 1$$

Stretched exponetial relaxation, KWW

Kohlrausch-Williams-Watts (KWW) decay function

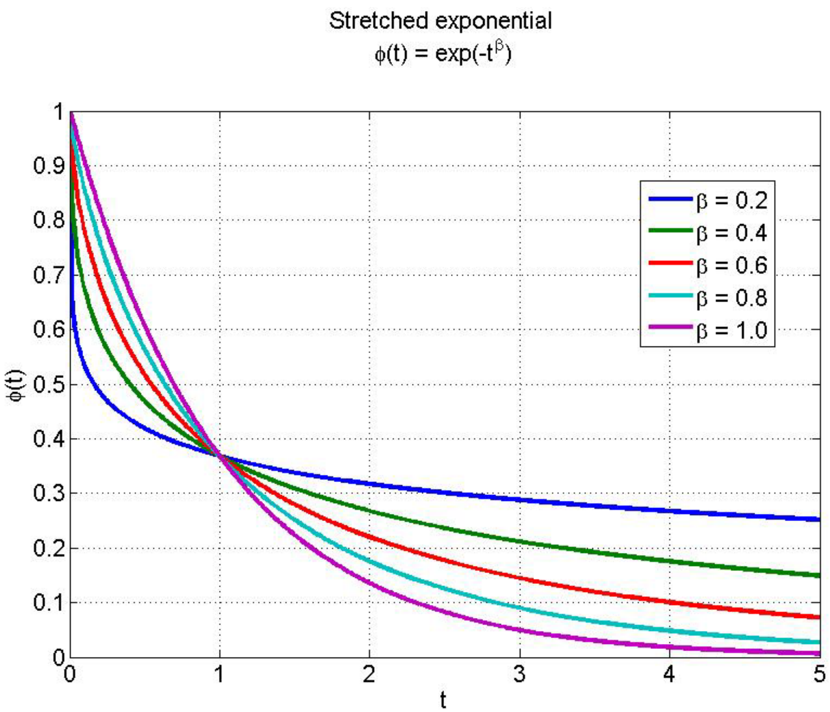
Williams & Watts, Trans. Faraday Soc **66,** 89 (1970

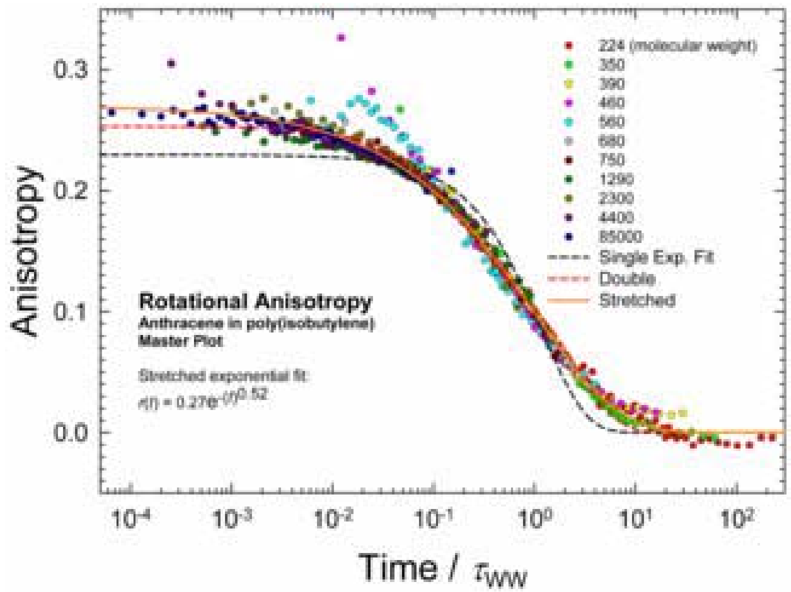
$$\phi_\beta(t) = \exp[-(t/\tau)^\beta];\ 0 < \beta \leq 1;\ \tau = const.$$

Originally introduced by Kohlrausch (1854) (Pogg. Ann. Phys. Chem. **91**, 179) for the fitting of dielectric loss data. He measured β for glasses and a modern fit to his data give $\beta = 0.426$. Remains a good estimate, 150 years later!

Found **empirically** in many different amorphous materials as for instance in many polymers and glass-like materials near the glass transition temperature

Stretched exponential function





Example of fitting

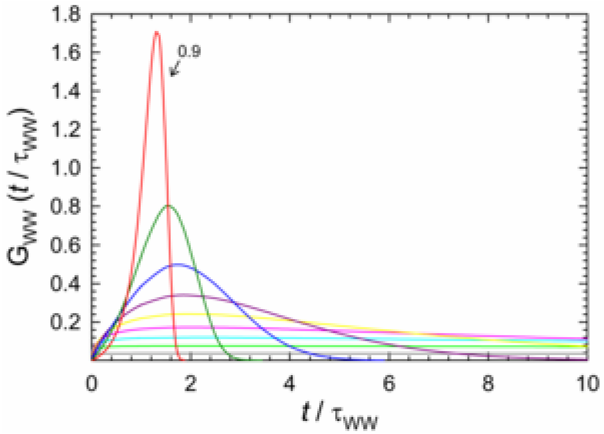
Phenomenological fitting tools or they reflect properties of fundamental significance?

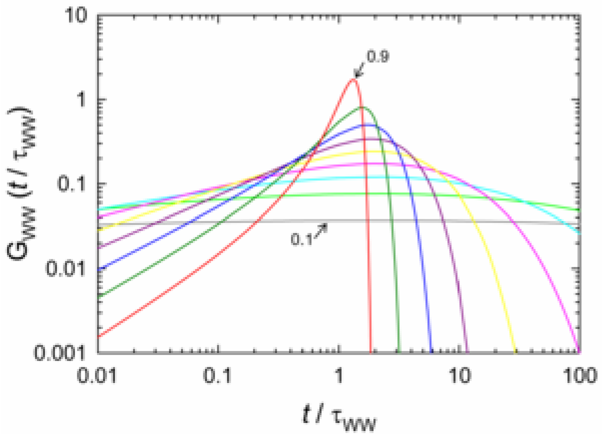
KWW and Lévy distributions

Expands into a weighted superposition of ordinary exponential decay functions, with a weighting function which is expressible in terms of a Lèvy (stable) distribution:

$$\phi_\beta(t) = \frac{\tau}{\mu^2} \int_0^\infty L_{\beta,-1}(\tau/\mu)\exp(-t/\mu)\,d\mu$$

Because of this connection with the statistics of stable laws, the KWW relaxation properties may be argued to develop naturally through the dynamics





Scaled Lévy distributions for various values of β; 0.1 to 0.9

ac-conductivity

- Universality of ac (alternating-current) conduction, which, for a range of relatively high frequencies, is expressible in terms of a power-law dependence of the real part of conductivity on frequency:

$$\sigma'(\omega) \propto \omega^{\eta} \qquad 0 \leq \eta < 1$$

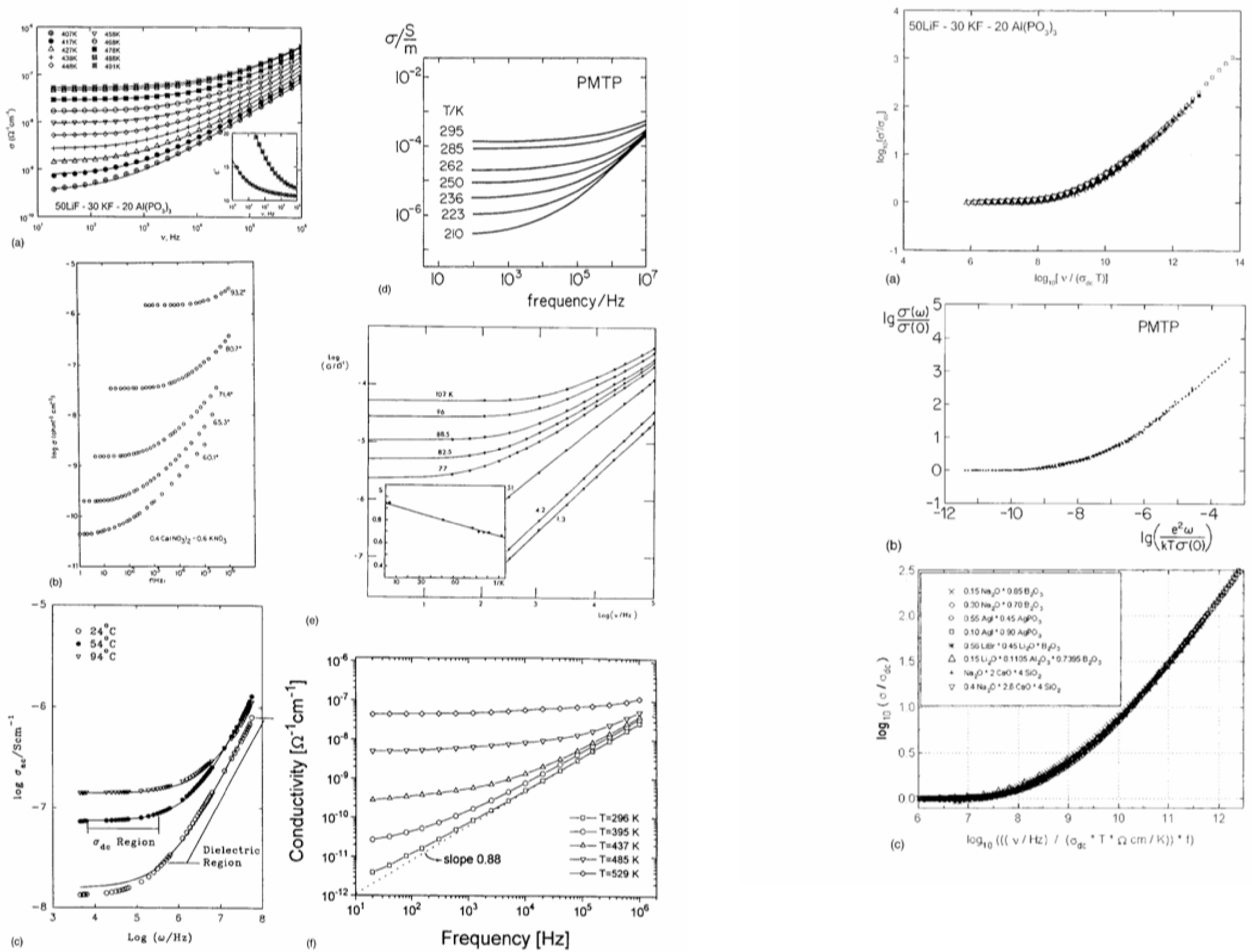
- Often found in disordered insulators and semi-conductors, including doped materials. A good estimate: η between 0.54 and 0.62 (Jacobs et al., J. Phys. Chem. B **110,** 20143 (2006))

Universality means...

- η values do not depend on the details of the underlying conducting lattice, nor on the microscopic charge transport mechanisms operating in the system (i.e., classical barrier crossing for ions and/or quantum mechanical tunneling for electrons)

- Both η and β depend on the chemical composition of the material and the absolute temperature

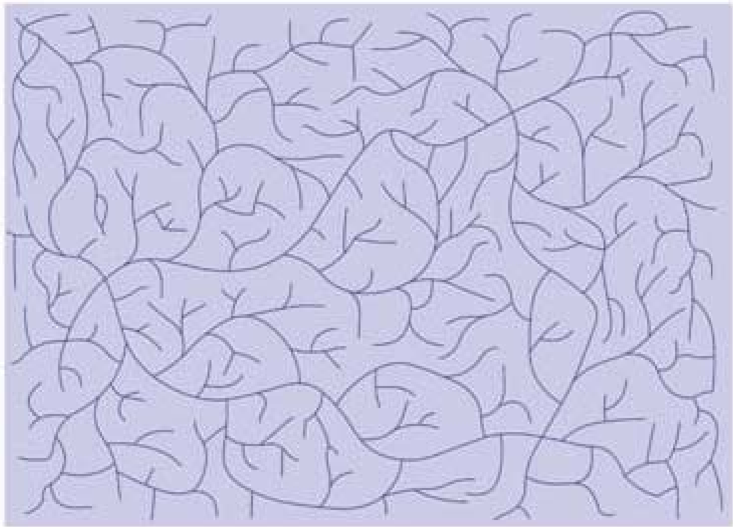
Universality demonstrated



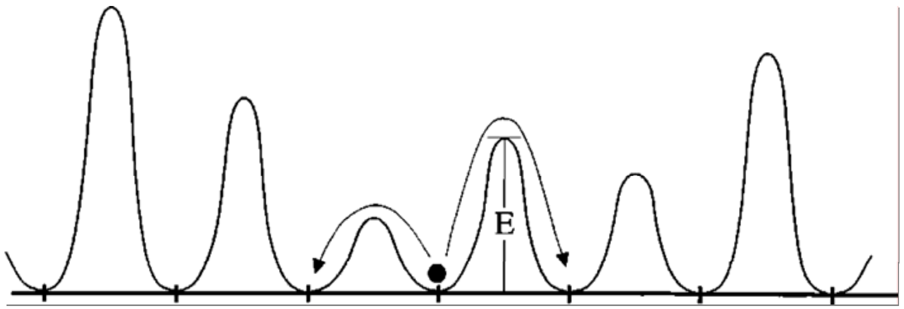
Dyre & Schrøder, Rev. Mod. Phys. **72**, 873 (2000).

Power-law ac conduction coefficient

$$\sigma'(\omega) \propto \omega^{\eta}$$



- Derives from a model, in which the conduction occurs as a result of random walks of charged particles on a percolating cluster (Milovanov and Rasmussen, PRB **64,** 212203 (2001); **66,** 134505 (2002))
- Universality of ac conduction is rooted in the universality of the percolation transition.



Hopping of charge between the localized states of the lattice

Cycles and dead-ends of the fractal acting as potential wells for the moving charged-particles

Using the known estimates for the percolation exponents: $\eta = 0.6$ in 3d

Response function

Homogeneous, isotropic dielectric exposed to external polarizing $\mathbf{E} = \mathbf{E}(t, \mathbf{r})$

$$\mathbf{P}(t, \mathbf{r}) = \int_{-\infty}^{+\infty} \chi(t - t')\mathbf{E}(t', \mathbf{r})dt'$$

$\chi(t - t')$ response (memory) function; Causality: $\chi(t - t') = 0$ for $t < t'$

$\mathbf{E}(t, \mathbf{r}) = \mathbf{E}(\mathbf{r})\delta(t) \quad \rightarrow \quad \mathbf{P}(t, \mathbf{r}) = \mathbf{E}(\mathbf{r})\chi(t)$, $\chi(t)$ response to a delta-pulse.

$\mathbf{E}(t, \mathbf{r}) = \mathbf{E}(\mathbf{r})\theta(-t)\exp(\nu t)$ with $\nu \rightarrow +0$; $\theta(t)$ Heaviside stepfunction

$\mathbf{P}(t, \mathbf{r}) = \mathbf{E}(\mathbf{r})\phi(t)$; $\phi(t)$: relaxation function.

$$\phi(t) = \theta(-t)\phi(0)\exp(\nu t) + \theta(t)\left(\phi(0) - \int_0^t \chi(t')\,dt'\right)$$

$\phi(0) = \int_0^\infty \chi(t)\,dt \;\rightarrow\; 1$

$$\chi(t) = -\frac{d\phi}{dt}$$

KWW relaxation function

Assume

$$\phi(t) = \theta(-t)\exp(\nu t) + \theta(t)\exp\left[-(t/\tau)^{\beta}\right]$$

$$\chi(t) = \frac{\beta\phi(0)}{\tau^{\beta}} t^{\beta-1}\theta(t)\exp\left[-(t/\tau)^{\beta}\right]$$

Stretched exponential relaxation function $\phi(t) \to \chi(t)$ with power law decay $t^{\beta-1}$ $(t < \tau)$, with stretched exponential cut-off $(t > \tau)$.

Fourier transforming

$$\phi(\omega) = \int_{-\infty}^{0} \exp(\nu t) e^{i\omega t} dt + \int_{0}^{+\infty} \exp[-(t/\tau)^{\beta}] e^{i\omega t} dt$$

$$\phi(\omega) = \tau \mathrm{Q}(\omega\tau) + i\tau\left(\mathrm{V}(\omega\tau) - \frac{1}{\omega\tau}\right)$$

The Lèvy functions:

$$\mathrm{Q}(z) = \int_{0}^{+\infty} \exp(-u^{\beta})\cos(uz)du; \quad \mathrm{V}(z) = \int_{0}^{+\infty} \exp(-u^{\beta})\sin(uz)du$$

AC-conductivity

Lèvy functions series expansion:

$$\mathrm{Q}(z) = \sum_{n=1}^{\infty} (-1)^{n-1} \frac{1}{z^{n\beta+1}} \frac{\Gamma(n\beta+1)}{\Gamma(n+1)} \sin \frac{n\beta\pi}{2}$$

$$\mathrm{V}(z) = \sum_{n=0}^{\infty} (-1)^{n} \frac{1}{z^{n\beta+1}} \frac{\Gamma(n\beta+1)}{\Gamma(n+1)} \cos \frac{n\beta\pi}{2}$$

Kaatz *et al*, Macromolecules **29**, 1666 (1996).
Montroll & Bendler, J. Stat. Phys. **34**, 129 (1984).

Define complex $\chi(\omega)$ as Fourier pair with $\chi(t)$, and use $\chi(t) = -d\phi/dt$

$$\chi(\omega) = i\omega\phi(\omega) = 1 - \omega\tau\mathrm{V}(\omega\tau) + i\omega\tau\mathrm{Q}(\omega\tau)$$

Leading terms in the expansions: $\chi(\omega) \propto \omega^{-\beta}$

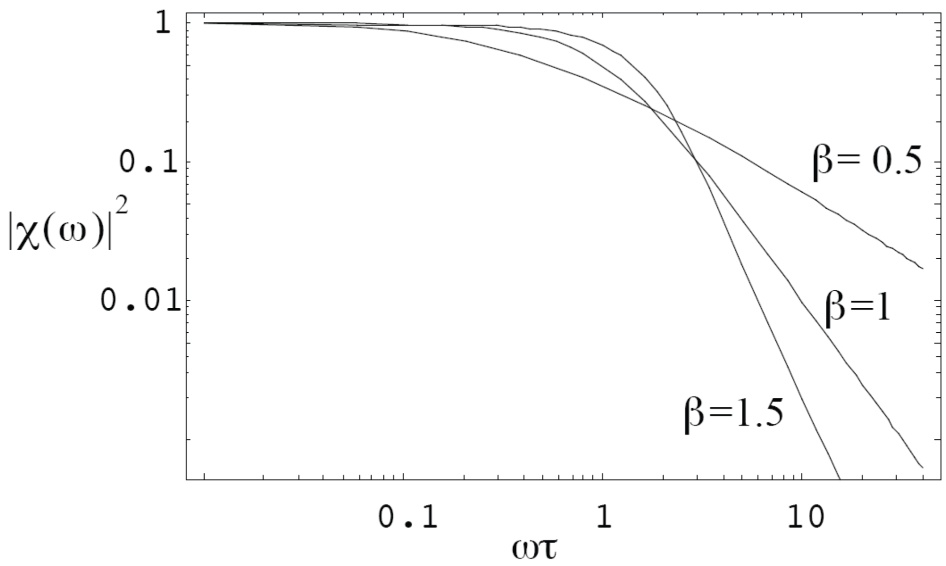
$\epsilon'(\omega) + i\epsilon''(\omega) = 1 + 4\pi\chi(\omega)$ and $\sigma'(\omega) = \omega\epsilon''(\omega)/4\pi$
Kramers-Kronig relation:

$$\sigma'(\omega) \propto \omega^{1-\beta} \quad \rightarrow \quad \eta = 1 - \beta$$

Power spectral density

PSD of polarization field

$$S(\omega) = \langle|\mathbf{P}(\omega,\mathbf{r})|^2\rangle = |\chi(\omega)|^2\langle|\mathbf{E}(\omega,\mathbf{r})|^2\rangle$$



PSD for uncorrelated white noise drive : $S(\omega) = |\chi(\omega)|^2$

Power law regime for $\omega\tau > 1$

Self-consistent relaxation model

Goal: to obtain the KWW decay function self consistently

Assume no external field and look for the response to the inherent E-field generated by polarization charge distribution $\rho(t, \mathbf{r})$

$$P(t,r) = P(0,r) + \int_0^t \chi(t-t')E(t',r)dt'$$

$$j(t,r) = \int_0^t \sigma(t-t')E(t',r)dt'$$

where the polarization current is obtained as time derivative of the polarization field:

$$j(t,r) = \frac{\partial}{\partial t}P(t,r) \Leftrightarrow \sigma(t-t') = \frac{\partial}{\partial t}\chi(t-t')$$

Electrostatic dynamics

Electrostatic equations:

$$\nabla \cdot E(t,r) = 4\pi\rho(t,r)$$

$$\nabla \cdot P(t,r) = -\rho(t,r)$$

Polarization and electric source fields are self-consistently determined by the distribution of the polarization charges

The continuity equation:

$$\frac{\partial}{\partial t}\rho(t,r) + \nabla \cdot j(t,r) = 0$$

Evolution of charge density

$$\frac{\partial}{\partial t}\rho(t,r) = -\nabla \cdot j(t,r)$$

$$\frac{\partial}{\partial t}\rho(t,r) = -\nabla \cdot \int_0^t \sigma(t-t')E(t',r)dt'$$

$$\frac{\partial}{\partial t}\rho(t,r) = -\int_0^t \sigma(t-t')\nabla \cdot E(t',r)dt'$$

$$\frac{\partial}{\partial t}\rho(t,r) = -4\pi \int_0^t \sigma(t-t')\rho(t',r)dt'$$

Laplace transformed charge density

$$s\rho(s,r) - \rho(0,r) = -4\pi\sigma(s)\rho(s,r)$$

Separating variables...

$$\rho(s,r) = \phi(s)g(r)$$

we find

$$\phi(s) = \frac{\phi(0)}{s + 4\pi\sigma(s)} \Rightarrow \frac{1}{s + 4\pi\sigma(s)}$$

where we set $\phi(0) = 1$ as the initial condition...

Postulate power law ac conduction

The form of the ac conduction coefficient...

$$\sigma(s) = \alpha s^{\eta}$$

...results in

$$\phi(s) = \frac{1}{s + 4\pi\alpha s^{\eta}}$$

Inverse Laplace transform:

$$\phi(t) = \frac{1}{2\pi i}\int_{-i\infty}^{+i\infty} \frac{e^{st}}{s + \tau^{-\beta} s^{1-\beta}} ds$$

where

$$\tau^{-\beta} = 4\pi\alpha$$

$$\beta = 1 - \eta$$

The definition of Mittag-Leffler function: $E_{\beta}[-(t/\tau)^{\beta}]$

Metzler & Klafter, Phys. Rep. **339,** 1 (2000);
Sokolov *et al.* Phys. Today **55,** 48 (2002)

Mittag-Leffler function

Series expansion

$$\phi(t) = \sum_{n=0}^{\infty} (-1)^n \frac{(t/\tau)^{n\beta}}{\Gamma(n\beta+1)}$$

For short times, the behavior is stretched-exponential:

$$\phi(t) \approx \exp\left[-(t/\tau)^{\beta} / \Gamma(\beta+1)\right]$$

This closed analytical form replicates the KWW decay function: thus given a power law ac conductivity results in stretched exponential decay: $\beta = 1 - \eta$

Fractional derivative representation

$$s^{\eta} \Leftrightarrow {}_0\hat{D}_t^{\eta}$$

Riemann-Liouville fractional operator

$${}_0\hat{D}_t^{\eta}\rho(t,r) = \frac{1}{\Gamma(1-\eta)}\frac{\partial}{\partial t}\int_0^t \frac{\rho(t',r)}{(t-t')^{\eta}}dt'$$

Provides an extension of the ordinary time derivative to fractional order

Fractional relaxation equation

$$s\rho(s,r)-\rho(0,r)=-4\pi\alpha s^{\eta}\rho(s,r)$$

$$s\rho(s,r)-\rho(0,r)=-\tau^{-\beta}s^{1-\beta}\rho(s,r)$$

In the time domain...

$$\frac{\partial}{\partial t}\rho(t,r)=-\tau^{-\beta}\,{}_0\hat{D}_t^{1-\beta}\rho(t,r)$$

which extends the ordinary relaxation equation to processes with memory as due to the Riemann-Liouville operator

Conclusions

- The KWW decay function can be obtained analytically from a self-consistent model of dielectric relaxation, in which both the polarization and electric source fields are self-consistently generated by the residual charge-density

- The exponent of the KWW decay function is related to the exponent of the ac conduction coefficient via $\beta = 1-\eta$

- The relaxations are described by a fractional extension of the relaxation equation, which naturally incorporates the power-law dependence of the ac conduction coefficient on frequency