Dielectric Modulus: Experiment, Application, and Interpretation

Tutorial on "Broadband Dielectric Spectroscopy and its Applications"

Lille, 10 July 2005

History

Basic Properties

Experimental Approach

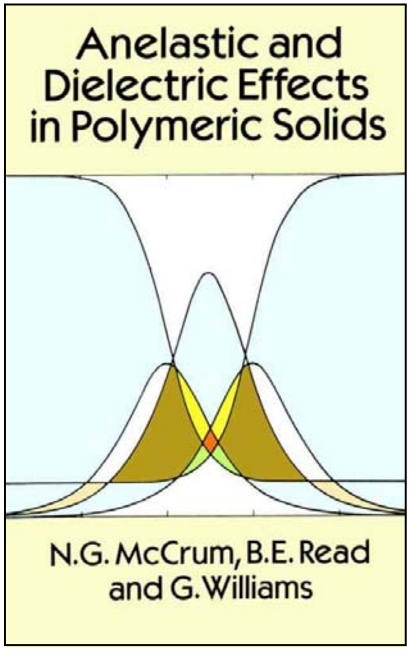
Applications

Ranko Richert

From shear modulus to electrical modulus

N. G. McCrum, B. E. Read, G. Williams,
Anelastic and Dielectric Effects in Polymeric Solids (Wiley, London, 1967)

MECHANICAL	DIELECTRIC (cgs)
stress σ	electric field E
strain γ	displacement D
shear compliance J	permittivity ε
$\gamma = J\,\sigma$	$D = \varepsilon\,E$
shear modulus G	
$\sigma = G\,\gamma$	?
$G = 1/J$	



(Dover, New York, 1991)

Constant Field vs. Constant Charge: The Modulus

H. Fröhlich, Theory of Dielectrics, Clarendon, Oxford, 1958

We shall now use equation 10.7 in the investigation of the approach to equilibrium of a condenser. The following two cases are to be considered:

(*a*) Constant charge on the condenser plates. Then

$$\frac{dD}{dt} = 0, \quad D = D_0,$$

and hence, using 10.7,

$$\tau' \frac{dE}{dt} + E = \frac{D_0}{\epsilon_s}, \quad \text{i.e.} \quad D_0 - \epsilon_s E \propto e^{-t/\tau'}, \qquad (10.9)$$

where

$$\tau' = \frac{\epsilon_\infty}{\epsilon_s}\tau. \qquad (10.10)$$

(*b*) Constant voltage at the condenser plates, i.e.

$$\frac{dE}{dt} = 0, \qquad E = E_0.$$

It follows with 10.7 that

$$\tau \frac{dD}{dt} + D = \epsilon_s E_0, \quad \text{i.e.} \quad D - \epsilon_s E_0 \propto e^{-t/\tau}. \qquad (10.11)$$

Both cases thus lead to exponential approach to equilibrium.

S.R. Elliott, J. Non-Cryst. Solids, 170 (1994) 97

The first drawback to the modulus is that it is not a directly measurable quantity; instead, it is a complicated function of the measured quantities ϵ', ϵ'' and σ_0 (Eq. (3)). Thus, significant experimental errors in, say, one of these quantities can be propagated into both the real and imaginary parts of the complex modulus. A further disadvantage is that the modulus is not directly related

$$M'' = \epsilon''/\left[\epsilon'^2 + (\epsilon'' + \sigma_0/\omega\epsilon_0)^2\right] + (\sigma_0/\omega\epsilon_0) / \left[\epsilon'^2 + (\epsilon'' + \sigma_0/\omega\epsilon_0)^2\right]. \qquad (3)$$

Electrical relaxation

N. G. McCrum, B. E. Read, G. Williams,
Anelastic and Dielectric Effects in Polymeric Solids (Wiley, London, 1967)

P.B. Macedo, C.T. Moynihan, R. Bose,
Phys. Chem. Glasses 13 (1972) 171

M. Hodge, K. L. Ngai, C. T. Moynihan,
J. Non-Cryst. Solids 351 (2005) 104

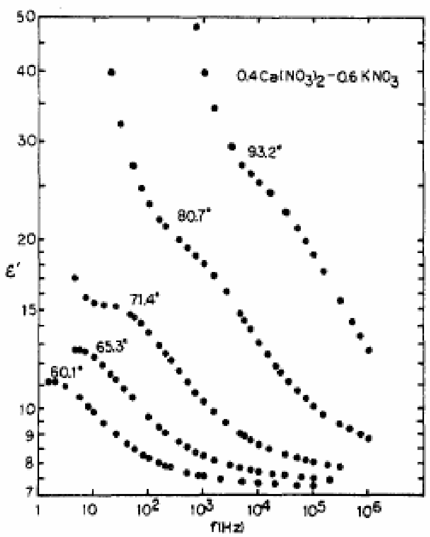


Figure 1. Dielectric constant *vs.* frequency for 0.4Ca(
0.6KNO$_3$ melt above the glass transition temperature.

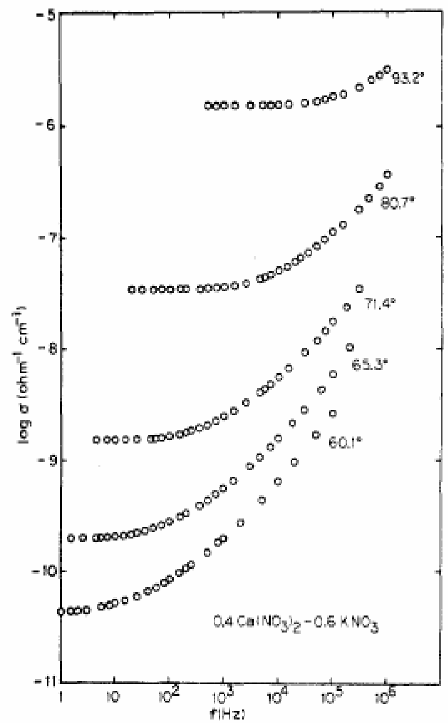


Figure 2. Conductivity *vs.* frequency for 0.4Ca(NO$_3$)$_2$–0.6KNO$_3$ melt above the glass transition temperature.

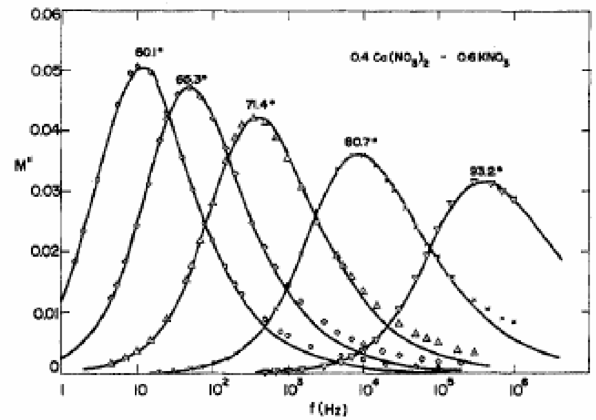
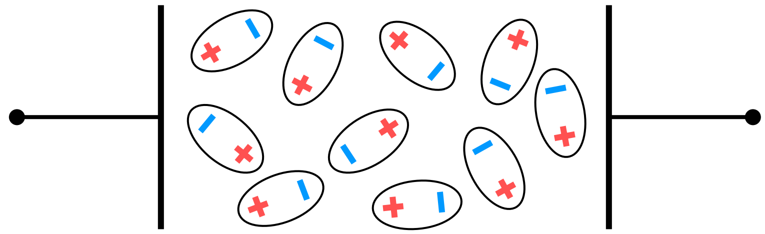


Figure 6. Imaginary part of the electric modulus *vs.* frequency for 0.4Ca(NO$_3$)$_2$–0.6KNO$_3$ melt above the glass transition temperature.

F. S. Howell, R. A. Bose, P. B. Macedo, C. T. Moynihan, J. Phys. Chem. 78 (1974) 639

BASIC PROPERTIES

Dielectric Relaxation and Retardation



dielectric displacement $\mathbf{D} \equiv \frac{\mathbf{Q}}{\mathbf{A}} \propto \frac{\mathbf{U}}{\mathbf{d}} \equiv \mathbf{E}$ *electric field*

$$\mathbf{D} = \varepsilon \ \varepsilon_0 \ \mathbf{E}$$

$$\varepsilon_0 \ \mathbf{E} = \frac{1}{\varepsilon} \mathbf{D} = \mathbf{M} \ \mathbf{D}$$

Retardation

$$\varepsilon^*(\omega) = \frac{Y^*(\omega)}{Y_0}$$

$$Y^*(\omega) = \frac{I^*(\omega)}{U^*(\omega)}$$

$$M = 1/\varepsilon$$

Relaxation

$$M^*(\omega) = \frac{Z^*(\omega)}{Z_0}$$

$$Z^*(\omega) = \frac{U^*(\omega)}{I^*(\omega)}$$

definitions of dielectric and electric quantities

V	voltage	I	current	Q	charge
D	displacement	E	electric field	P	polarization
ε	dielectric function	M	electric modulus	χ	susceptibility
j	current density	σ	conductivity	ρ	resistivity

'permittivity of vacuum'

ε_0 = 8.854×10^{-12} pF m^{-1}
= 8.854×10^{-12} A s V^{-1} m^{-1}
= 8.854×10^{-14} S s cm^{-1}

---

steady state relations

$$D = \varepsilon \cdot \varepsilon_0 \cdot E \qquad E = \frac{M}{\varepsilon_0} \cdot D$$

$$P = D - \varepsilon_0 E = (\varepsilon - 1)\varepsilon_0 E = \chi \varepsilon_0 E \qquad \chi = \varepsilon - 1$$

$$j = \sigma \cdot E = j_\sigma + j_\varepsilon = j_\sigma + \dot{D} \qquad E = \rho \cdot j \qquad j = \dot{D}$$

$$D = \frac{Q}{A} \qquad E = \frac{V}{d} \qquad j = \frac{I}{A} \qquad Q = \int_0^t I(t')dt'$$

$$\hat{\varepsilon} = \varepsilon' - i\varepsilon'' \qquad \hat{\sigma} = i\omega\varepsilon_0\hat{\varepsilon} \qquad \hat{\sigma} = \sigma' + i\sigma''$$

$$\hat{M} = 1/\hat{\varepsilon} \qquad \hat{\rho} = 1/\hat{\sigma}$$

$$\hat{M} = M' + iM'' \qquad \hat{\rho} = \hat{M}/i\omega\varepsilon_0 \qquad \hat{\rho} = \rho' - i\rho''$$

constant field step E(t) = E_0 θ(t)

$$\varepsilon(t) = \frac{D(t)}{\varepsilon_0 \cdot E_0}$$

$$\sigma(t) = \frac{j_\sigma + j_\varepsilon}{E_0} = \frac{j_\sigma + \dot{D}(t)}{E_0} = \frac{j_\sigma + \varepsilon_0 \cdot E_0 \cdot \dot{\varepsilon}(t)}{E_0}$$

$$\sigma(t) = \sigma_{dc} + \varepsilon_0 \cdot \dot{\varepsilon}(t)$$

$$P(t) = D(t) - \varepsilon_0 \cdot E_0 = \varepsilon_0 \cdot E_0 \cdot [\varepsilon(t) - 1] = \varepsilon_0 \cdot E_0 \cdot \chi(t)$$

constant charge step D(t) = D_0 θ(t)

$$M(t) = \frac{\varepsilon_0 \cdot E(t)}{D_0}$$

$$P(t) = D_0 - \varepsilon_0 \cdot E(t) = D_0 \cdot [1 - M(t)]$$

Relations for time/frequency, epsilon/modulus, and probability densities

complex dielectric function $\varepsilon^*(\omega)$

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

complex electric modulus $M^*(\omega)$

$$\varepsilon^*(\omega)=i\omega\int_0^\infty \varepsilon(t)\, e^{-i\omega t}dt$$

$$M^*(\omega)=i\omega\int_0^\infty M(t)\, e^{-i\omega t}dt$$

$$\varepsilon(t)=\frac{1}{2\pi}\int_0^\infty \frac{\varepsilon^*(\omega)}{i\omega}\, e^{i\omega t}d\omega$$

$$M(t)=\frac{1}{2\pi}\int_0^\infty \frac{M^*(\omega)}{i\omega}\, e^{i\omega t}d\omega$$

retardation function $\varepsilon(t)$

$$\int_0^t M(\tau)\cdot\varepsilon(t-\tau)=\int_0^t \varepsilon(\tau)\cdot M(t-\tau)=t\theta(t)$$

relaxation function $M(t)$

$$\varepsilon(t)=\varepsilon_\infty+(\varepsilon_s-\varepsilon_\infty)\int_0^\infty g_\varepsilon(\tau)\left(1-e^{-t/\tau}\right)d\tau$$

$$M(t)=M_s+(M_\infty-M_s)\int_0^\infty g_M(\tau)\, e^{-t/\tau}d\tau$$

probability density $g_\varepsilon(\tau)d\tau$

probability density $g_M(\tau)d\tau$

$$\varepsilon^*(\omega)=\varepsilon_\infty+(\varepsilon_s-\varepsilon_\infty)\int_0^\infty \frac{g_\varepsilon(\tau)}{1+i\omega\tau}d\tau$$

$$M^*(\omega)=M_s+(M_\infty-M_s)\int_0^\infty \frac{g_M(\tau)\, i\omega\tau}{1+i\omega\tau}d\tau$$

Kramers-Kronig relations

$$\left.\begin{aligned}\varepsilon'(\omega)&=\varepsilon_\infty+\frac{2}{\pi}\int_0^\infty \varepsilon''(x)\frac{x}{x^2-\omega^2}\,dx\\ \varepsilon''(\omega)&=-\frac{2}{\pi}\int_0^\infty \left[\varepsilon'(x)-\varepsilon_\infty\right]\frac{\omega}{x^2-\omega^2}\,dx\end{aligned}\right\}\Rightarrow \frac{2}{\pi}\int_{-\infty}^{\infty}\varepsilon''(\ln\omega)d\ln\omega=\varepsilon_s-\varepsilon_\infty$$

time-scale relations: M(ω) - ε(ω) for the Debye case

$$\hat{M}(\omega) = \frac{1}{\hat{\varepsilon}(\omega)} \qquad M_\infty = \frac{1}{\varepsilon_\infty} \qquad M_s = \frac{1}{\varepsilon_s}$$

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

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

$$= \frac{1}{\varepsilon_\infty} + \frac{1 + i\omega\tau - \dfrac{1}{\varepsilon_\infty}(\varepsilon_\infty i\omega\tau + \varepsilon_s)}{\varepsilon_\infty i\omega\tau + \varepsilon_s} = \frac{1}{\varepsilon_\infty} + \frac{1 + i\omega\tau - i\omega\tau - \dfrac{\varepsilon_s}{\varepsilon_\infty}}{\varepsilon_s + \varepsilon_\infty i\omega\tau} = \frac{1}{\varepsilon_\infty} + \frac{\dfrac{1}{\varepsilon_s} - \dfrac{1}{\varepsilon_\infty}}{1 + \dfrac{\varepsilon_\infty}{\varepsilon_s} i\omega\tau}$$

$$= M_\infty + \frac{M_s - M_\infty}{1 + i\omega\left(\dfrac{\varepsilon_\infty}{\varepsilon_s}\tau\right)} = \underbrace{M_\infty + \frac{M_s - M_\infty}{1 + i\omega\tau'}} \quad \text{with} \quad \tau' = \frac{\varepsilon_\infty}{\varepsilon_s}\tau$$

same function as ε(ω), but different parameters

time-scale relations: M(ω) - ε(ω) for the non-Debye cases

$$\hat{M}(\omega) = \frac{1}{\hat{\varepsilon}(\omega)} \qquad M_\infty = \frac{1}{\varepsilon_\infty} \qquad M_s = \frac{1}{\varepsilon_s}$$

Kohlrausch-Williams-Watts (KWW)

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

Cole-Cole (CC)

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{1}{1 + (i\omega\tau)^\alpha} \qquad \tau_M = \tau_\varepsilon \times \left(\frac{\varepsilon_\infty}{\varepsilon_s}\right)^{\frac{1}{\alpha}}$$

Cole-Davidson (CD)

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{1}{[1 + i\omega\tau]^\gamma} \qquad \tau_M \approx \tau_\varepsilon \times \left(\frac{\varepsilon_\infty}{\varepsilon_s}\right)^{\frac{1}{\gamma}}$$

R. Richert, Physica A 287 (2000) 26
N. Ito, R. Richert, J. Chem. Phys.

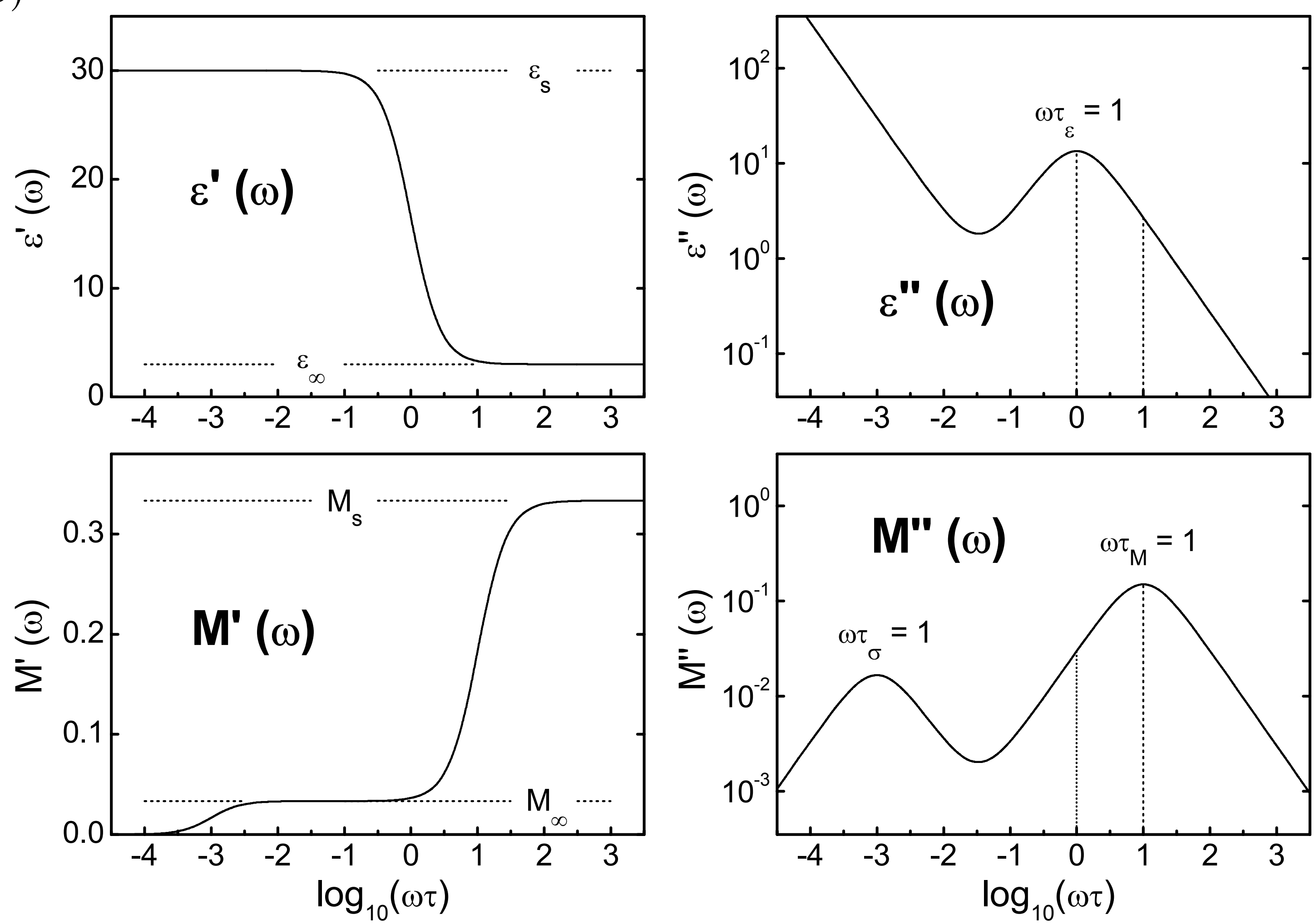
Model calculation for Debye process + dc-conductivity

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\frac{1}{1+i\omega\tau} + \frac{\sigma_{dc}}{i\omega\varepsilon_0}$$

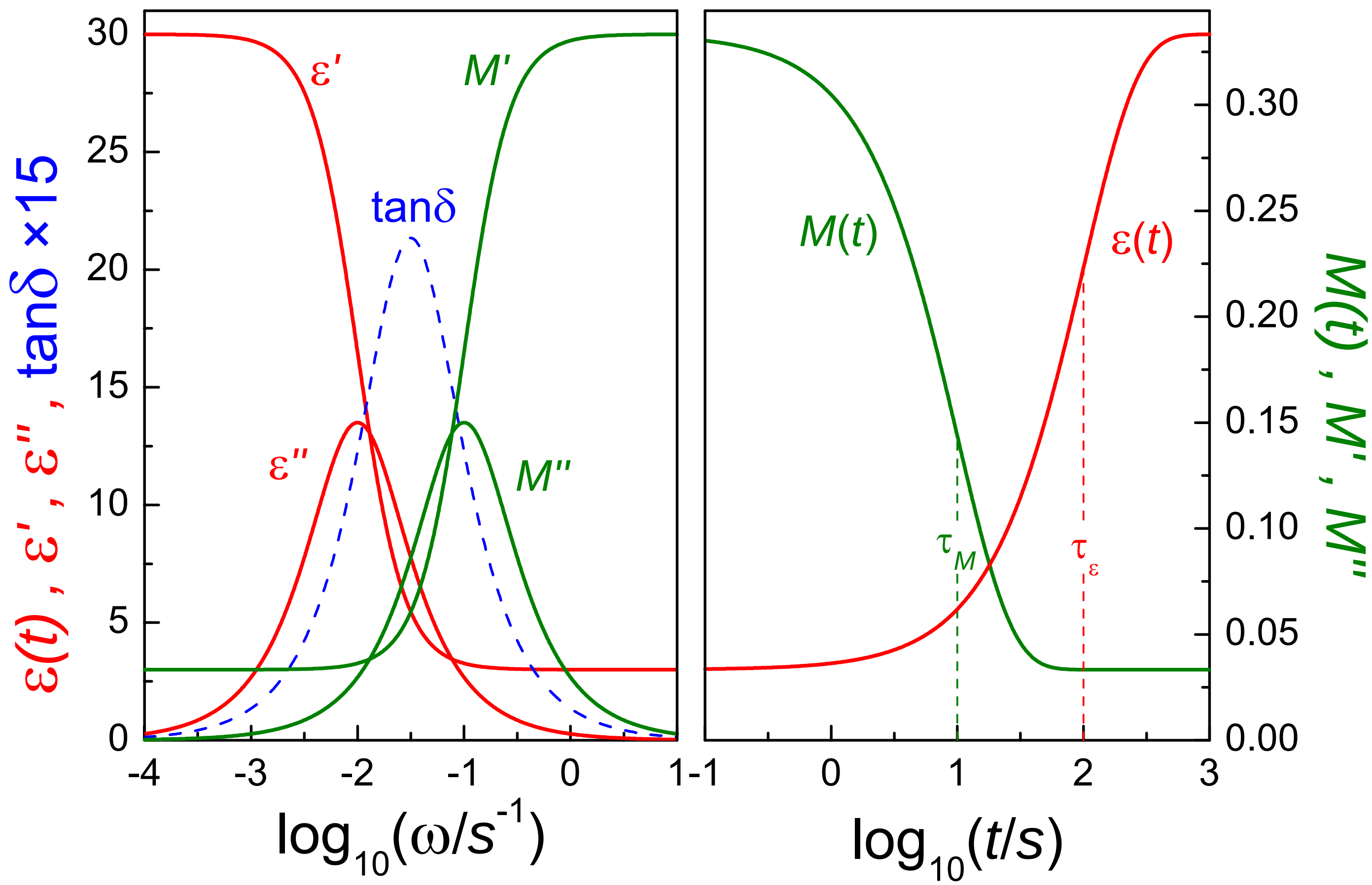
$$\hat{M}(\omega) = 1/\hat{\varepsilon}(\omega)$$

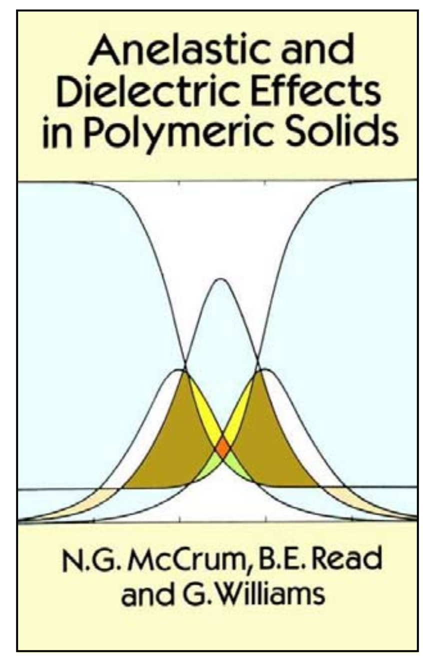
$$M_s = 1/\varepsilon_s$$

$$M_\infty = 1/\varepsilon_\infty$$



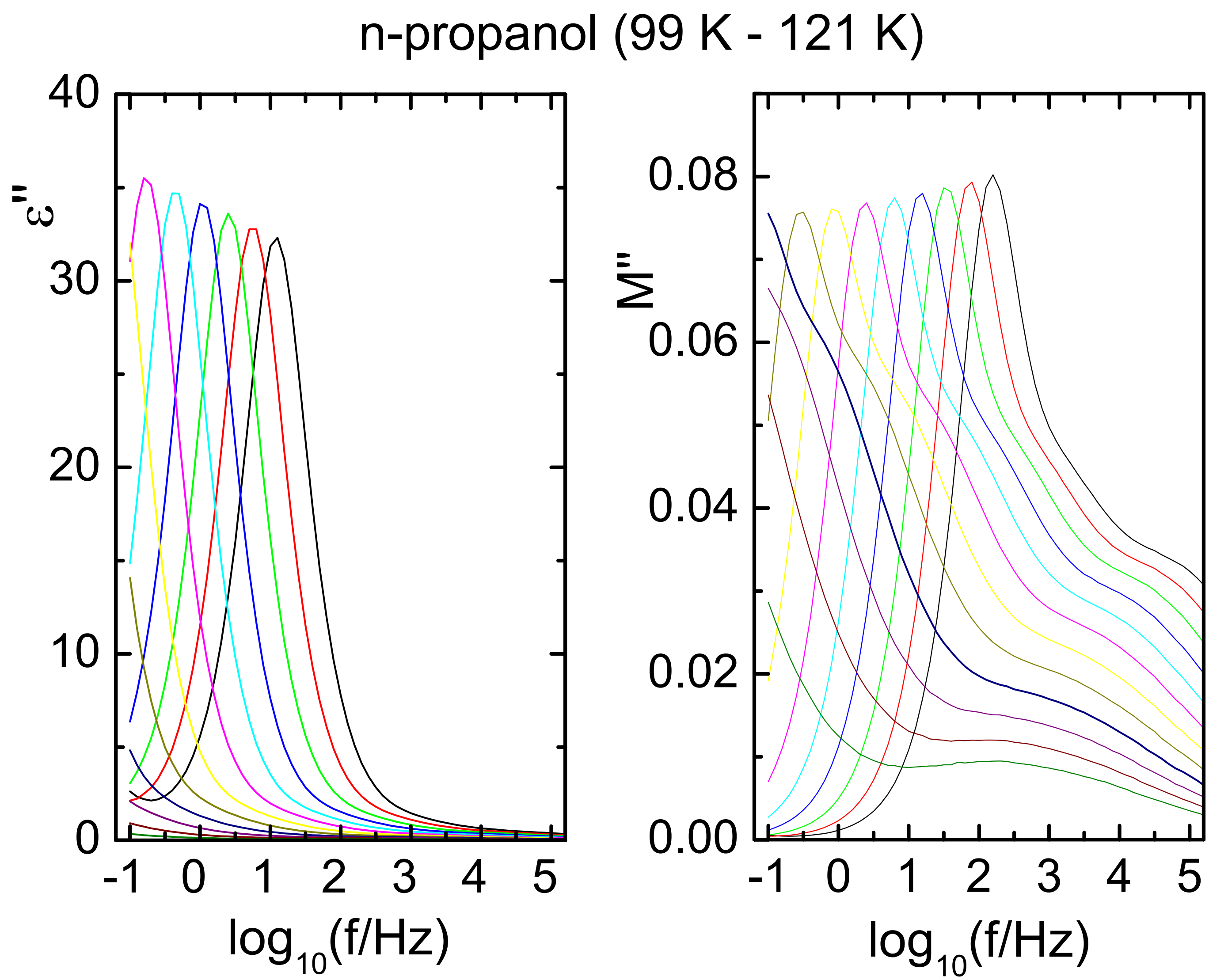
Relaxation versus Retardation



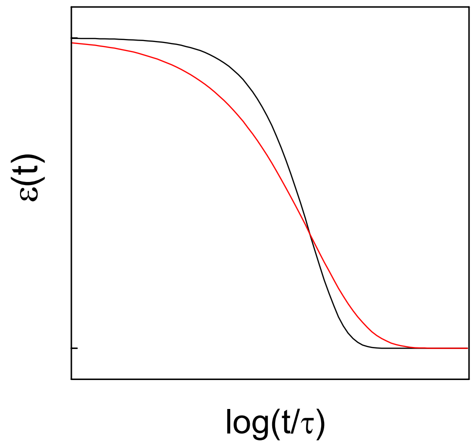


see: N. G. McCrum, B. E. Read, G. Williams,
Anelastic and Dielectric Effects in Polymeric Solids (Dover, New York, 1991)

Identical Information – Different Emphasis



Different Techniques - Identical Information

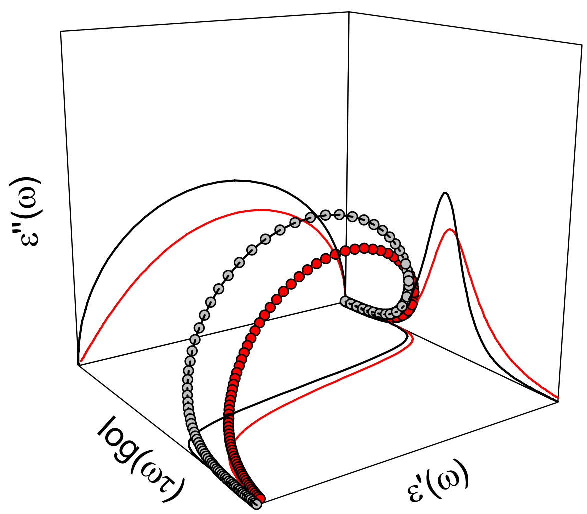


Time domain: ε(t)

$$\varepsilon(t) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\left[1 - e^{-t/\tau}\right]$$

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

Kohlrausch-Williams-Watts



Frequency domain: ε*(ω)

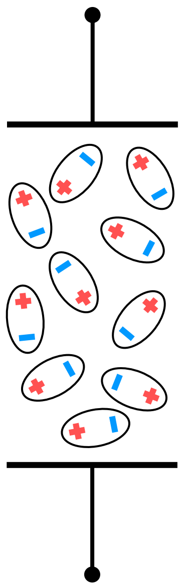
$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + i\omega\tau}$$

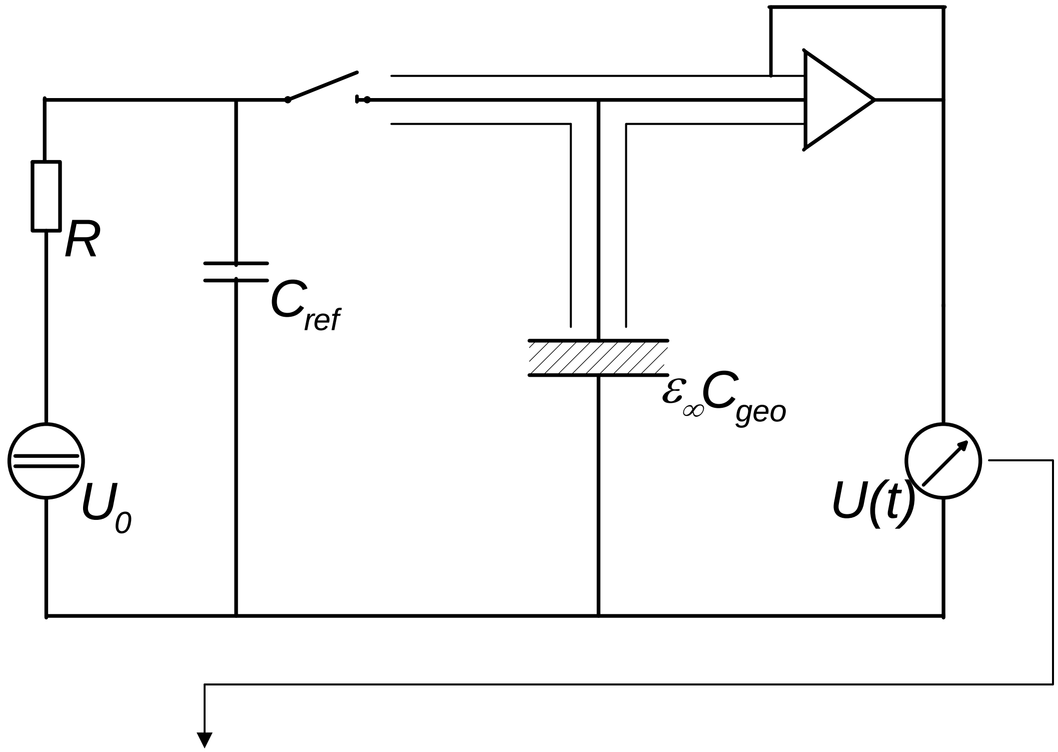
$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{\left[1 + (i\omega\tau)^\alpha\right]^\gamma}$$

Havriliak-Negami

DIELECTRIC MODULUS TECHNIQUE

Real Dielectric Relaxation: The Electric Modulus





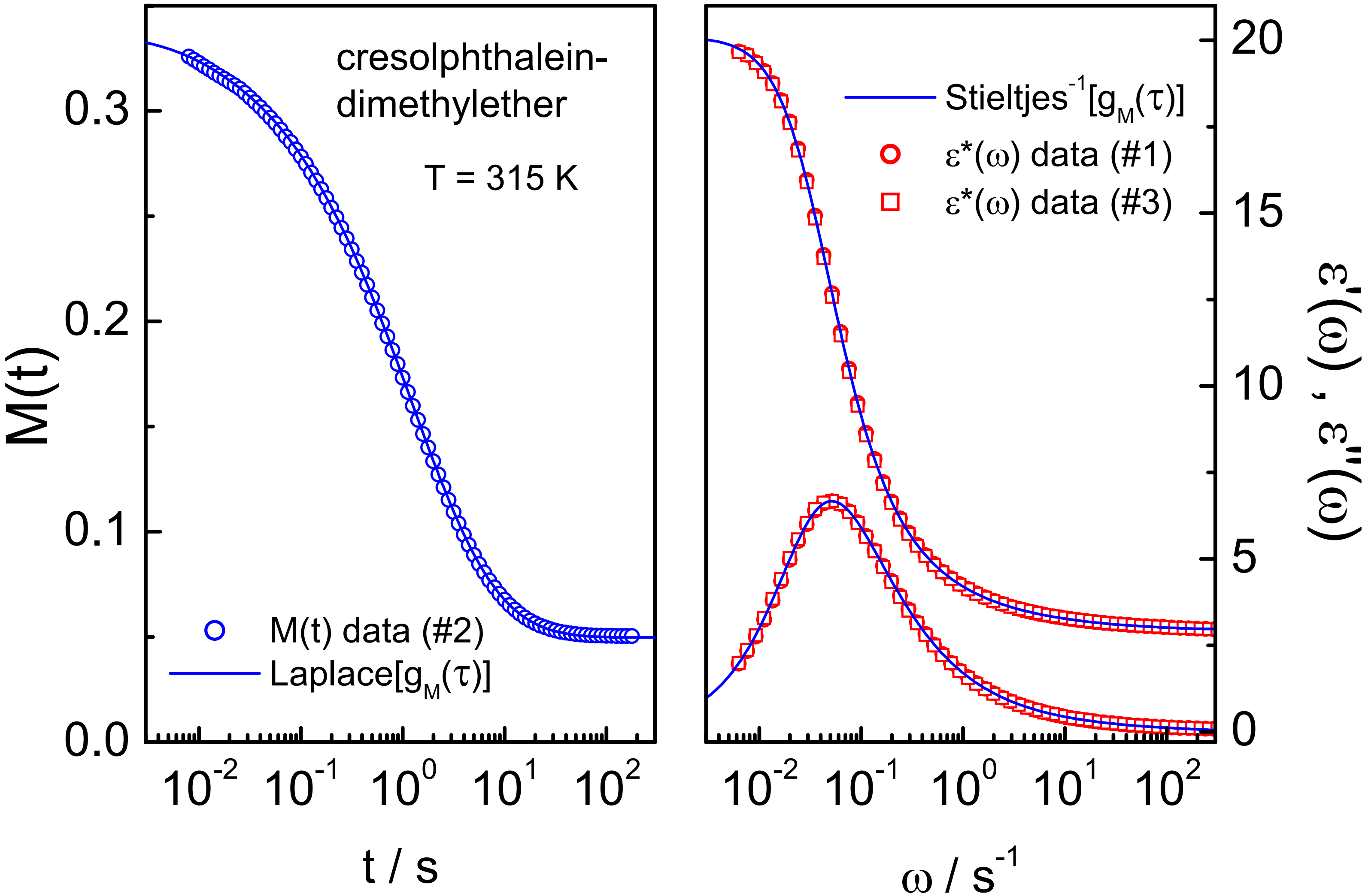
$$U(t) \propto E(t) \propto P_{\text{const. charge}}(t) \propto M(t)$$

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)}$$

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

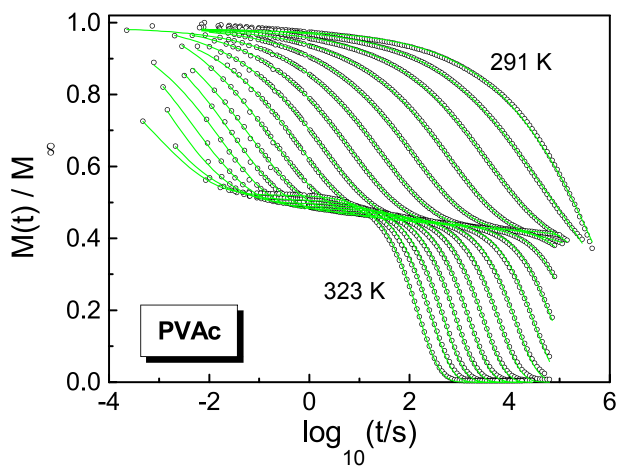
H. Wagner, R. Richert, Polymer 38 (1997) 255

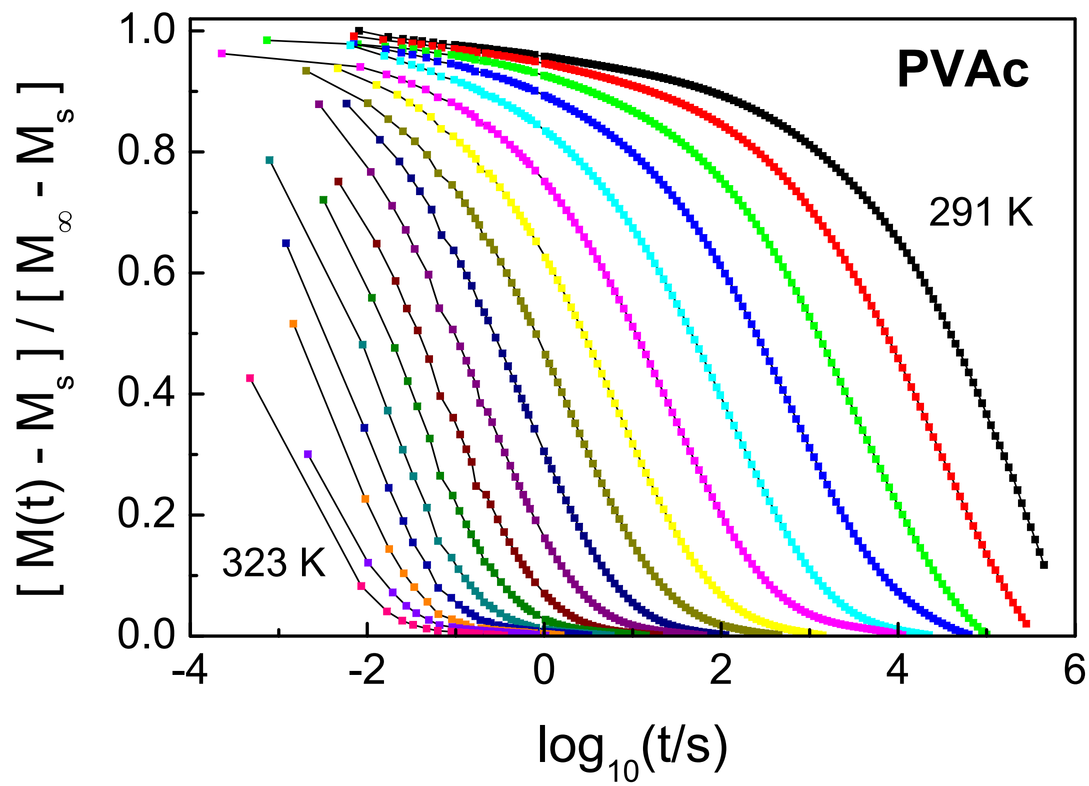
Comparing *M(t)* with *ε*(ω)*



H. Wagner, Dissertation, 1999, Mainz
R. Richert, J. Non-Cryst. Solids 305 (2002) 29

Dielectric Modulus of Poly(vinyl acetate)



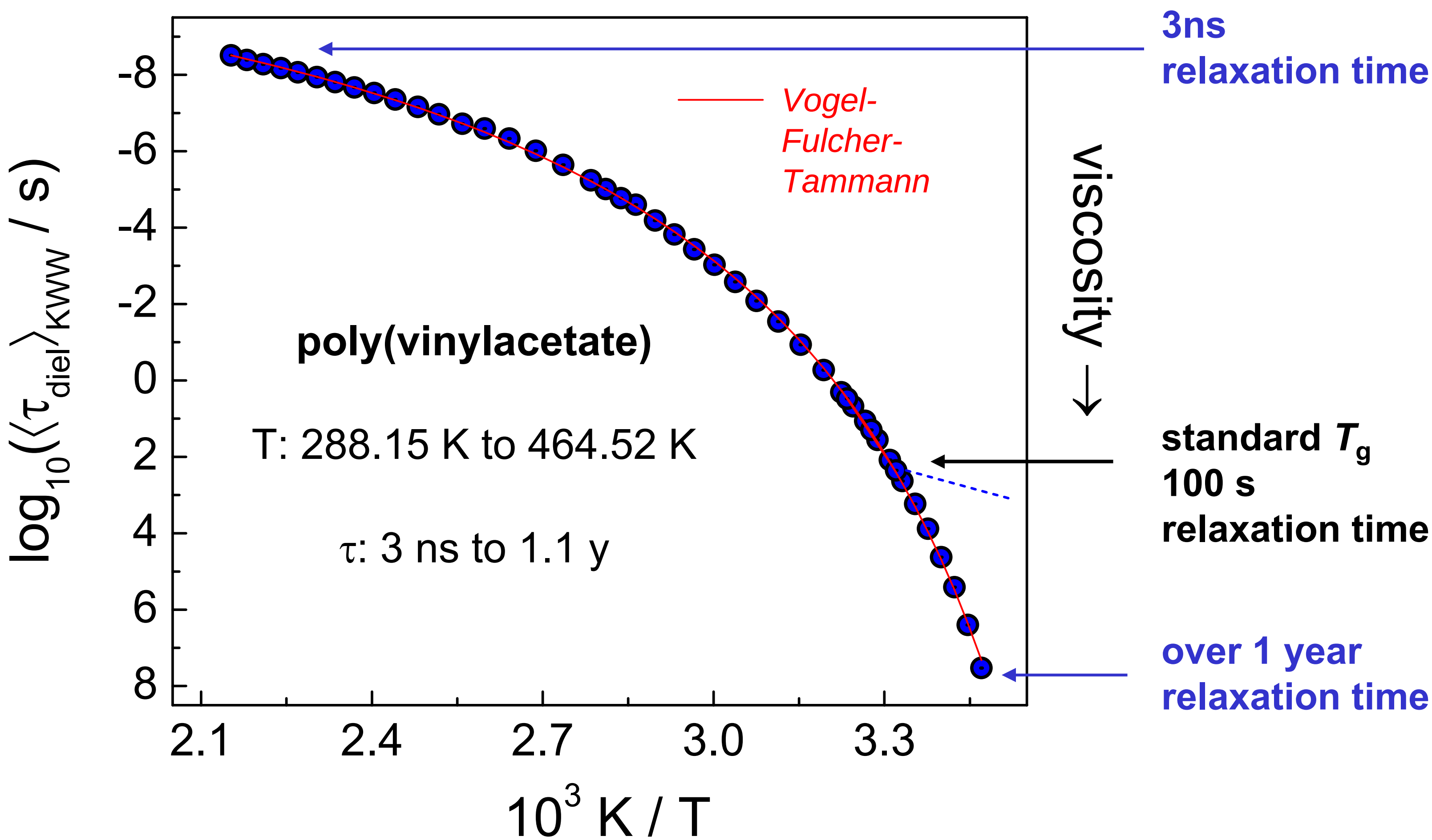


$$M(t) = (M_\infty - M_s) \times \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right] + M_s \cdot \exp\left[-\frac{t \cdot \sigma_{dc} \cdot M_s}{\varepsilon_o}\right]$$

$$\frac{M(t) - M_s}{M_\infty - M_s} = \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right]$$

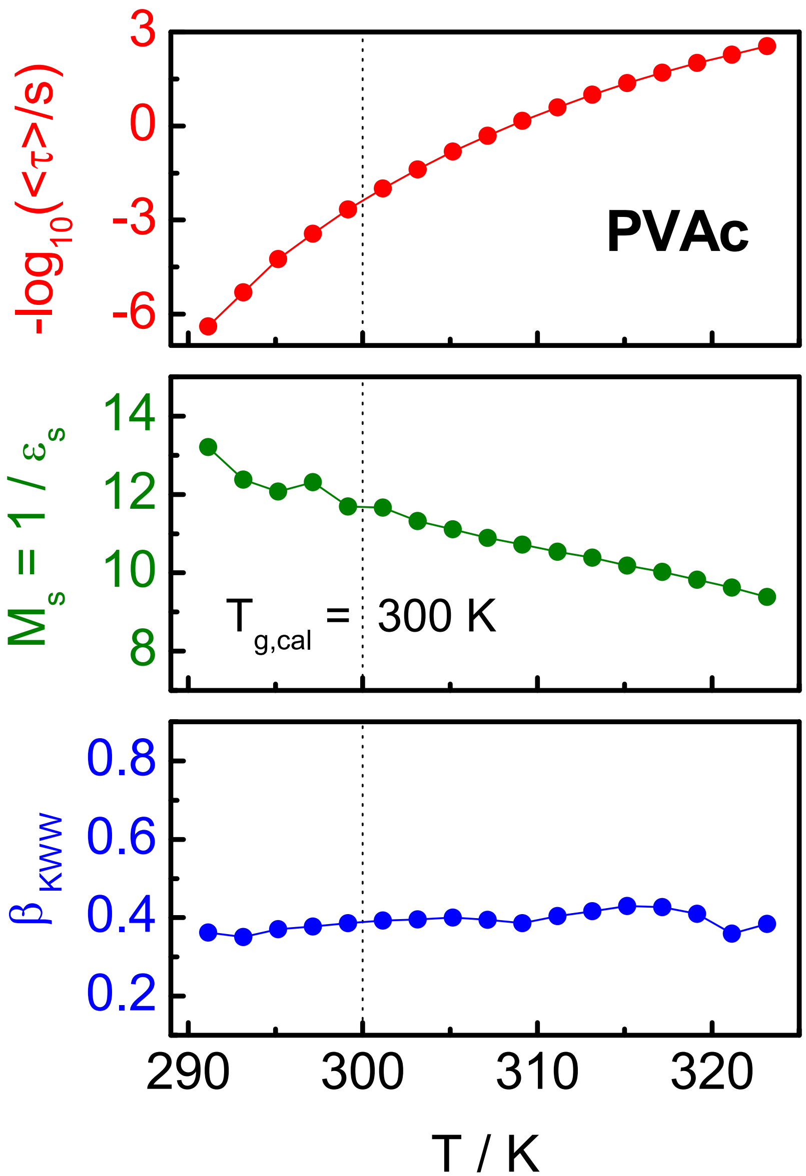
H. Wagner, R. Richert, Polymer 38 (1997) 255

Dynamics of Poly(vinyl acetate) across 16 Decades in Time



H. Wagner, R. Richert, Polymer 38 (1997) 255
H. Wagner, R. Richert, Polymer 38 (1997) 5801
R. Richert, Physica A 287 (2000) 26

Same Dynamics Above and Below '100s - T_g'

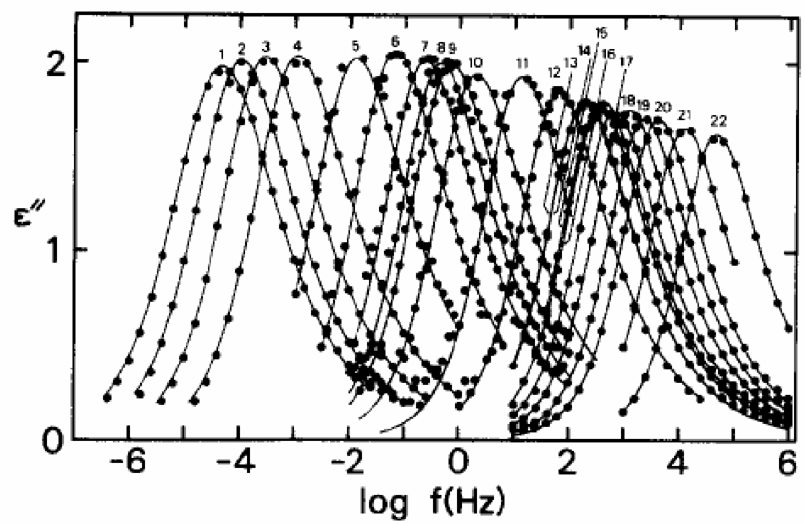


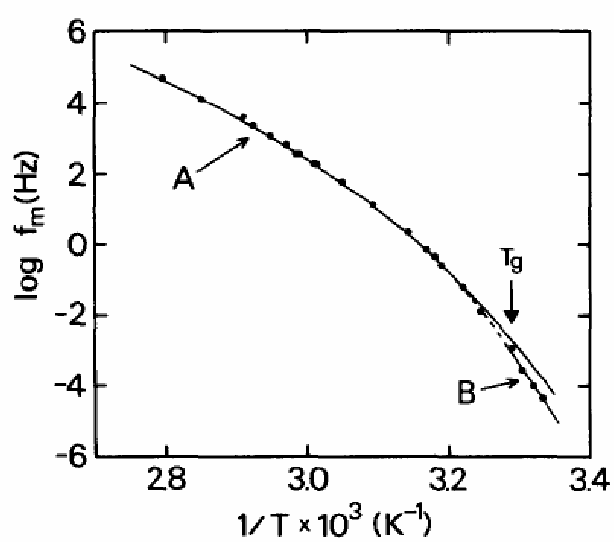
- T_g is purely kinetic
- all dipoles remain active
- time temperature superposition (TTS)

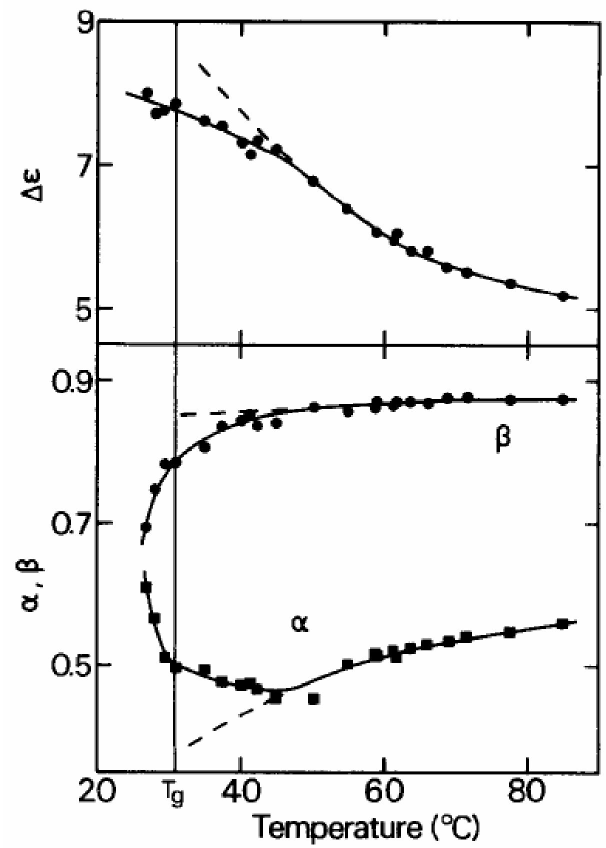
H. Wagner, R. Richert, Polymer 38 (1997) 255

Nozaki, Mashimo: poly(vinyl acetate) in the frequency range 10^{-6} - 10^{6} Hz

different dynamics above and below T_g ?



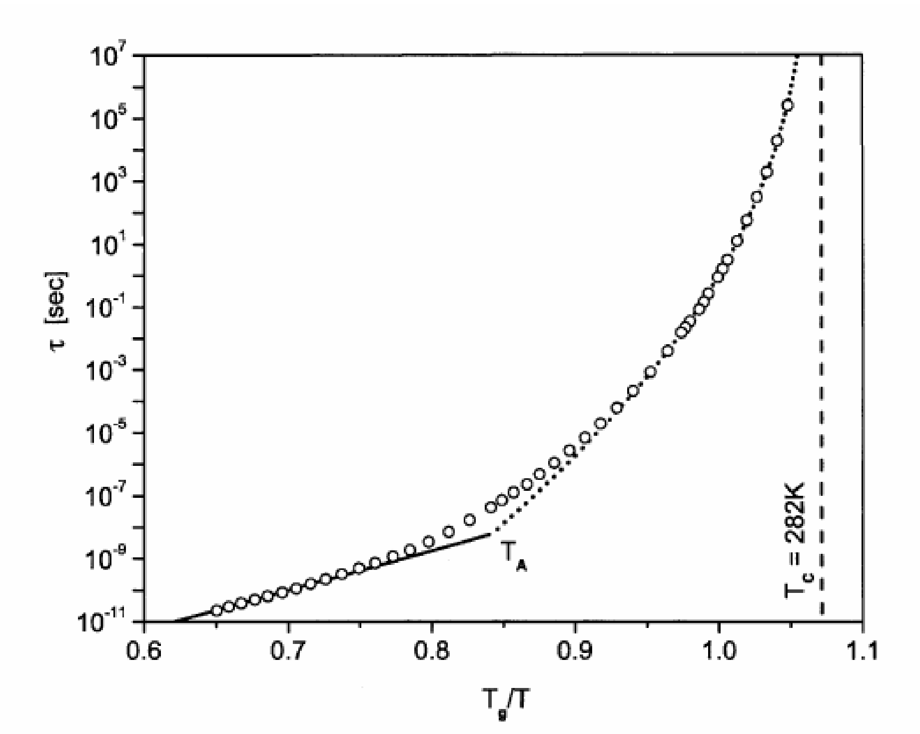




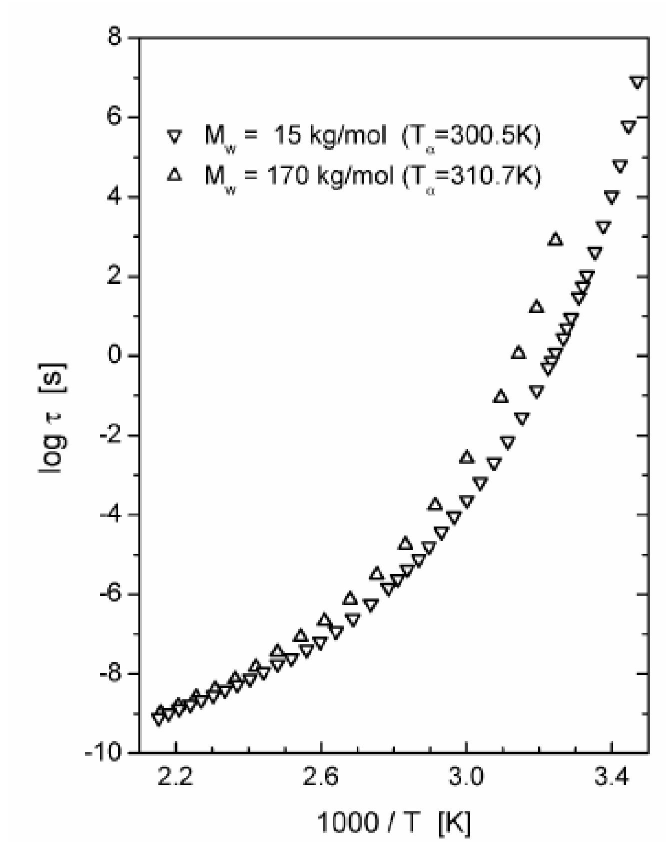
Dielectric relaxation measurements of poly(vinyl acetate) in glassy state in the frequency range 10^{-6}-10^{6} Hz
R. Nozaki, S. Mashimo, J. Chem. Phys. 87 (1987) 2271

Is Ultra-Long Relaxation Time Data Useful ?

Temperature dependence of relaxation times and the length scale of cooperative motion for glass-forming liquids
B. M. Erwin, R. H. Colby,
J. Non-Cryst. Solids 307-310 (2002) 225

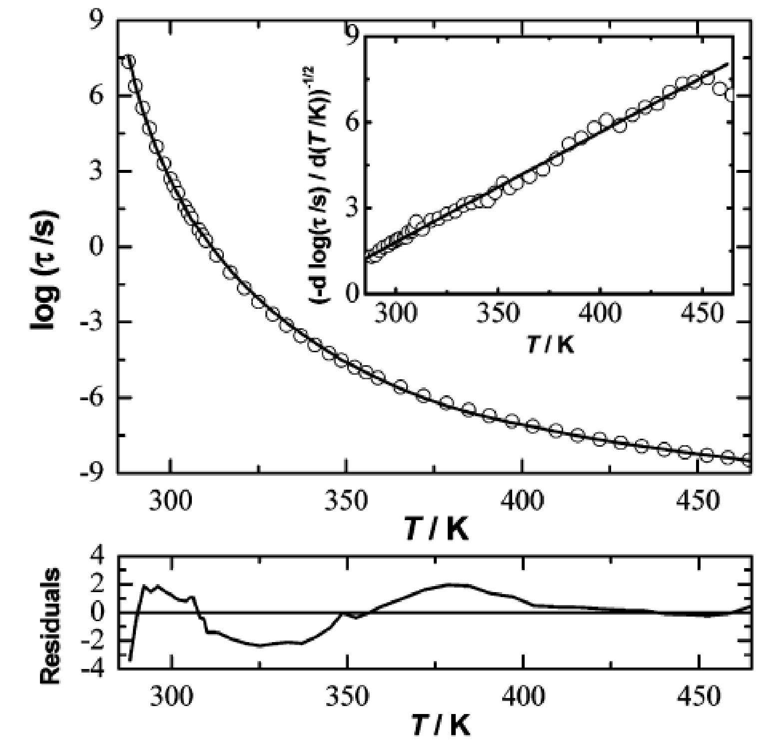


Temperature and volume effects on local segmental relaxation in poly(vinyl acetate)
C. M. Roland, R. Casalini,
Macromol. 36 (2003) 1361

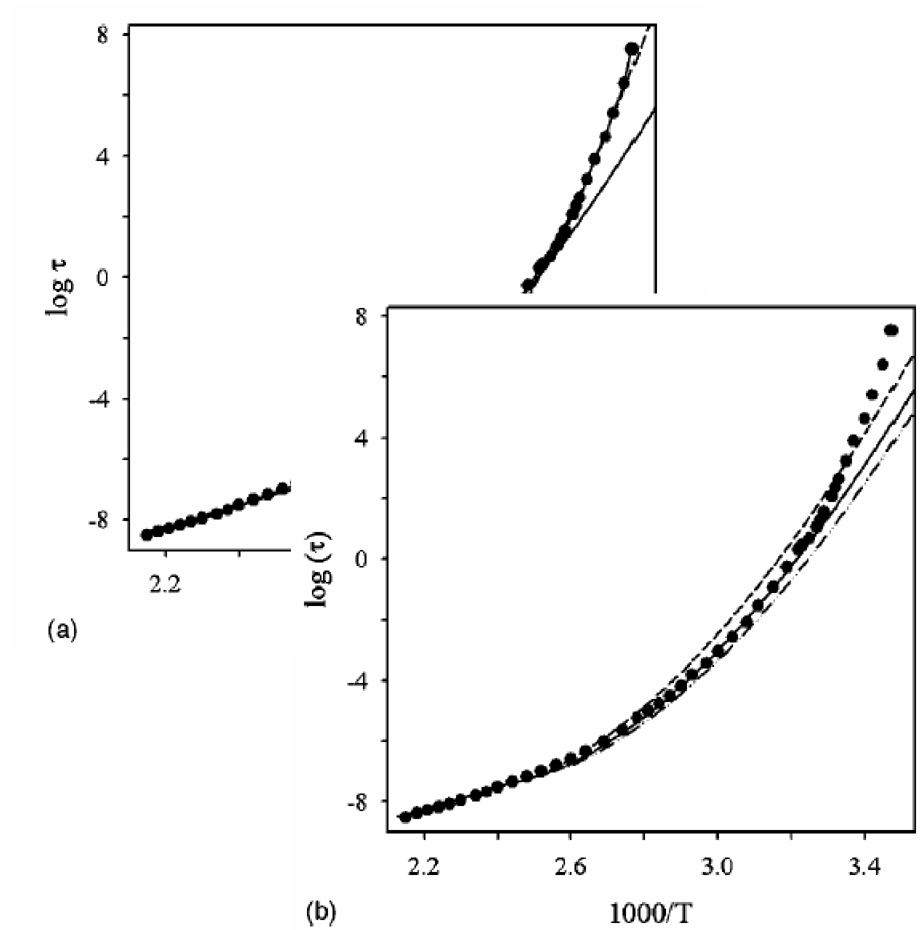


Is Ultra-Long Relaxation Time Data Useful ?

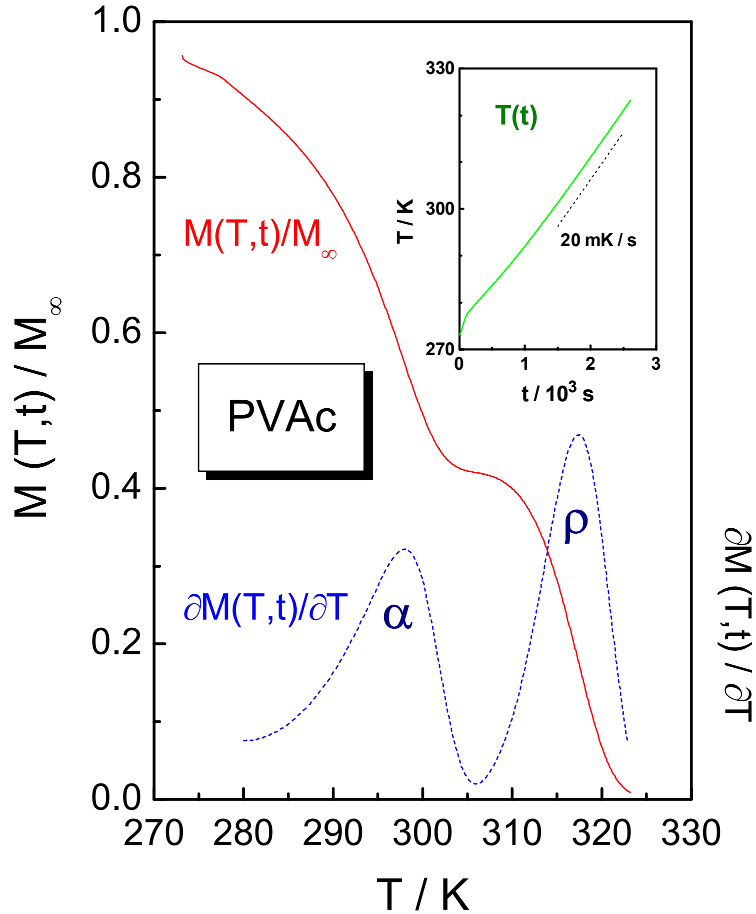
Data analysis with the Vogel-Fulcher-Tammann-Hesse equation
J. F. Mano, E. Pereira,
J. Phys. Chem. A 108 (2004) 10824

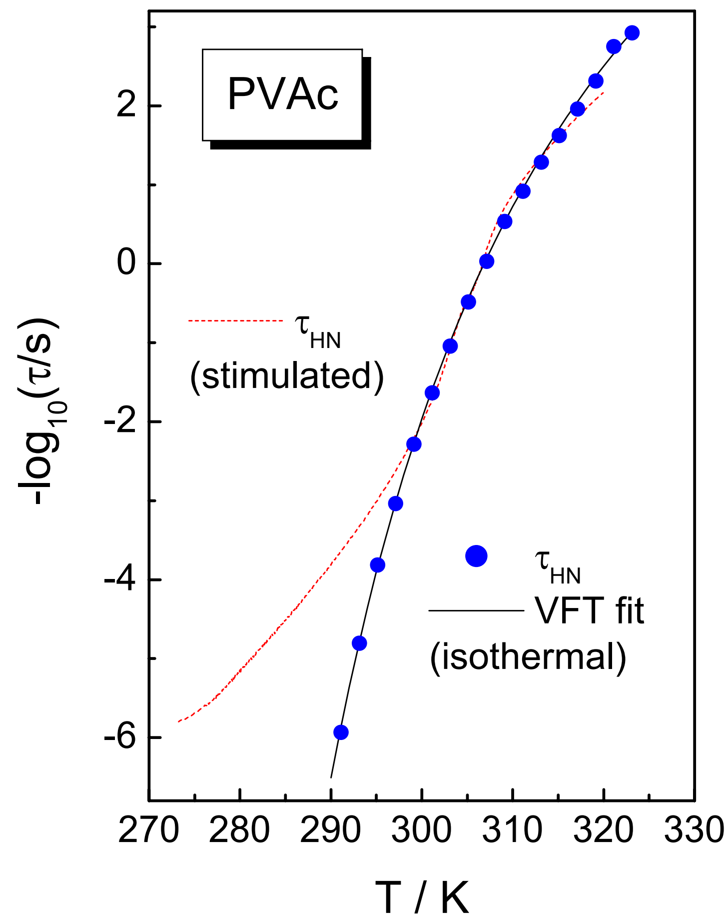


Universal scaling, dynamic fragility, segmental relaxation, and vitrification in polymer melts
E. J. Saltzman, K. S. Schweizer,
J. Chem. Phys. 121 (2004) 2001



Thermally Stimulated Modulus Relaxation

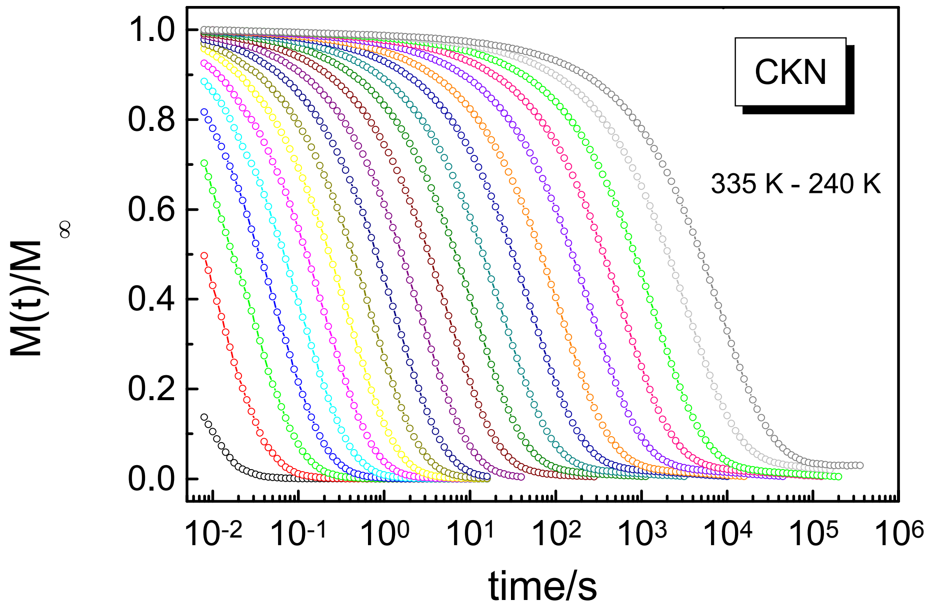




advantage: sample is cooled at zero field

H. Wagner, R. Richert, Polymer 38 (1997) 5801

Electric Modulus of Ionic Glasses



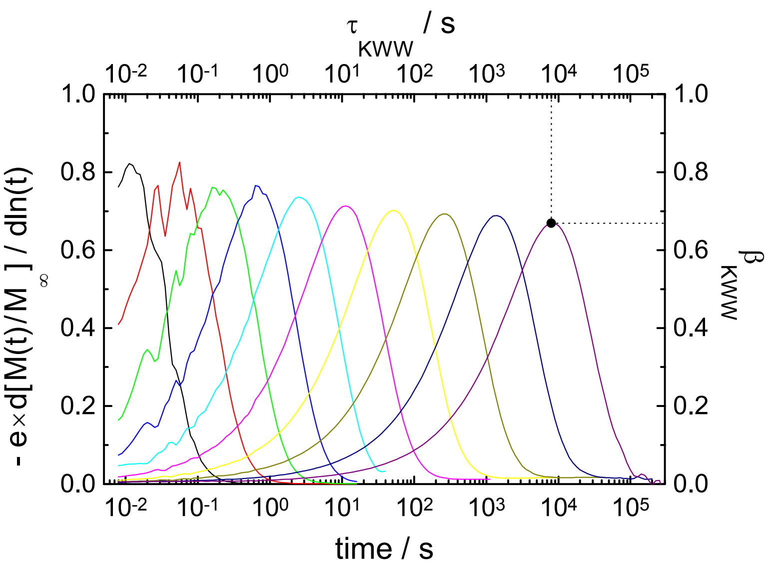
0.4 $Ca(NO_3)_2$ – 0.6 KNO_3

E_0 = 19 V

d = 66 μm

$$\sigma_s = \sigma(t \to \infty) = \frac{\varepsilon_o\, \varepsilon_\infty}{\langle \tau \rangle}$$

$$\langle \tau^n \rangle_{KWW} = \tau^n_{KWW} \frac{\Gamma(n/\beta_{KWW})}{\beta_{KWW}\Gamma(n)}$$

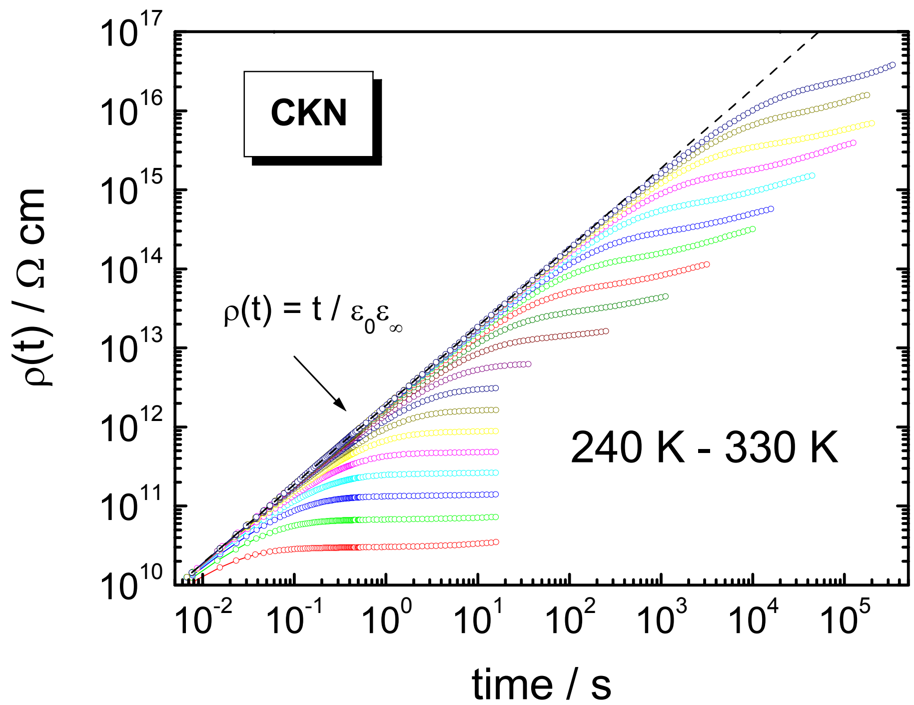


$$\left.\frac{d^2\Phi(t)}{d(\ln t)^2}\right|_{t=\tau_{KWW}} = 0$$

$$\left.\frac{d\Phi(t)}{d\ln t}\right|_{t=\tau_{KWW}} = -\frac{\beta_{KWW}}{e}$$

H. Wagner, R. Richert, J. Appl. Phys. <u>85</u> (1999) 1750

Electric Modulus of Ionic Glasses



$$\rho(t) = \frac{1}{\varepsilon_0 \varepsilon_\infty} \int_0^t \frac{M(t')}{M_\infty} dt'$$

$$\hat{\varepsilon} = \varepsilon' - i\varepsilon'' \qquad \leftarrow \hat{\sigma} = i\omega\varepsilon_0\hat{\varepsilon} \rightarrow \qquad \hat{\sigma} = \sigma' + i\sigma''$$

$$\uparrow \qquad\qquad \uparrow$$

$$\hat{M} = 1/\hat{\varepsilon} \qquad\qquad \hat{\rho} = 1/\hat{\sigma}$$

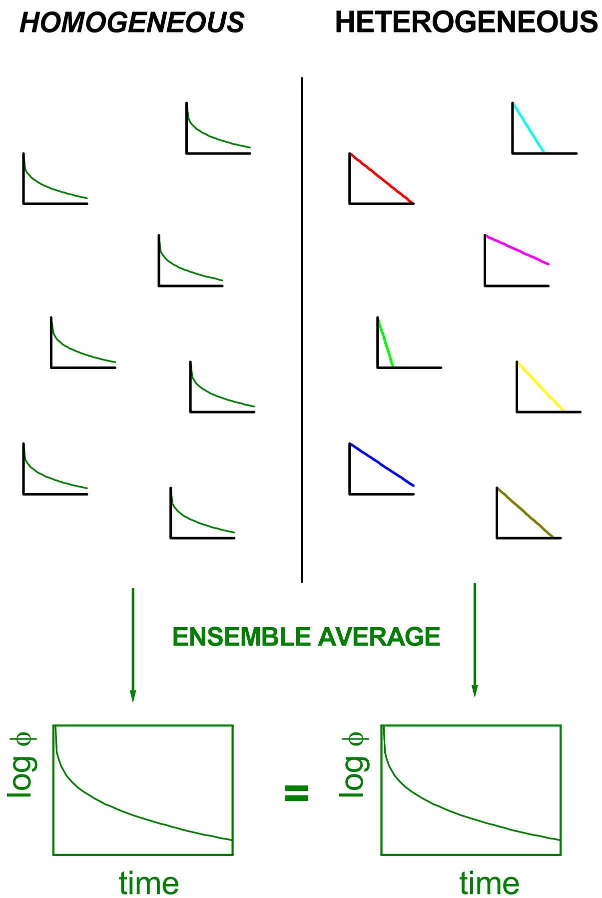
$$\downarrow \qquad\qquad \downarrow$$

$$\hat{M} = M' + iM'' \qquad \leftarrow \hat{\rho} = \hat{M} / i\omega\varepsilon_0 \rightarrow \qquad \hat{\rho} = \rho' - i\rho''$$

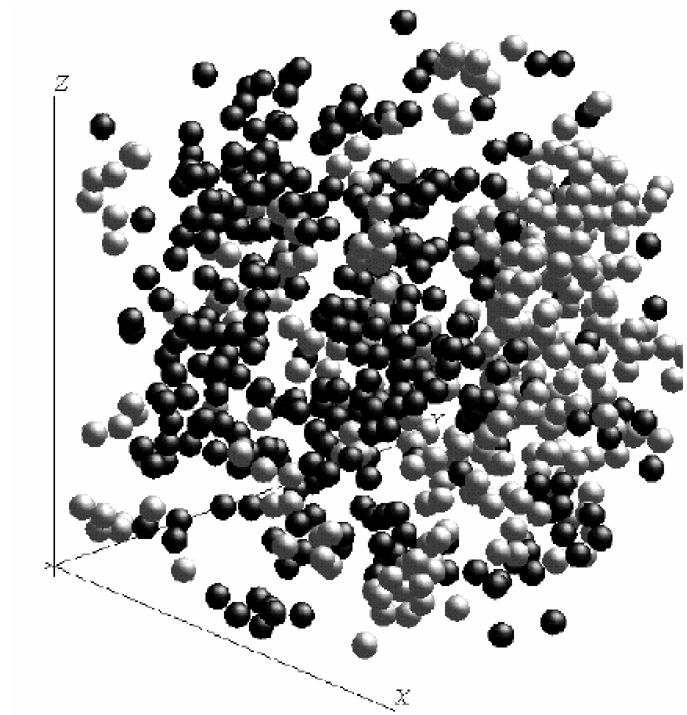
H. Wagner, R. Richert, J. Appl. Phys. 85 (1999) 1750

DIELECTRIC HOLE-BURNING EXPERIMENTS

Homogeneous versus heterogeneous dynamics



MD Simutation: Binary 80:20
Lennard-Jones Liquid



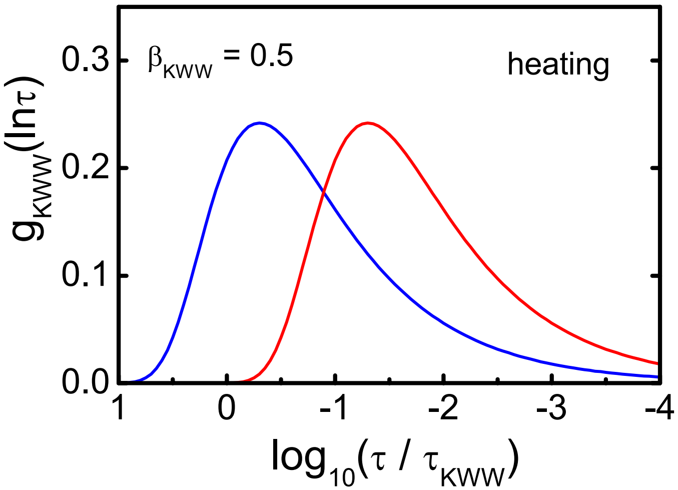
<u>dark:</u>
5 % least
mobile
particles

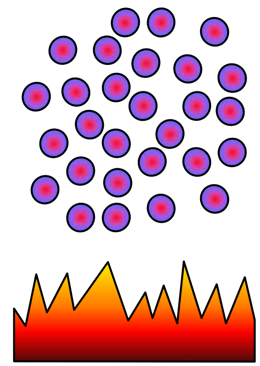
<u>light:</u>
5 % most
mobile
particles

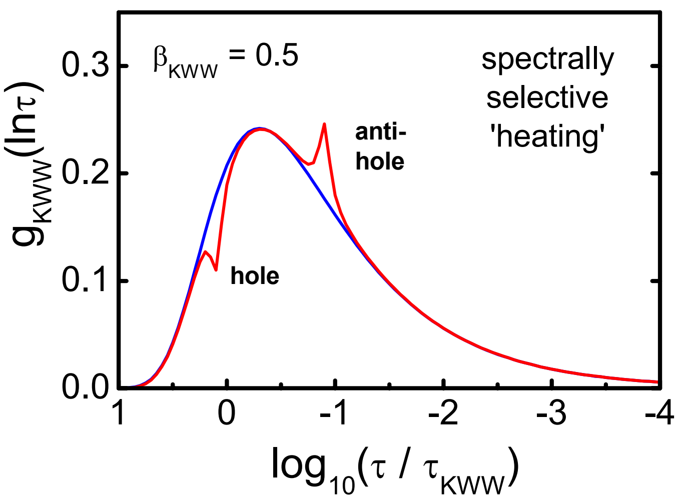
R. Richert, Chem. Phys. Lett. <u>216</u> (1993) 223

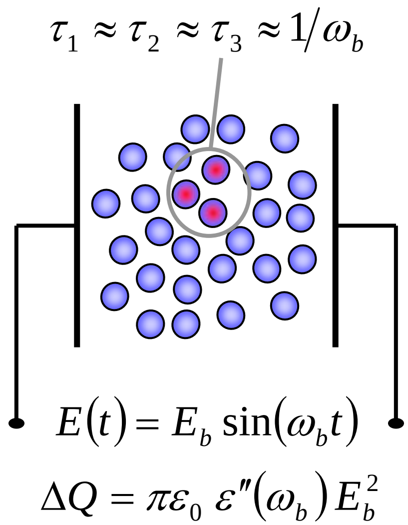
S.C. Glotzer, C. Donati, J. Phys.: Condens. Matter <u>11</u> (1999) A285

Spectrally selective dielectric experiments



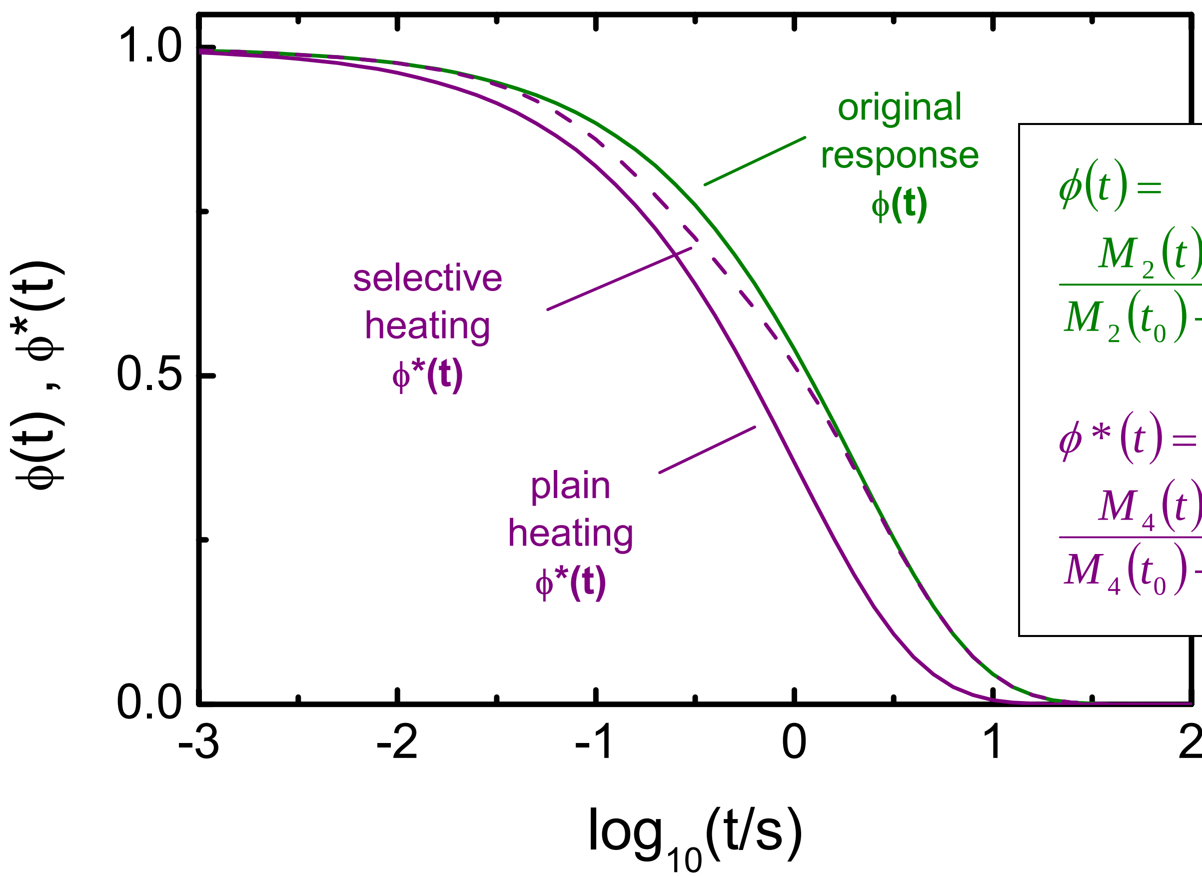






B. Schiener, R. Böhmer, A. Loidl, R.V. Chamberlin, Science 274 (1996) 752

Dielectric hole-burning technique: What do we look for?

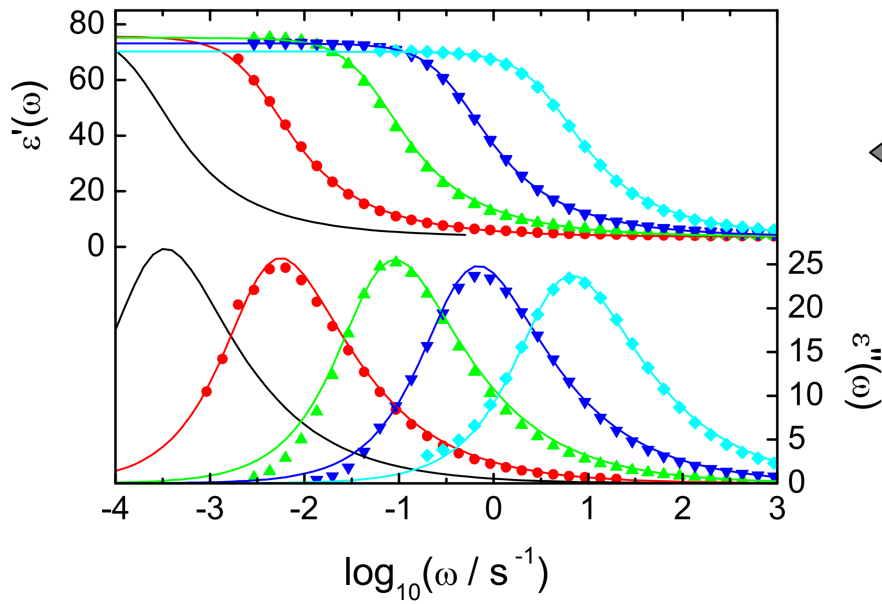


$$\phi(t) = \frac{M_2(t) - M_3(t) + M_8(t) - M_9(t)}{M_2(t_0) - M_3(t_0) + M_8(t_0) - M_9(t_0)}$$

$$\phi^*(t) = \frac{M_4(t) - M_5(t) + M_6(t) - M_7(t)}{M_4(t_0) - M_5(t_0) + M_6(t_0) - M_7(t_0)}$$

Dielectric relaxation and retardation in viscous glycerol

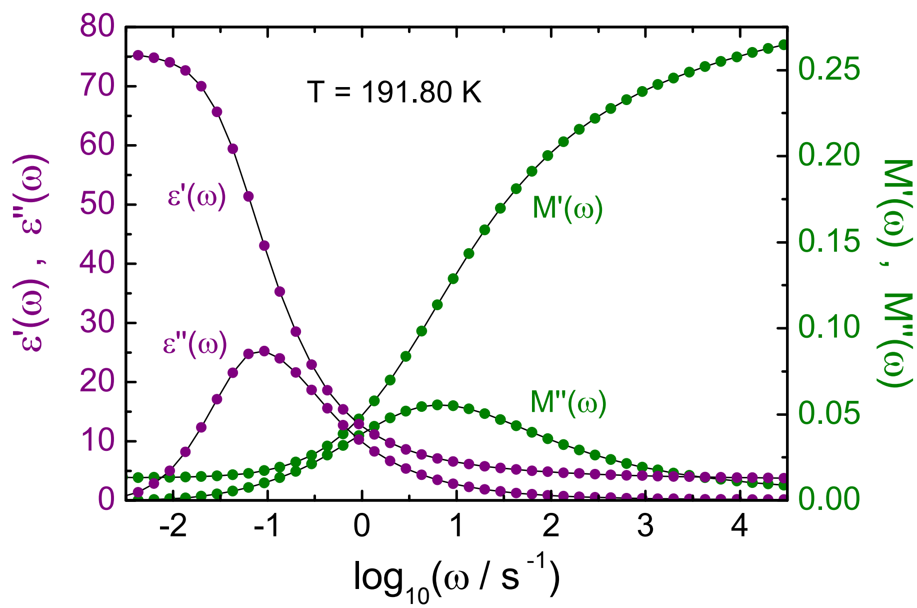
sample thickness: 6.4 μm



frequency domain data ε*(ω,T)

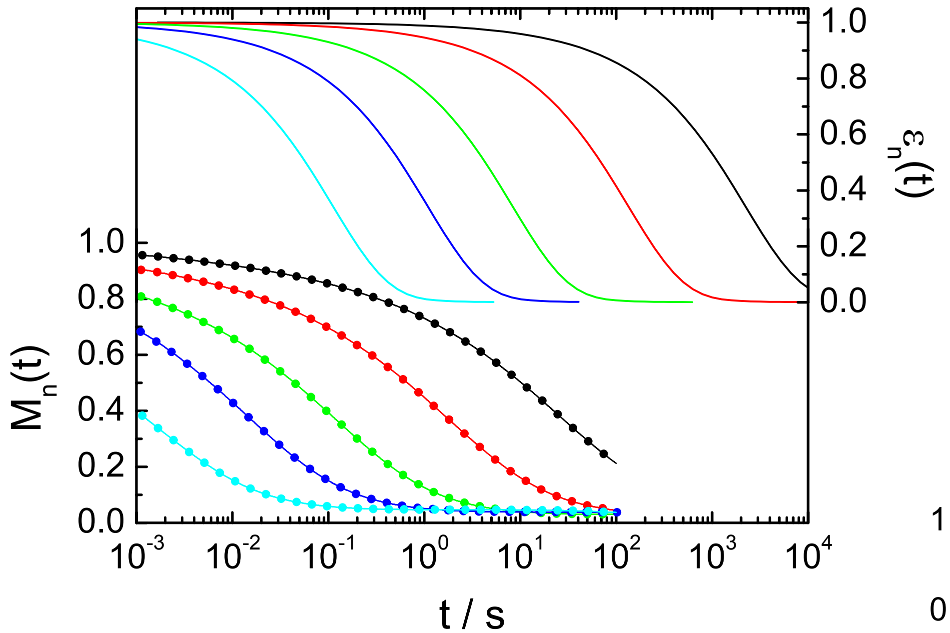
T = 183.50 K
T = 187.30 K
T = 191.80 K
T = 195.80 K
T = 200.50 K

ε*(ω) **versus** ***M*(ω)***



K. Duvvuri, R. Richert, J. Chem. Phys. 118 (2003) 1356

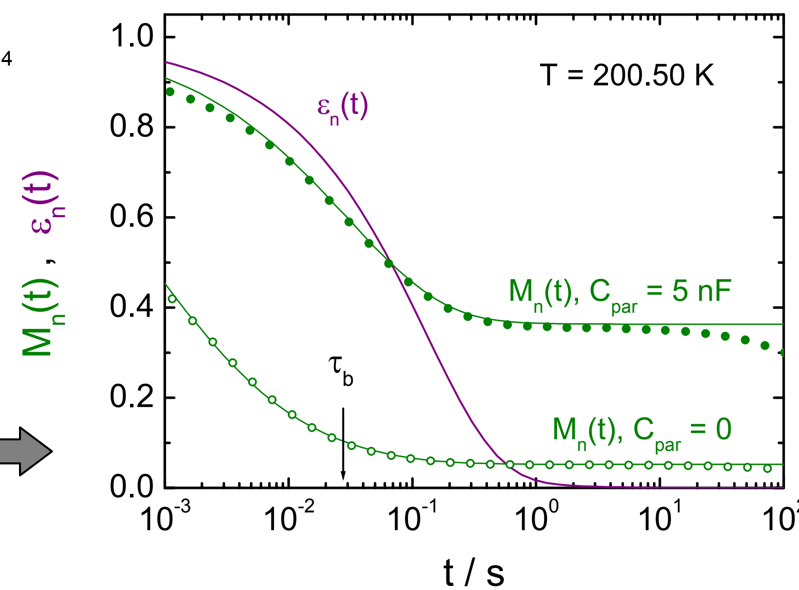
Exploiting M(t) for high frequency hole-burning



$$\tau_M \approx \frac{1}{80} \times \tau_\varepsilon$$

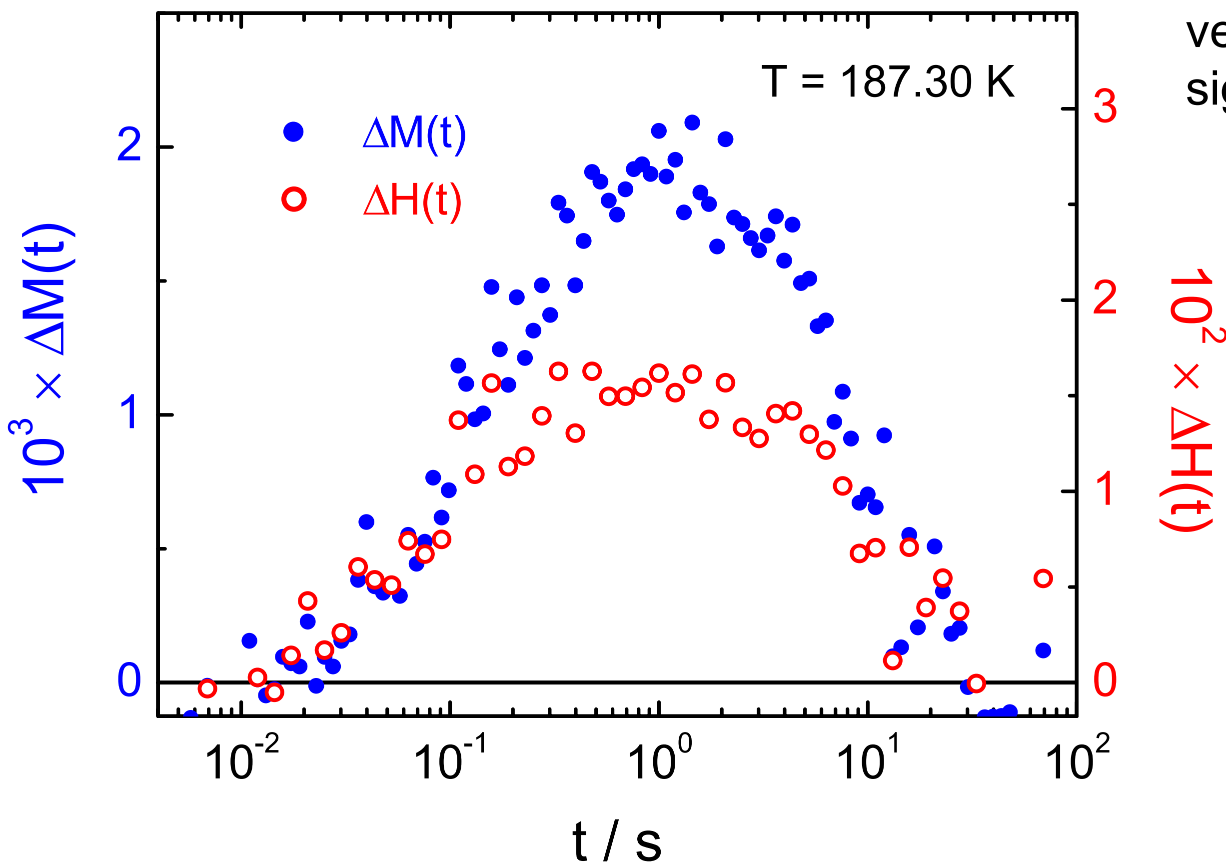
variable τ: $\tau_M \ldots \tau_\varepsilon$
using parallel capacitance

$$\frac{\tau_M}{\tau_\varepsilon} \approx \frac{\varepsilon_\infty}{\varepsilon_s} \rightarrow \frac{\varepsilon_\infty + \varepsilon_{par}}{\varepsilon_s + \varepsilon_{par}} \rightarrow 1$$



K. Duvvuri, R. Richert, J. Chem. Phys. 118 (2003) 1356

DHB results for glycerol: Vertical and horizontal differences

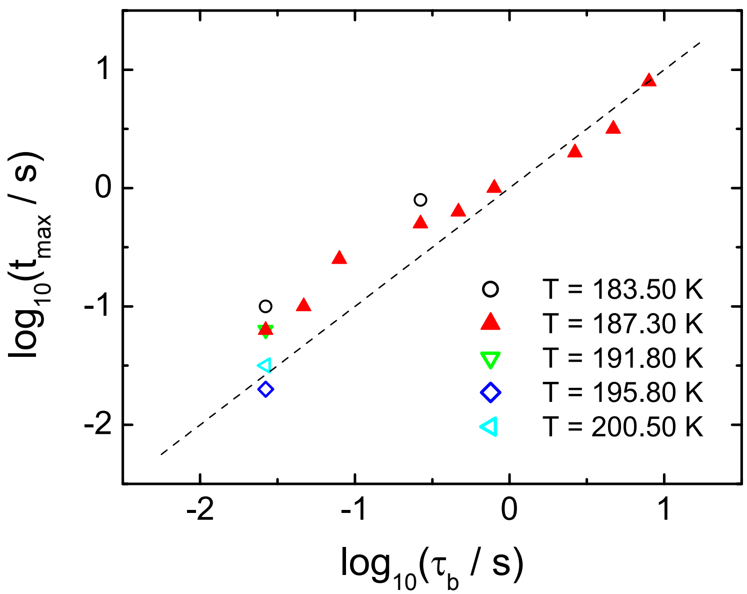


vertical & horizontal signal at:

n = 6
t_w = 1s
f_b = 0.2 Hz
V_b = 90 V
E_b = 140 kV/cm
T = 187.30 K

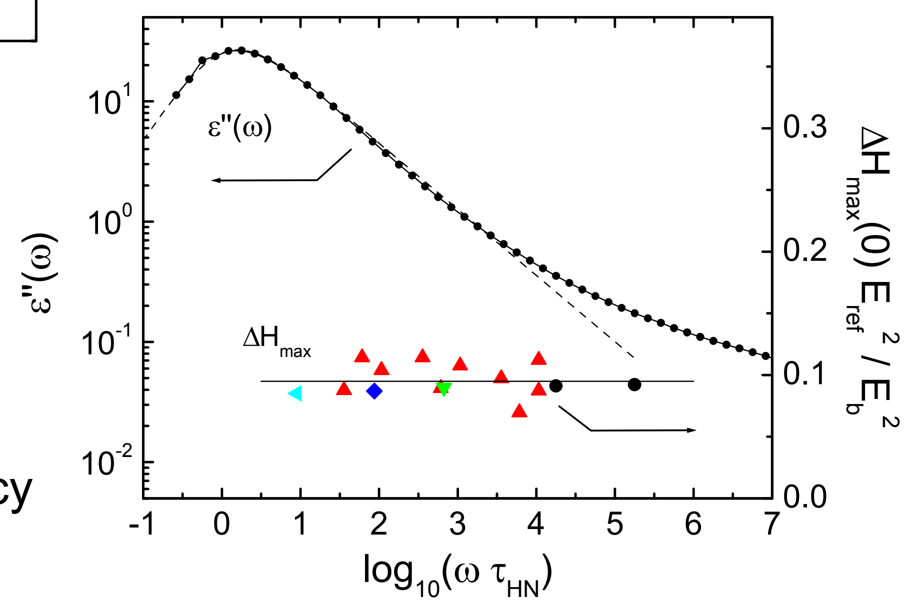
K. Duvvuri, R. Richert, J. Chem. Phys. 118 (2003) 1356

DHB results for glycerol: Burn-frequency dependence



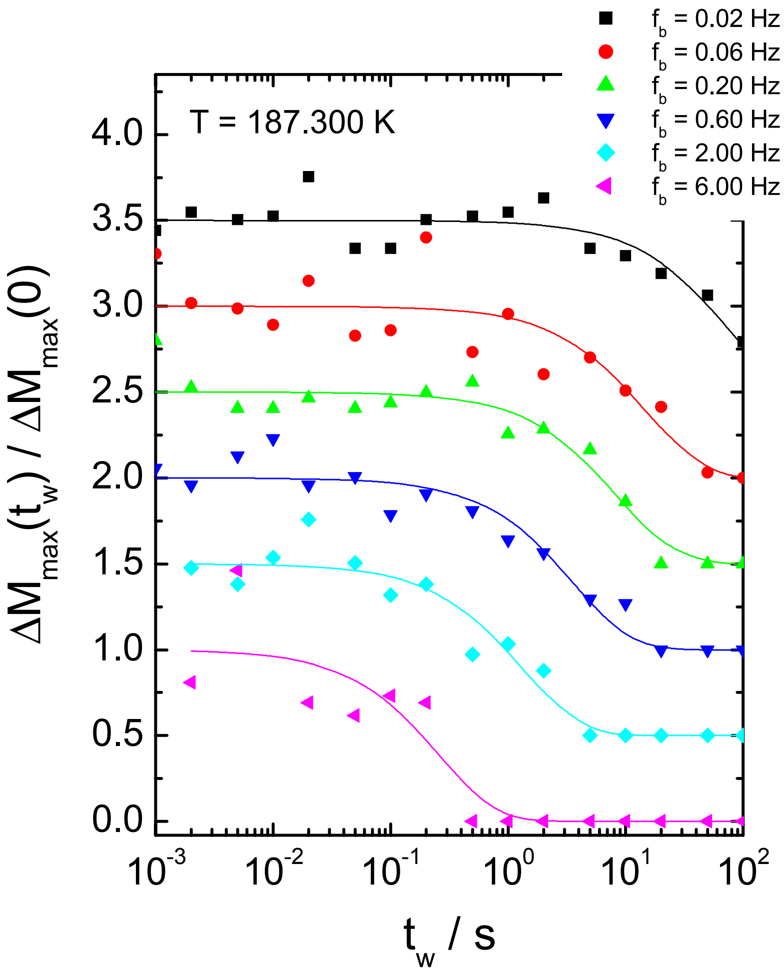
position of vertical hole
versus
burn frequency

amplitude of horizontal hole
versus
relative burn frequency



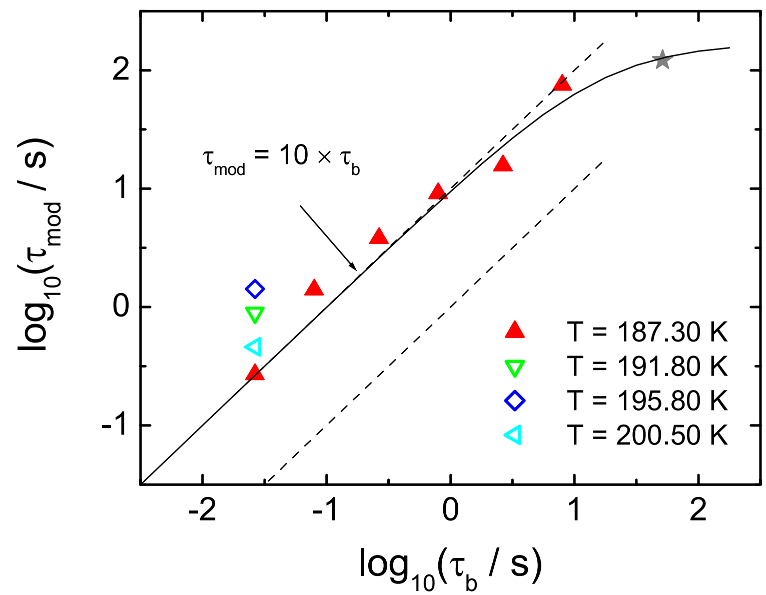
K. Duvvuri, R. Richert, J. Chem. Phys. 118 (2003) 1356

DHB results for glycerol: Waiting-time dependence



pump - wait - probe
t_w

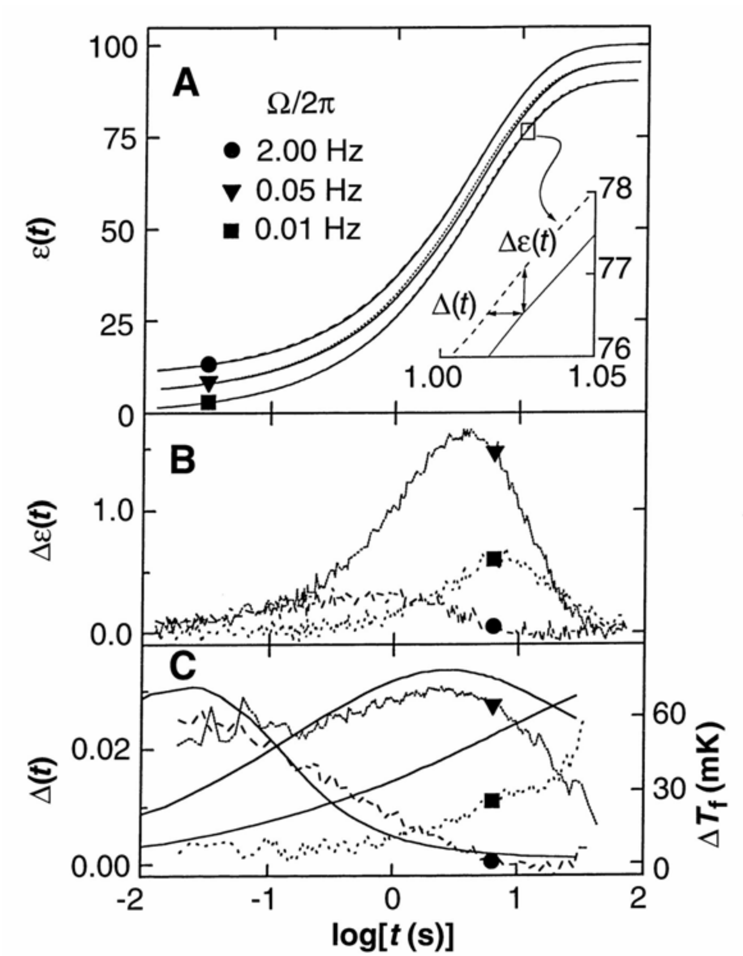
$$\frac{\Delta M_{\max}(t_w)}{\Delta M_{\max}(0)} = \exp\left(-\frac{t_w}{\tau_{\mathrm{mod}}}\right)$$

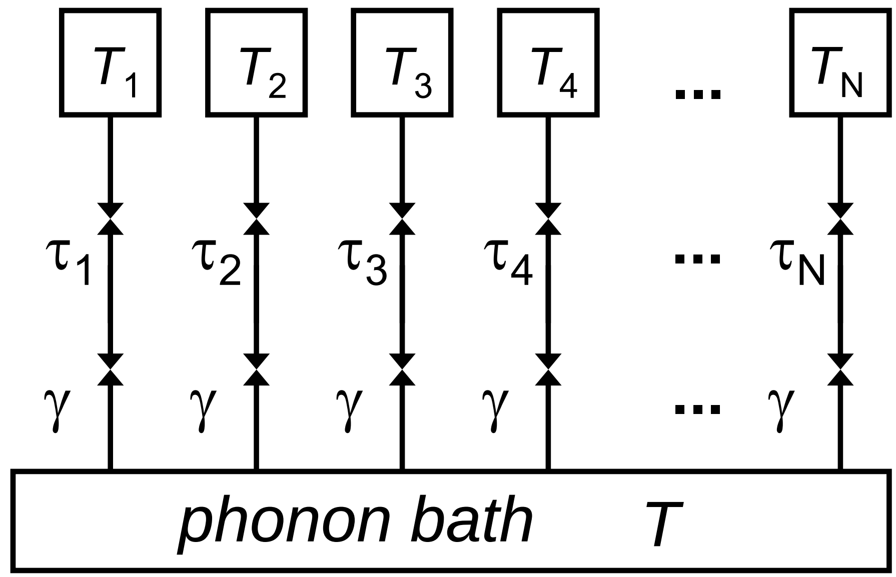


K. Duvvuri, R. Richert, J. Chem. Phys. 118 (2003) 1356

DIELECTRIC HOLE-BURNING MODEL

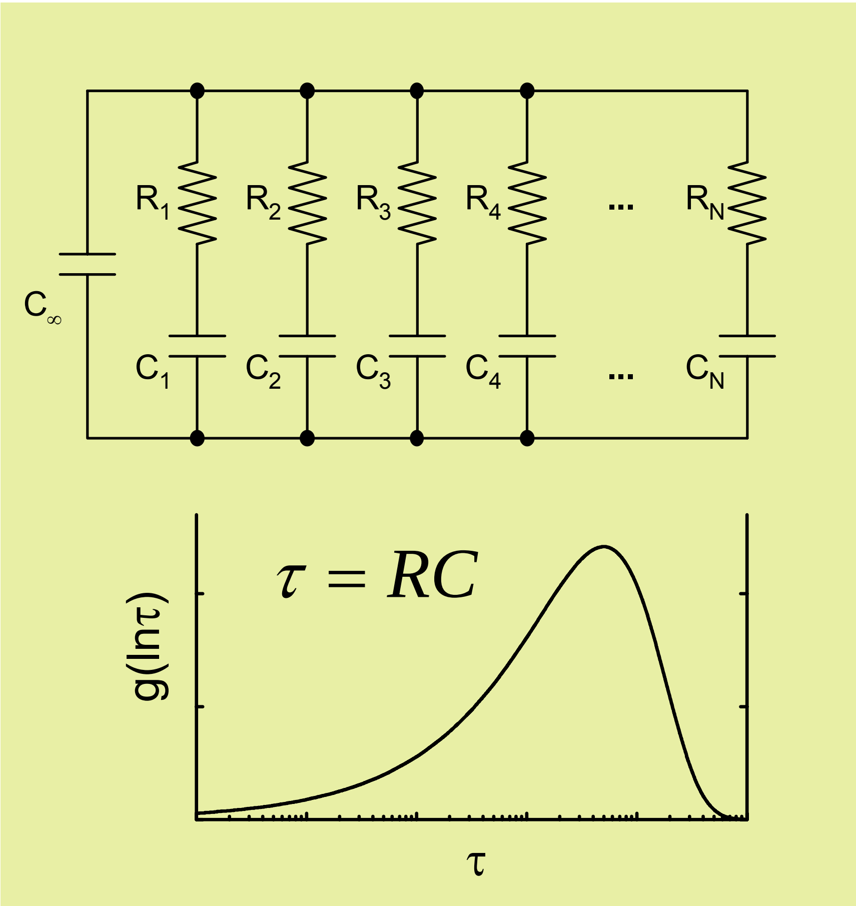
Original observation and 'box-model'





B. Schiener, R. Böhmer, A. Loidl, R. V. Chamberlin, Science 274 (1996) 752
B. Schiener, R. V. Chamberlin, G. Diezemann, R. Böhmer, J. Chem. Phys. 107 (1997) 7746
R. V. Chamberlin, B. Schiener, R. Böhmer, Mat. Res. Soc. Symp. Proc. 455 (1997) 117

Calculation of energy loss (heating) for RC network



$$\frac{dV_C(t)}{dt} = \frac{V_X(t) - V_C(t)}{RC}, \; V_C(t<0) = 0$$

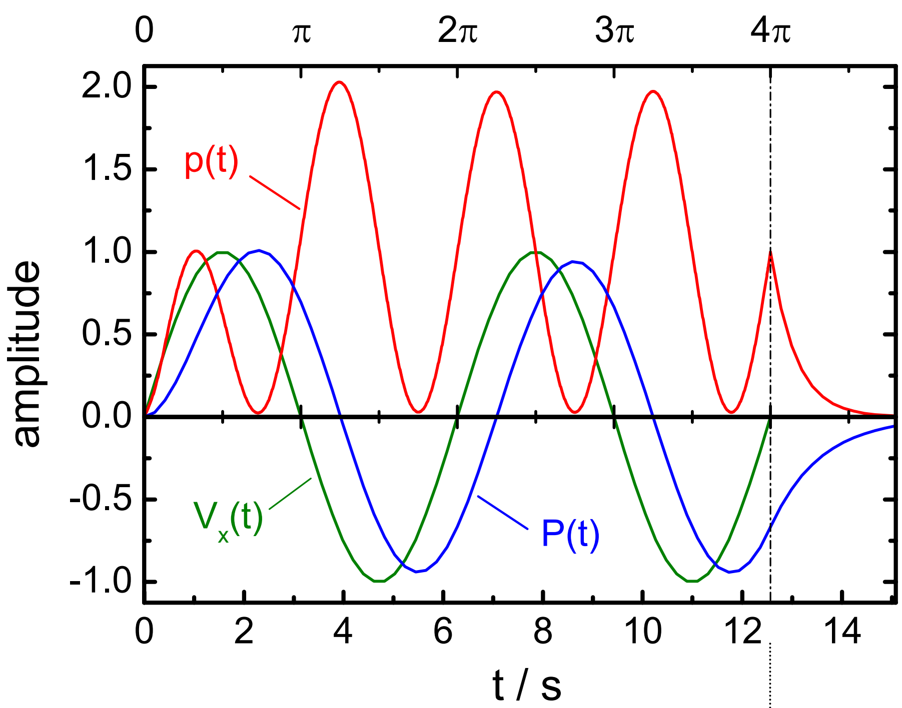
$$P(t) = \frac{Q(t)}{A} = C\frac{V_C(t)}{A}$$ polarization

$$p(t) = V_R(t) I_R(t) = \frac{V_R^2(t)}{R}$$ power

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + \Delta\varepsilon \frac{1}{C_{geo}} \left[C_\infty + \sum_{i=1}^{N} C_i \frac{1}{1 + i\omega R_i C_i} \right]$$

R. Richert, Physica A <u>322</u> (2003) 143

Calculation of heating p(t) for RC network



$$0 \le t \le n2\pi/\omega_b \qquad t > n2\pi/\omega_b$$

previous steady state case:

$$q_{eq} = \pi\varepsilon_0 \upsilon E_0^2 \varepsilon''(\omega_b)$$

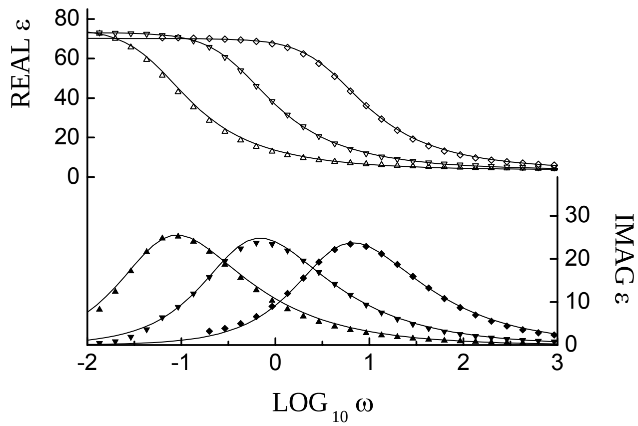
$$0 \le t \le n2\pi/\omega_b$$

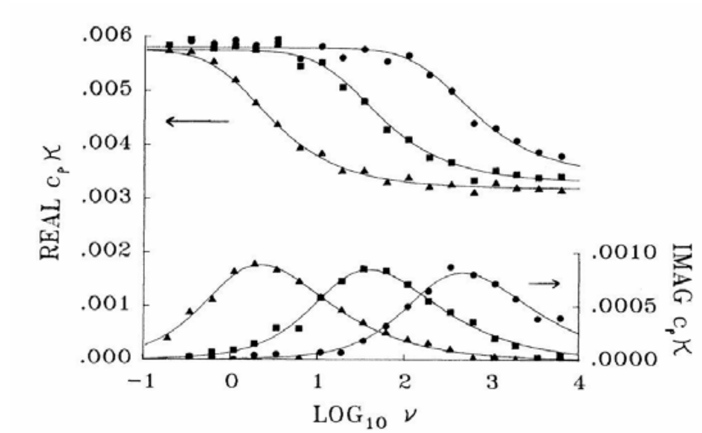
$$E_x(t) = \begin{cases} E_0 \sin(\omega_b t) & , \quad 0 \le t \le n2\pi/\omega_b \\ 0 & , \quad \text{otherwise} \end{cases}$$

$$p(t) = \frac{\varepsilon_0 \upsilon E_0^2 \varepsilon''(\omega_b)\omega_b}{1+\omega_b^2\tau^2} \times \begin{cases} \left[\omega_b\tau\sin(\omega_b t) + \cos(\omega_b t) - \exp(-t/\tau)\right]^2 & , \quad 0 \le t \le n2\pi/\omega_b \\ \left[1-\exp(n2\pi/\omega_b\tau)\right]^2 \exp(-2t/\tau) & , \quad t > n2\pi/\omega_b \end{cases}$$

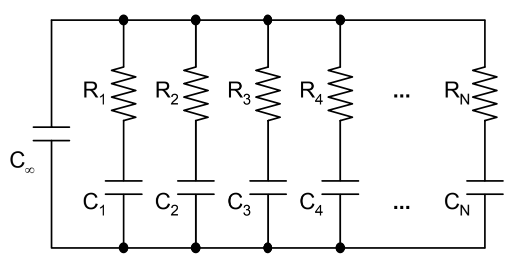
R. Richert, Physica A 322 (2003) 143

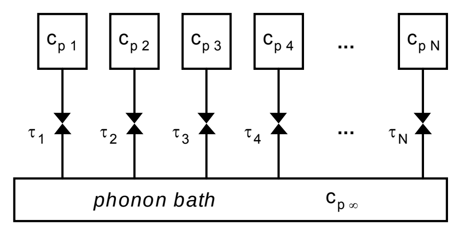
Dielectric and thermal relaxation times in glycerol

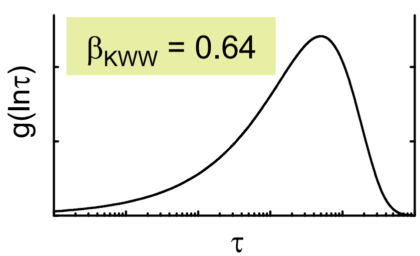




N. O. Birge, S. R. Nagel, Phys. Rev. Lett. 54 (1985) 2674







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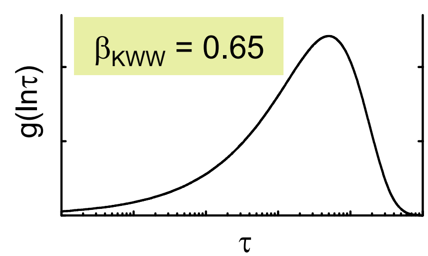
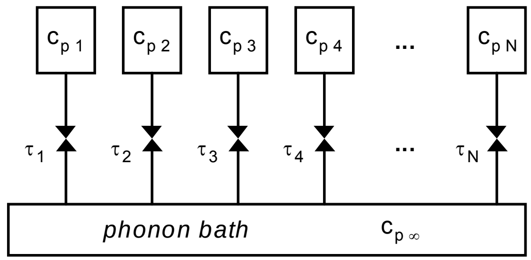
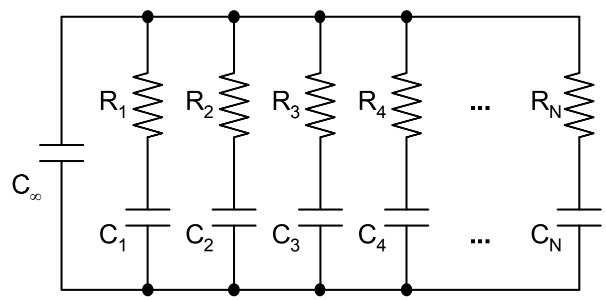
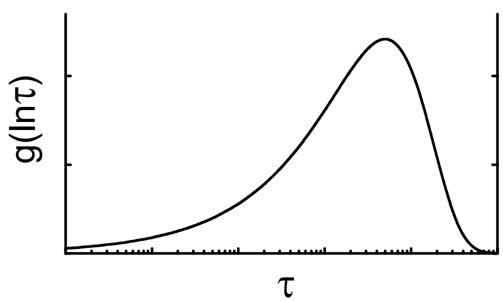


K. Schröter and E. Donth, J. Chem. Phys. 113 (2000) 9101

Only one step further: Tau's are locally correlated







$$\Delta c_p = 1.5\,\mathrm{JK^{-1}cm^{-3}}$$

$$E_A^{eff} = \frac{\partial \ln \tau}{\partial (1/T)} = 2\times 10^4\ \mathrm{K}$$

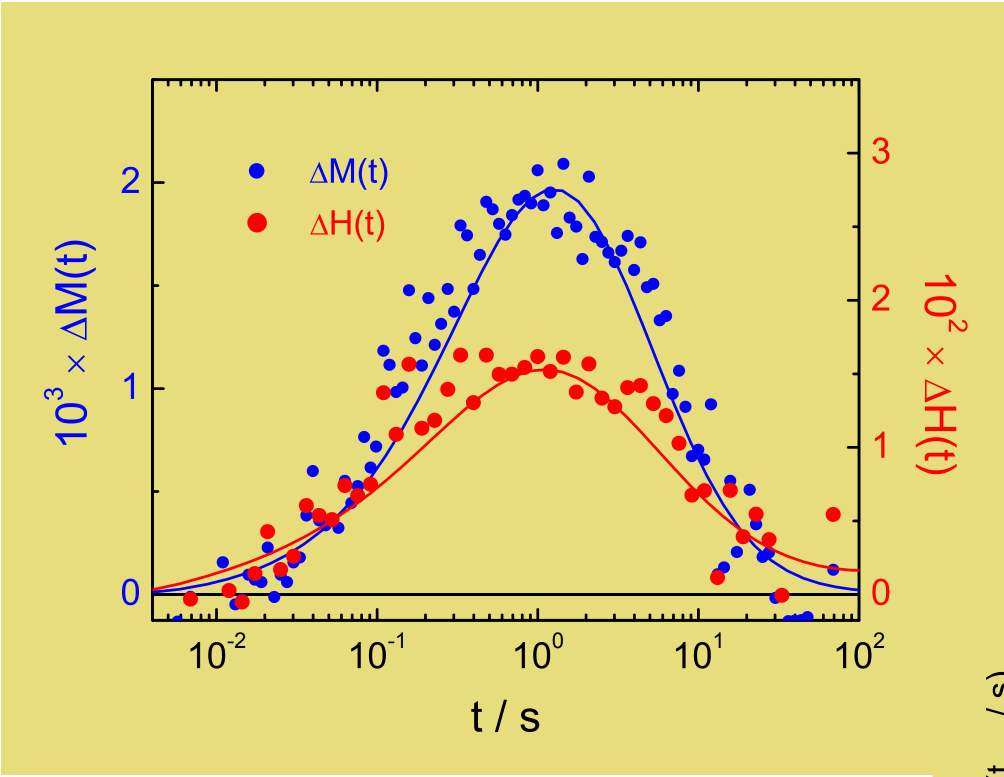
$$\varepsilon_\infty = 3.7, \varepsilon_s = 75.7$$

$$\alpha_{HN} = 0.95, \gamma_{HN} = 0.58, \tau_{HN} = 285\,\mathrm{s}$$

Model:
locally correlated structural and
thermal relaxation time heterogeneity

K.R. Jeffrey, R. Richert, K. Duvvuri, J. Chem. Phys. 119 (2003) 6150

DHB in glycerol: Calculated vs. measured results



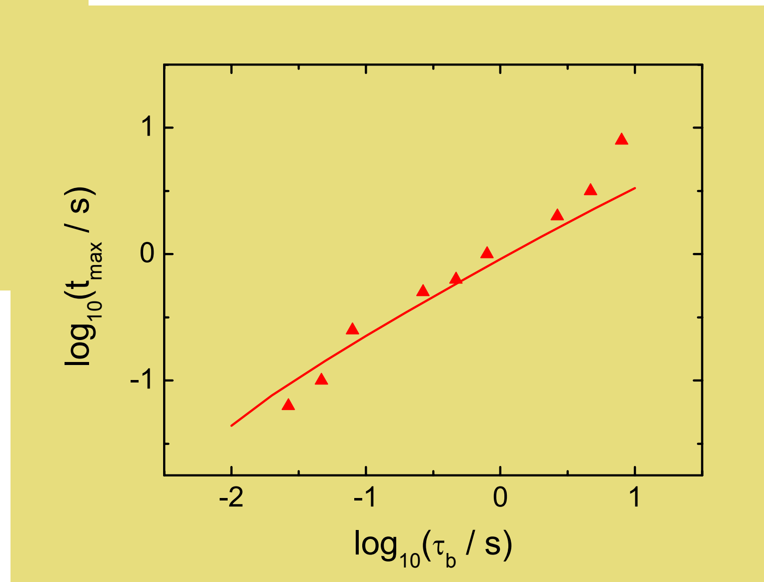
vertical & horizontal signal at n = 6

t_w = 1s

f_b = 0.2 Hz

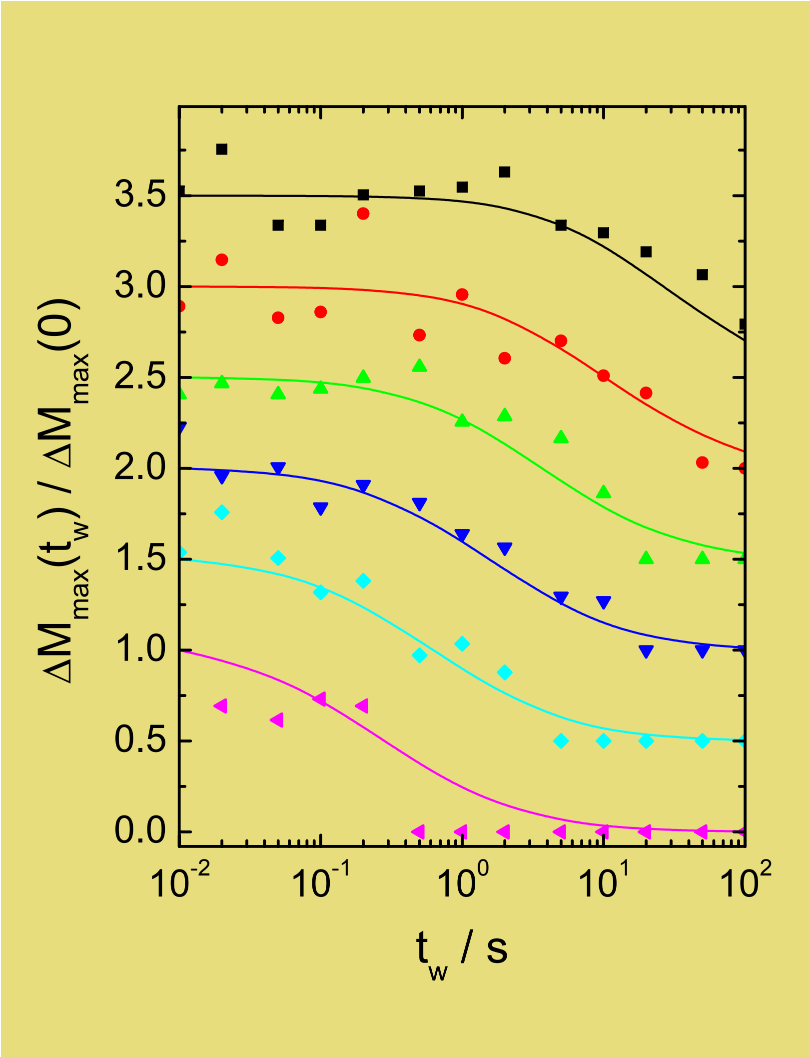
V_b = 90 V

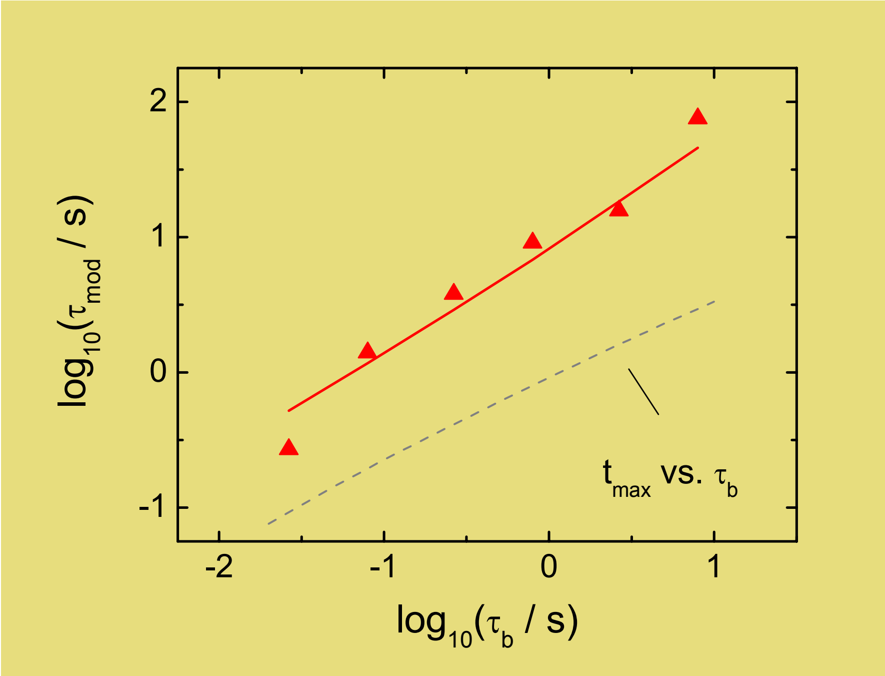
E_b = 140 kV/cm



K.R. Jeffrey, R. Richert, K. Duvvuri, J. Chem. Phys. 119 (2003) 6150

DHB in glycerol: Calculated vs. measured results





K.R. Jeffrey, R. Richert, K. Duvvuri, J. Chem. Phys. 119 (2003) 6150

Summary

- standard impedance: $\varepsilon^*(\omega)$ from 10^{-3} Hz to 10^{7} Hz yields dynamics with high resolution
- modulus shifts time by a factor of $\tau_M \approx (\varepsilon_\infty / \varepsilon_s)^{1/x} \tau_\varepsilon$
- dielectric modulus is a directly measurable quantity: time constants of > 1 y are accessible
- thermally stimulated M(t) uses low fields only
- shows kinetic nature of T_g, advantageous for discriminating various models of relaxations

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Hermann Wagner
Franz Stickel

Deutsche Forschungsgemeinschaft
Sonderforschungsbereich 262 (Mainz)

Kalyan Duvvuri
Susan Weinstein

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ACS/PRF - 42364-AC7