Fractional approaches to dielectric broadband spectroscopy

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Dielectric Broadband Spectroscopy

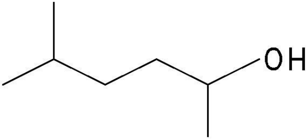
- Use composite fractional time evolution to describe dielectric spectroscopy data of glasses.
- Modified Debye relaxation equation with fractional derivatives
- Fitting with only 3/4 parameters

Fractional Calculus

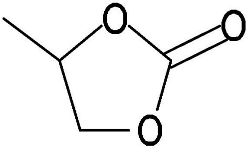
- Solution to modifed Debye relaxation equation
- Fractional differential equation (FDE) is solved directly.

Dielectric Broadband Spectroscopy

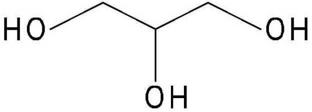
Dielectric Relaxation in Glasses



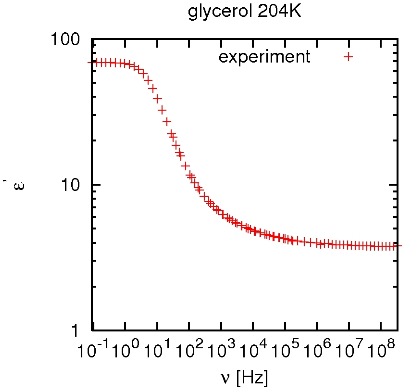
(a) 5-methyl-2-hexanol

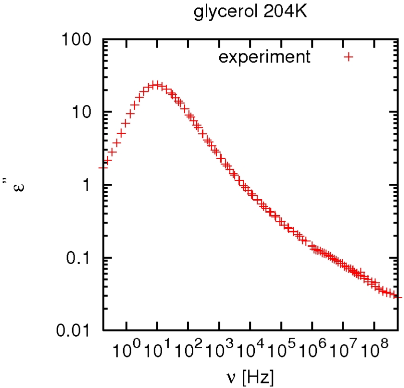


(b) propylene carbonate



(c) glycerol





data: Loidl, Phys. Rev. E **59** 6924, (1999)

Fit Models

normalised relaxation function e.g. polarisation

$$f(t) = \Phi(t)/\Phi(0)$$

Debye:

$$\tau \frac{d}{dt} f(t) + f(t) = 0, f(0) = 1 \qquad f(t) = e^{-t/\tau}$$

$$\mathscr{L}\left\{f(t)\right\}(u) = \int_0^\infty e^{-ut} f(t)\, dt$$

normalised complex dielectric susceptibility:

$$\chi(u) = 1 - u\mathscr{L}\left\{f(t)\right\}(u)$$

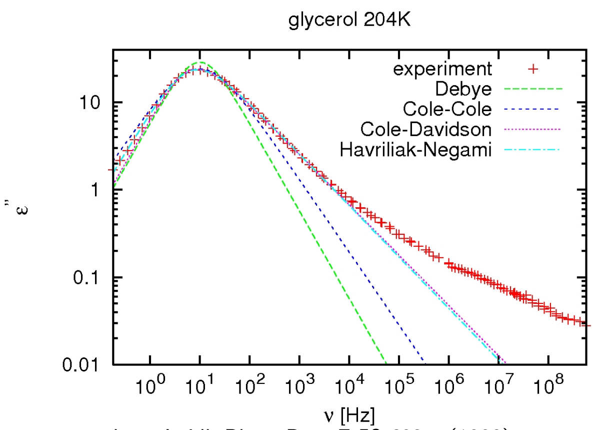
$$\chi(u) = \frac{1}{1+u\tau} = \frac{\hat{\chi}(u) - \hat{\chi}_\infty}{\hat{\chi}(0) - \hat{\chi}_\infty}$$

$$u = 2\pi i \nu$$

Fit Models

Debye:	$\chi(u) = \frac{1}{1+u\tau}$	$n_{\mathrm{param}} = 1$
Cole-Cole:	$\chi(u) = \frac{1}{1+(u\tau)^{\alpha}}$	$n_{\mathrm{param}} = 2$
Cole-Davidson:	$\chi(u) = \frac{1}{(1+u\tau)^{\gamma}}$	$n_{\mathrm{param}} = 2$
Havriliak-Negami [1]:	$\chi(u) = \frac{1}{[1+(u\tau)^{\alpha}]^{\gamma}}$	$n_{\mathrm{param}} = 3$

[1] Havriliak, Negami, Polymer **8** (4) 161, (1967)



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- Excess wing cannot be fitted with one function.
- superposition (Havriliak-Negami + Cole-Davidson ⇒ 6 fit parameters)

Fractional Relaxation Model

Apply the idea of composite fractional time evolution [Hilfer, Chem. Phys. **284** 399-408, (2002)]

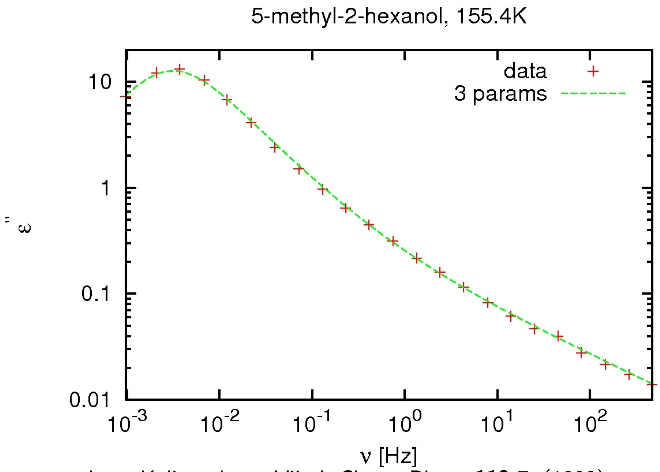
Modified relaxation equations:

$$\begin{aligned} \tau_1 Df(t) + \tau_2^{\alpha} D^{\alpha} f(t) + f(t) &= 0 \\ \tau_1 Df(t) + \tau_1^{\alpha_1} D^{\alpha_1} f(t) + \tau_2^{\alpha_2} D^{\alpha_2} f(t) + f(t) &= 0 \end{aligned}$$

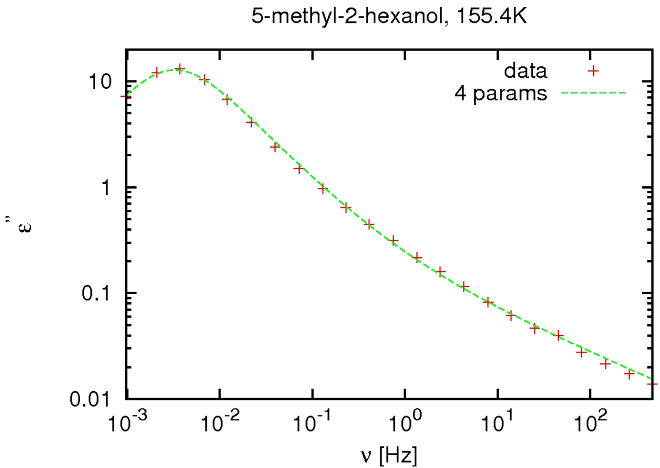
corresponding susceptibilities:

3params: $\chi(u) = \frac{1+(\tau_2 u)^{\alpha}}{1+(\tau_2 u)^{\alpha}+\tau_1 u}$ $\quad n_{\mathrm{param}} = 3$

4params: $\chi(u) = \frac{1+(\tau_1 u)^{\alpha_1}+(\tau_2 u)^{\alpha_2}}{1+\tau_1 u+(\tau_1 u)^{\alpha_1}+(\tau_2 u)^{\alpha_2}}$ $\quad n_{\mathrm{param}} = 4$



data: Kalinovskaya, Vij, J. Chem. Phys., **112** 7, (1999)



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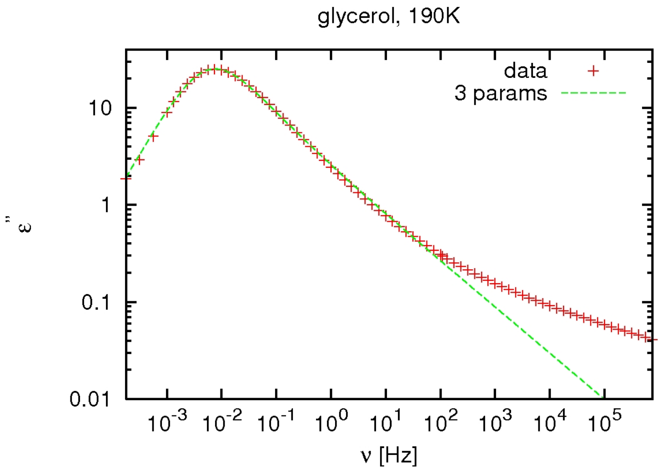

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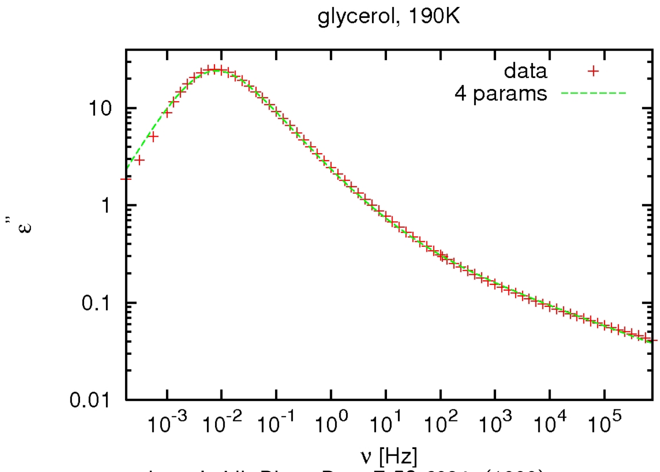

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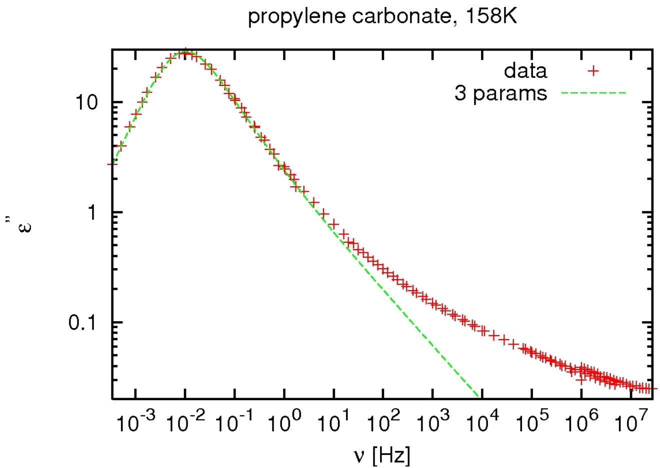

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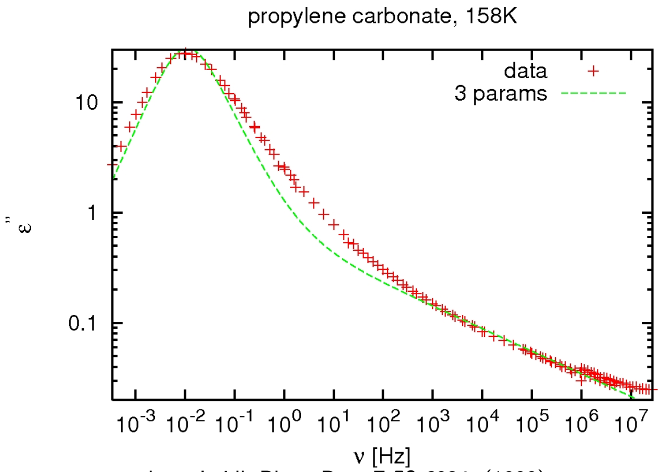
Fits
fractional model



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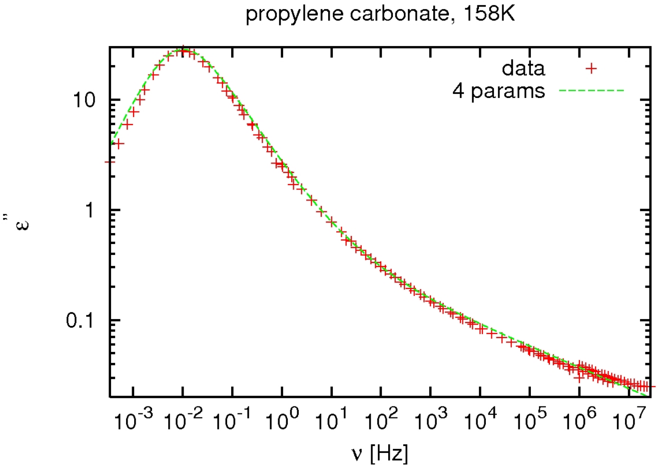
Fits
fractional model



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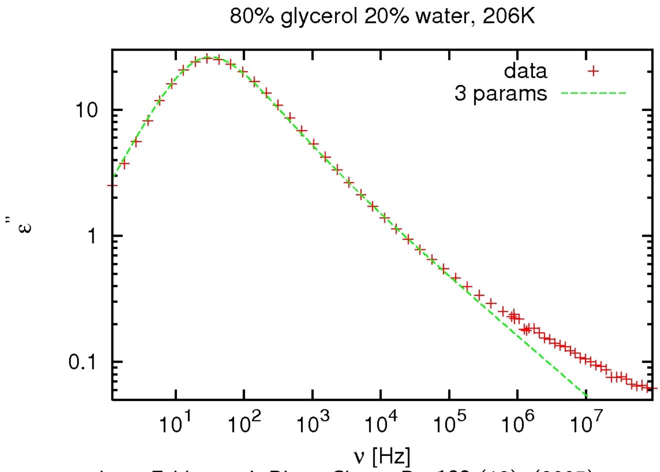

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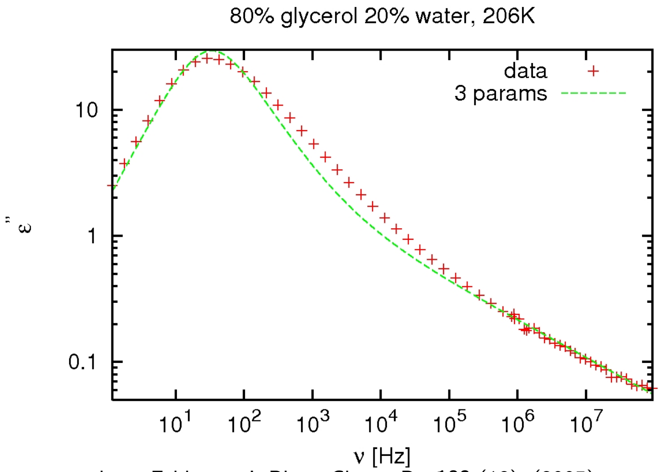

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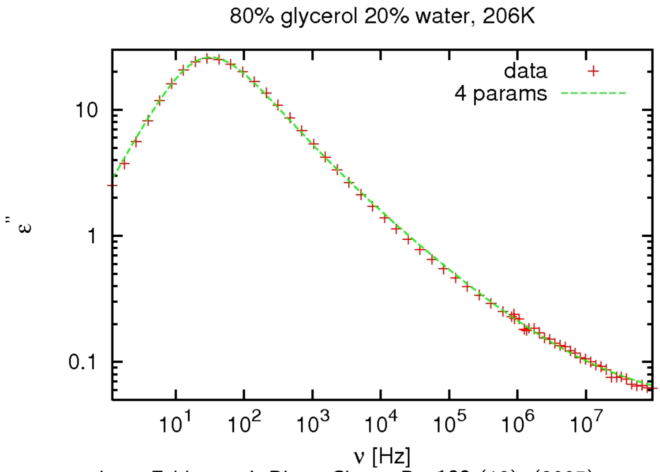

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Fractional Calculus

Problem

solve the modified relaxation equations

$$\begin{aligned} \tau_1 Df(t) + \tau_2^{\alpha} D^{\alpha} f(t) + f(t) &= 0 \\ \tau_1 Df(t) + \tau_1^{\alpha_1} D^{\alpha_1} f(t) + \tau_2^{\alpha_2} D^{\alpha_2} f(t) + f(t) &= 0 \end{aligned}$$

$$f(0) = 1$$

fractional integral:

$$I_0^\mu f(t) = \frac{1}{\Gamma(\mu)} \int_0^t (t-\xi)^{\mu-1} f(\xi)\ d\xi$$

Riemann-Liouville:

$$\begin{aligned} D_0^\nu f(t) &= D^{\lceil\nu\rceil} I_0^{(\lceil\nu\rceil-\nu)} f(t) \\ D_0^{3.2} &= D^4 I_0^{0.8} \end{aligned}$$

Caputo-Liouville:

$$D_0^\nu f(t) = I_0^{(\lceil\nu\rceil-\nu)} D^{\lceil\nu\rceil} f(t)$$

Hilfer:

$$D_0^{\nu,\beta} f(t) = I_0^{\beta(\lceil\nu\rceil-\nu)} D^{\lceil\nu\rceil} I_0^{(1-\beta)(\lceil\nu\rceil-\nu)} f(t)$$

$$
\begin{aligned}
I_0^{\mu} e^{at} &= \frac{e^{at}}{a^{\mu}\Gamma(\mu)}\gamma(\nu, at) \\
&= E(\mu, a; t) \qquad \text{fractiogene e-function } E_t(\mu, a) \\
&= t^{\mu} E_{1,\mu+1}(at) \qquad \text{generalised Mittag-Leffler function}
\end{aligned}
$$

Properties:

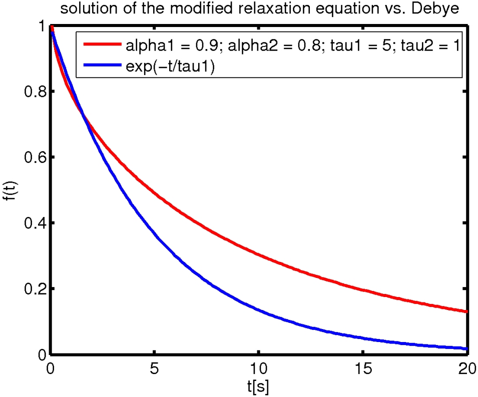
$$
\begin{aligned}
D^{\nu} E(\mu, a; t) &= E(\mu - \nu, a; t) \\
E(\mu, a; t) &= aE(\mu + 1, a; t) + \frac{t^{\mu}}{\Gamma(\mu + 1)}
\end{aligned}
$$

$$\tau_1 Df(t) + \tau_1^{\alpha_1} D^{\alpha_1} f(t) + \tau_2^{\alpha_2} D^{\alpha_2} f(t) + f(t) = 0$$

more general	$\sum_{i=0}^{N} a_i D^{i/N} f(t) = 0$
indicial polynomial	$\sum_{i=0}^{N} a_i c_j^i = 0$ j=1,..N
solution	$f(t) = \sum_{j=1}^{N} \left(\sum_{k=0}^{N-1} c_j^{N-k-1} E(-k/N, c_j^N; t) \right) B_j$
with	$\sum_{j=1}^{N} B_j \sum_{i=0}^{k-1} c_j^i a_{N-k+i+1} = 0 \quad 1 \leq k \leq N-1$

modified relaxation equation:

$$\tau_1 Df(t) + \tau_1^{\alpha_1} D^{\alpha_1} f(t) + \tau_2^{\alpha_2} D^{\alpha_2} f(t) + f(t) \quad = \quad 0$$



Summary

- Modified relaxation equation describes spectroscopy data better than Havriliak-Negami and Cole-Cole
- Less parameters (3/4) than Havriliak-Negami + Cole-Cole (6)
- 4 parameters to fit over 9 decades

- Fractiogene e-function to solve FDE independently of the type of derivative
- Solution of modified relaxation equation slower than Debye relaxation

Contact

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