Dielectric and Shear Mechanical Relaxation in Viscous Liquids: Are they Connected?

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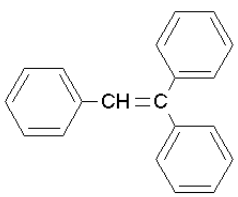
Motivation and Background

- To get information about $G(\omega)$ from $\epsilon(\omega)$
- To understand the relaxation in viscous liquids
- Starting with Debyes model [Debye, 1929]
  - The Debye-Stoke-Einstein relation
  - Onsager-like local field [Cole, 1938, Fatuzzo & Mason, 1967, Nee & Zwanzig, 1970]
  - Visco-elastic properties [DiMarzio & Bishop, 1974, Christensen & Olsen, 1994]
    a different approach [Havrilak & Havrilak, 1995]

Substances

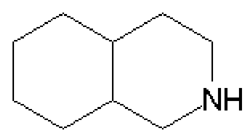
	T_m	T_g	n^2	$\Delta\epsilon$	$\log(\nu_{\beta,lp})$
DC704 Silicone oil	–	211K	2.42	0.2	–
TPE Triphenylethylene	343K	249K	–	0.05	–
DHIQ Decahydroisoquinoline	–	179K	2.2	1	2.7
TPG Tripropylene glycol	–	190K	2.9	20	4
Squalane Perhydrosqualene	235K	167K	2.1	0.01	4.5



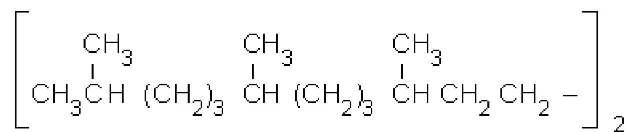
TPE

$HOCH_2CH_2CH_2(OCH_2CH_2CH_2)_2OH$

TPG

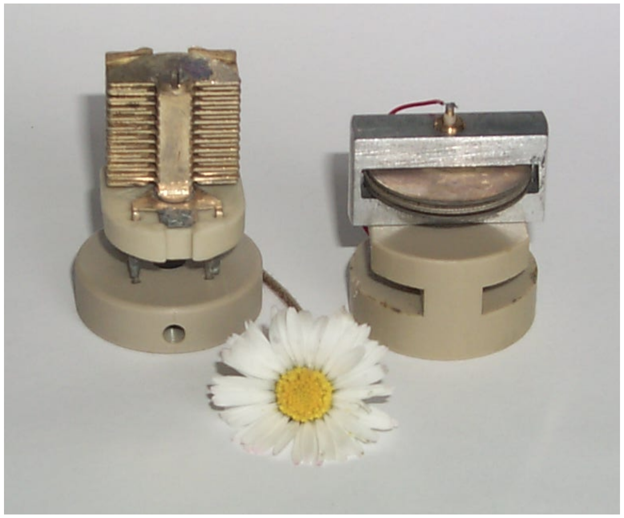


DHIQ



Squalane

Methods of measurement



Dielectric: 22-layer gold platen capacitor with empty capacitance of 68pF. $10^{-3} - 10^{6}$Hz

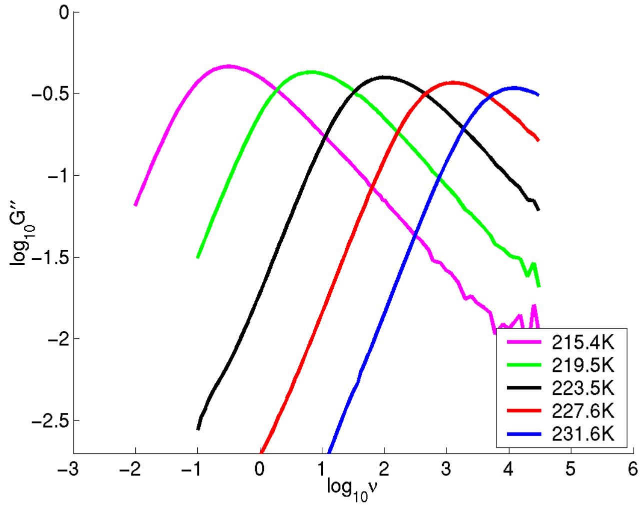
Shear modulus: Piezoelectric shear modulus gauge (PSG) [Christensen & Olsen, 1995] $10^{-3} - 10^{4.5}$Hz

Measurement: Standard equipment.
$10^{-3} - 10^{2}$Hz: HP3458A multimeter in conjunction with a Keithley AWFG.
$10^{2}4 - 10^{6}$Hz: HP 4284A LCR meter

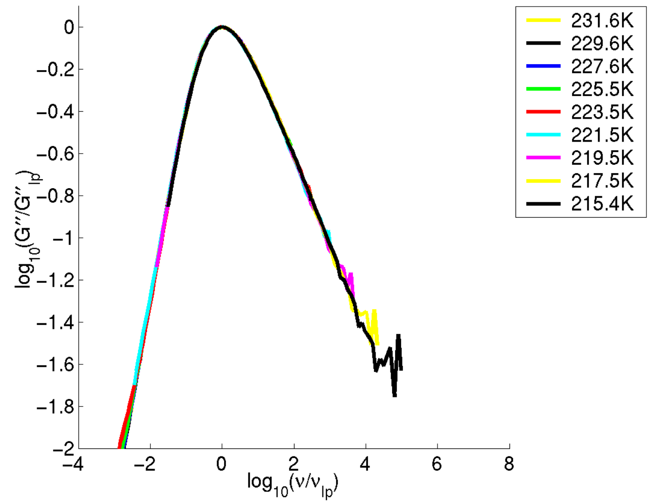
Temperature: Nitrogen cooled cryostat.
Absolute temperature: better than 0.2K
Temperature stability: better that 20mK

DC704

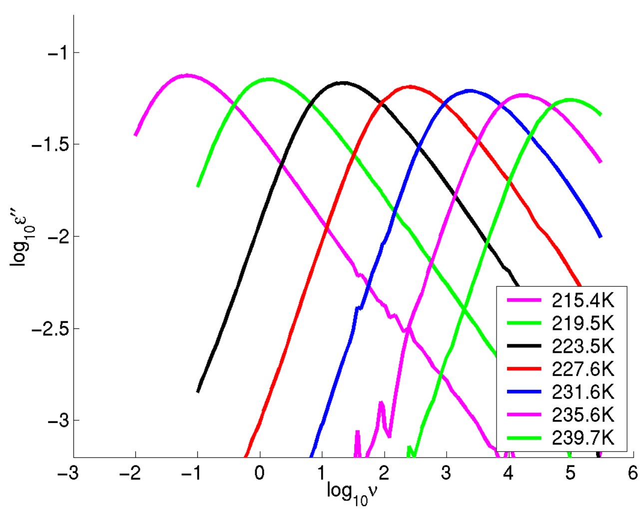
shear



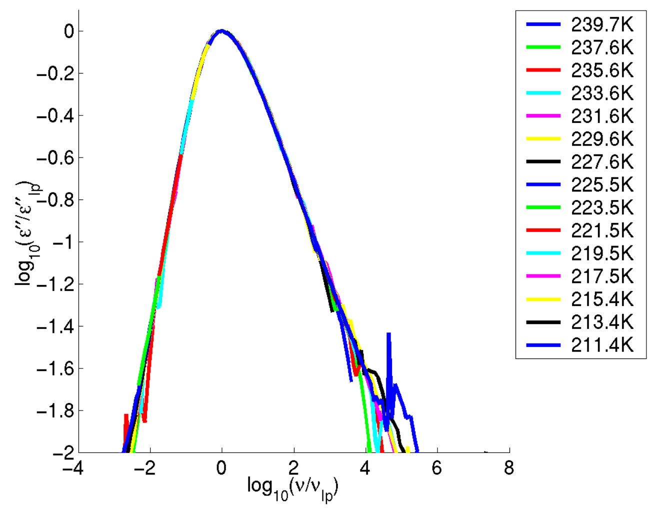
TTS shear



dielectric

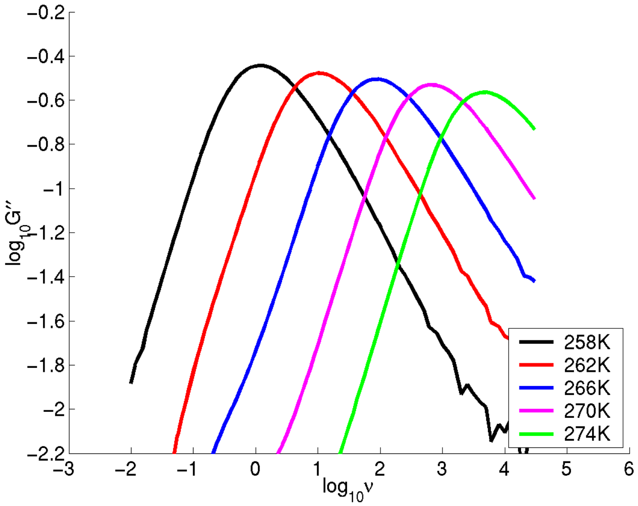


TTS dielectric

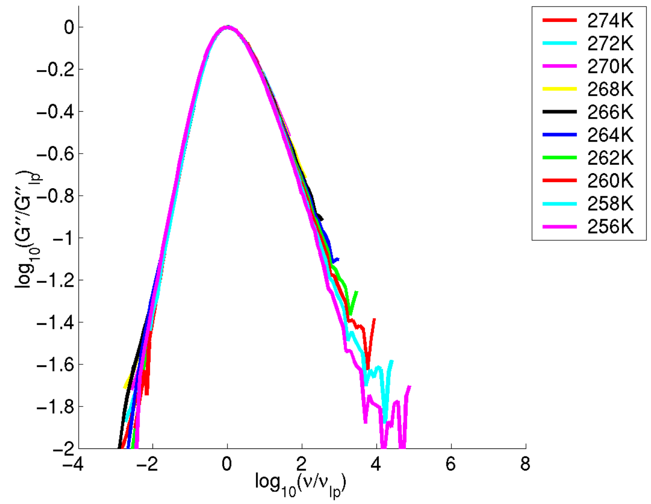


TPE

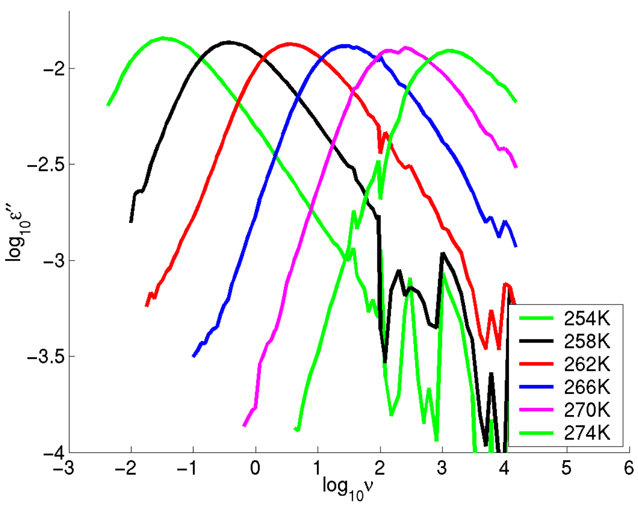
shear



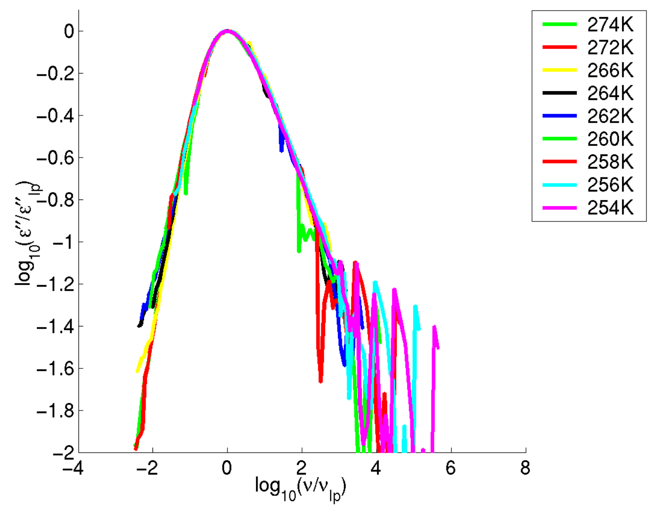
TTS shear



dielectric

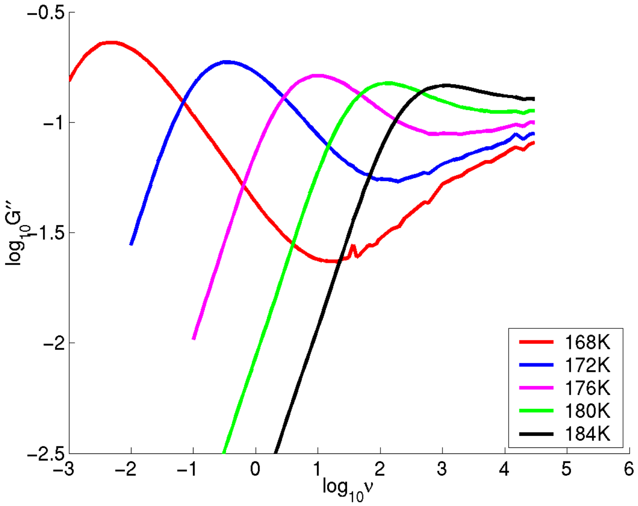


TTS dielectric

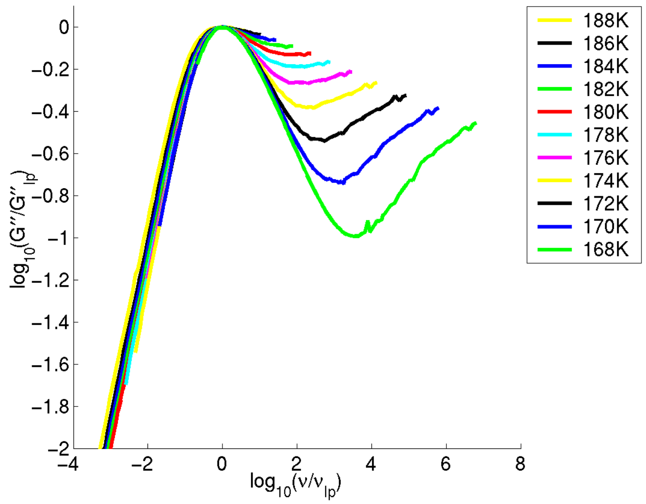


Squalan

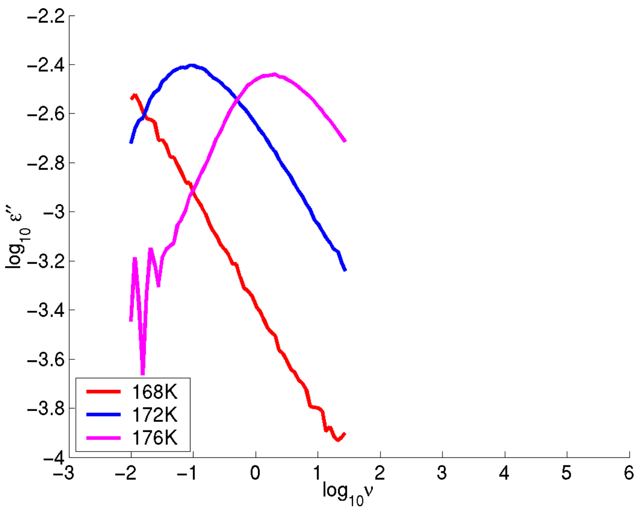
shear



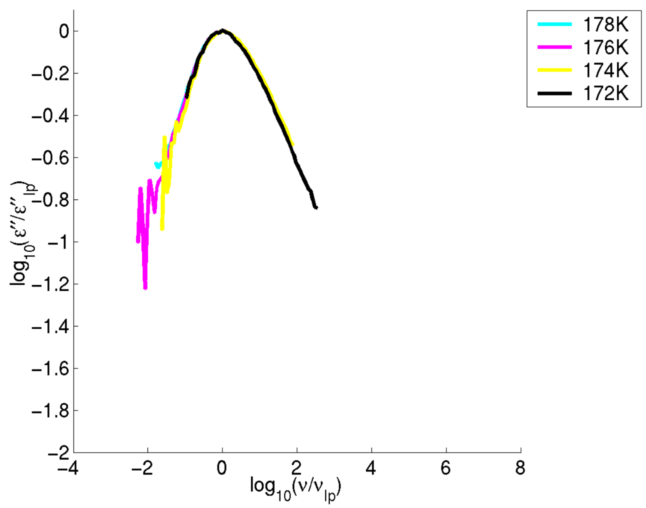
TTS shear



dielectric

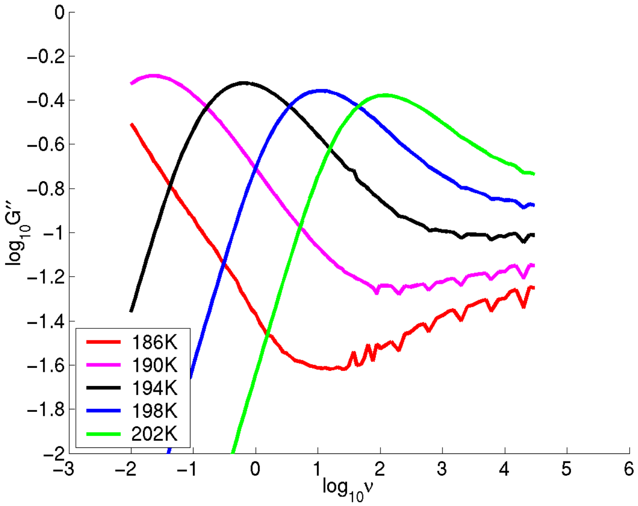


TTS dielectric

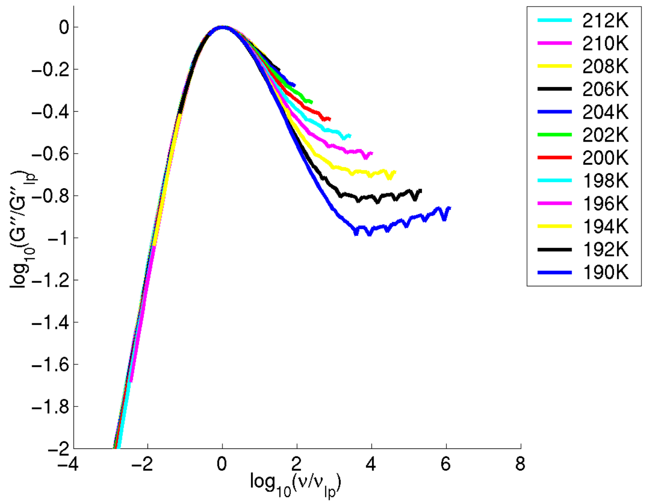


TPG

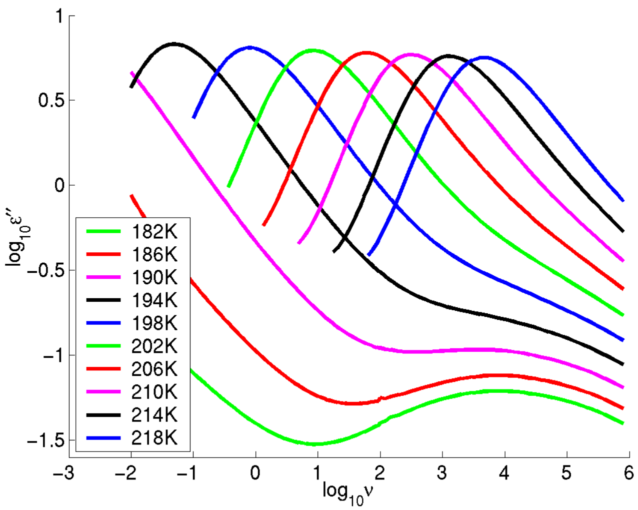
shear



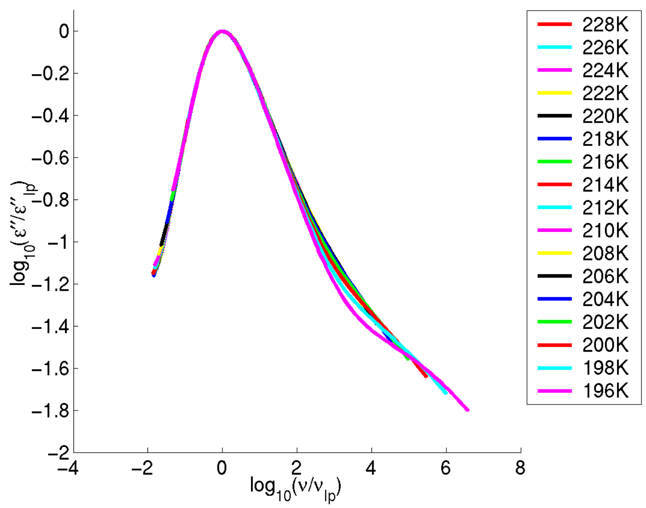
TTS shear



dielectric

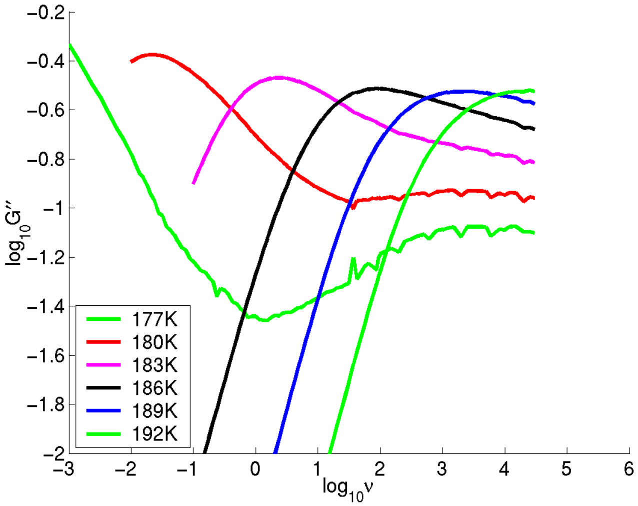


TTS dielectric

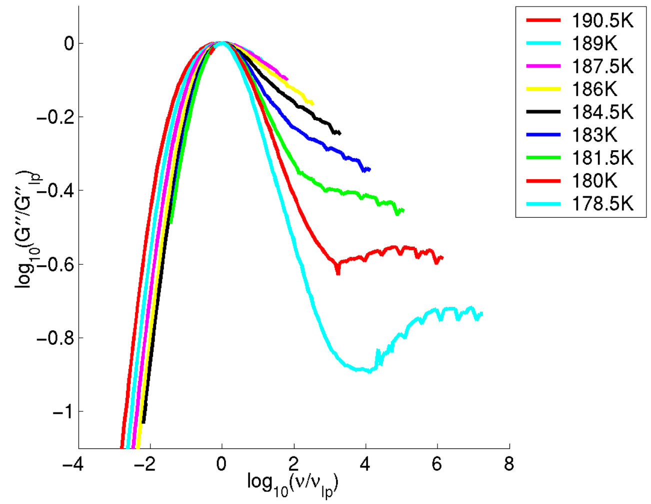


DHIQ

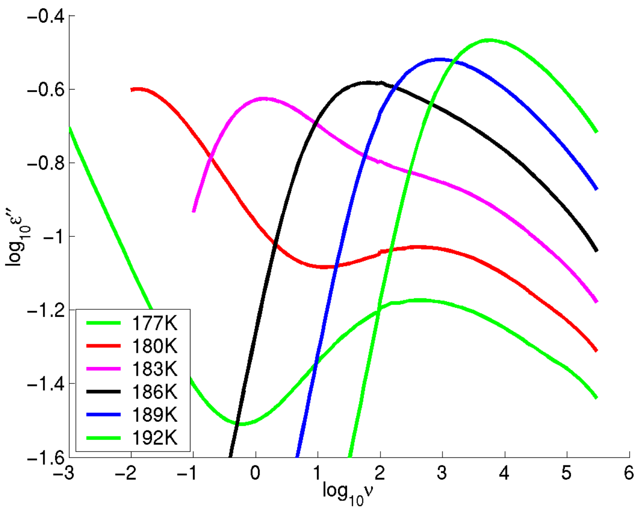
shear



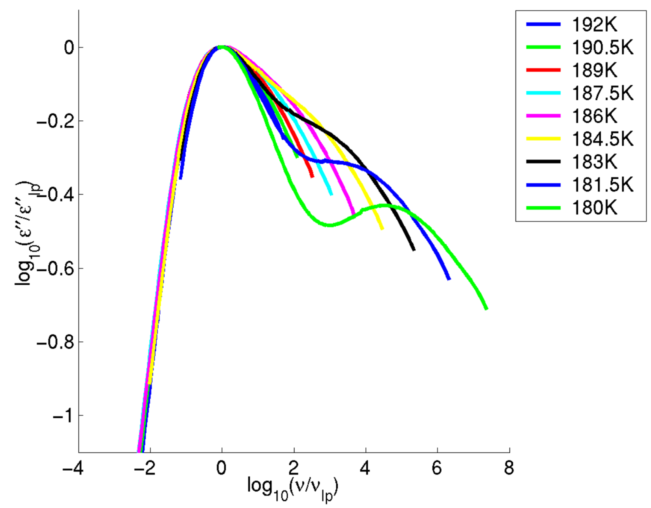
TTS shear



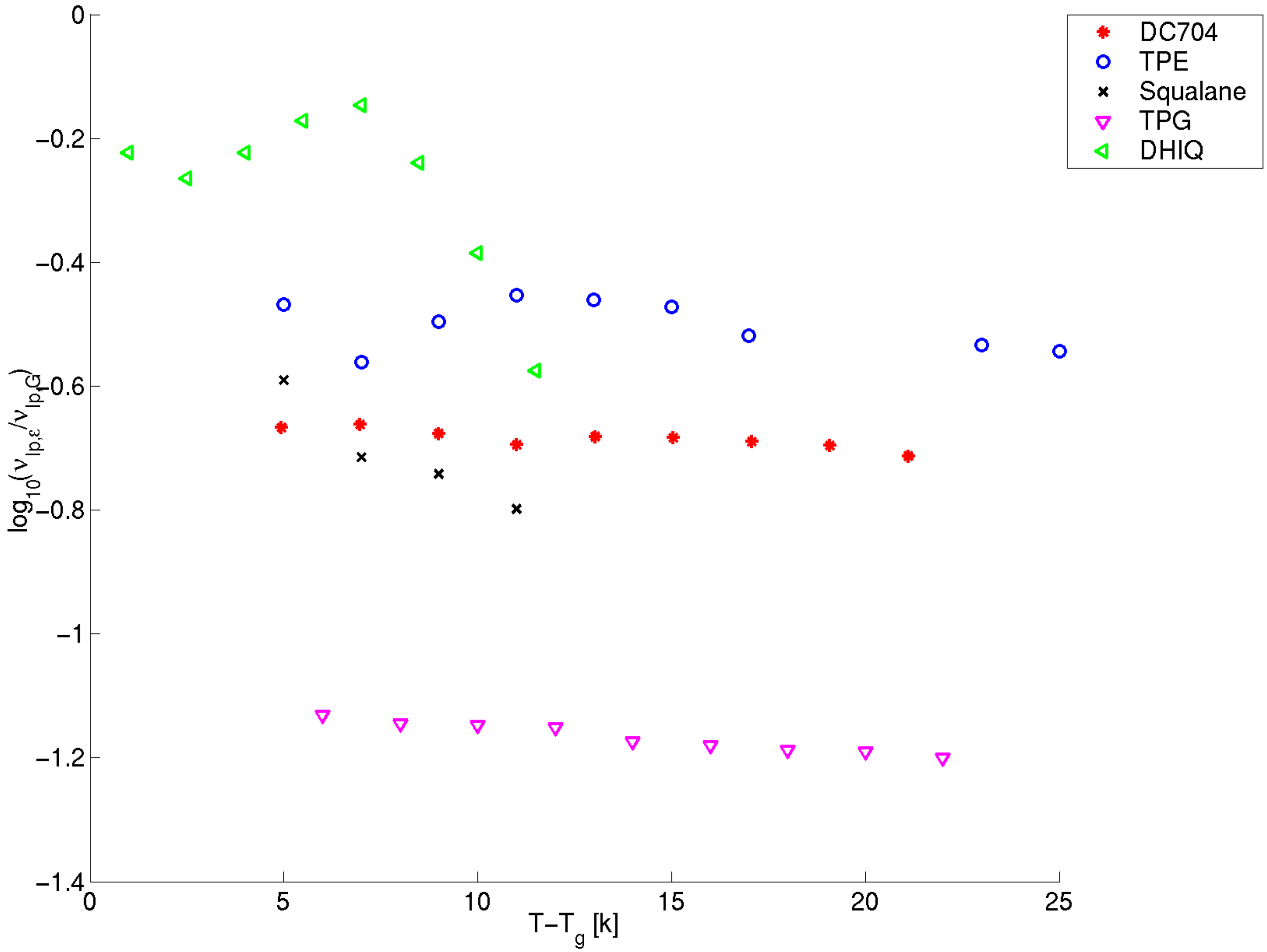
dielectric



TTS dielectric



Comparison of loss peak positions



Microscopic DiMarzio-Bishop model

The Debye "rotational diffusion equation":

$$\frac{\partial f}{\partial t} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\left(D_0\frac{\partial f}{\partial\theta} - \frac{M}{\zeta_0}f\right)\right]$$

The generalized rotational diffusion equation by DiMarzio & Bishop [1974]:

$$\frac{\partial f}{\partial t} = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\left(\frac{\partial}{\partial\theta}\int_{-\infty}^{t} D(t-\tau)f(\tau)d\tau - f\int_{-\infty}^{t} V(t-\tau)M(\tau)d\tau\right)\right]$$

The Stokes friction term is used

$$\zeta(\omega) = 8\pi r^3\eta(\omega)$$

A first order solution is found

$$\alpha_r(\omega) = \frac{\mu^2}{3k_BT\left(1+\left(\frac{4\pi r^3}{k_BT}\right)i\omega\eta(\omega)\right)} = \frac{\mu^2}{3k_BT\left(1+\left(\frac{4\pi r^3}{k_BT}\right)G(\omega)\right)}$$

This microscopic polarizability has to be connected to macroscopic measurable quantities.

Earlier formulations

Based on unphysical assumptions.

DiMarzio & Bishop [1974]

$$\frac{\epsilon(\omega)-\epsilon_\infty}{\epsilon_e-\epsilon_\infty}=\frac{1}{\left(1+\left(\frac{4\pi r^3}{k_B T}\right)\left(\frac{\epsilon_e+2}{\epsilon_\infty+2}\right)G(\omega)\right)}$$

Based on the assumption that $G(\omega)\to\infty$ when $\omega\to\infty$.
This is inconsistent if ∞ is interpreted as the limit which can be reached with dielectric measurements.

Christensen & Olsen [1994]

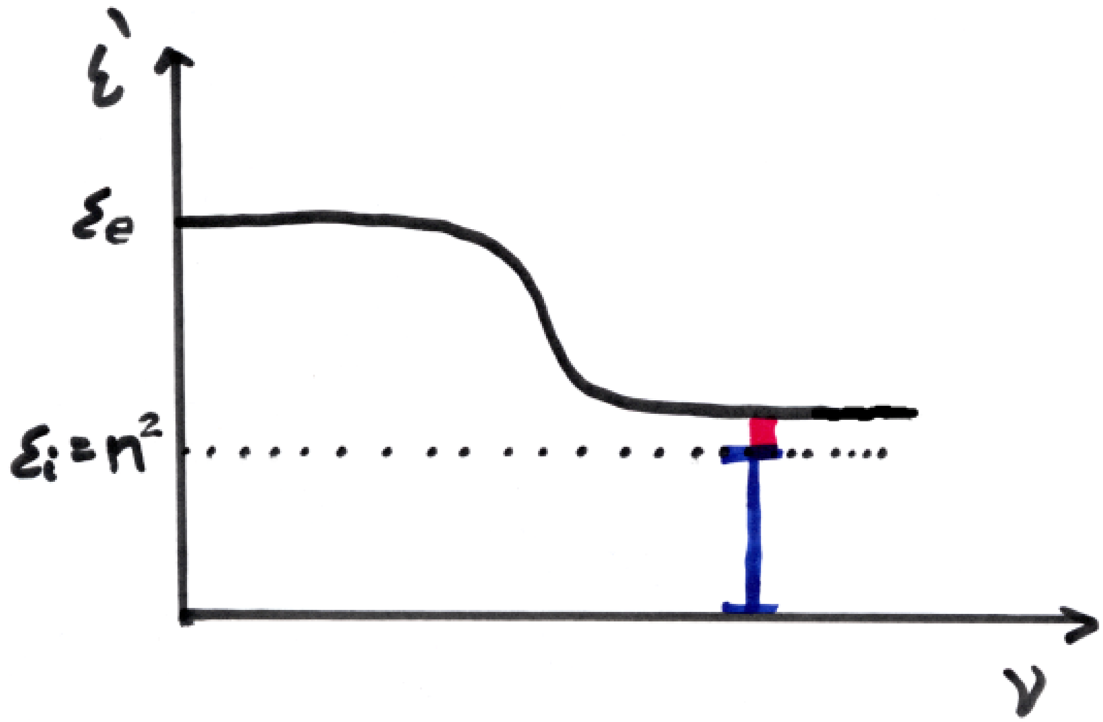
$$\frac{\epsilon(\omega)-1}{\epsilon_e-1} = \frac{1}{\left(1+\left(\frac{4\pi r^3}{k_B T}\right)\left(\frac{\epsilon_e+2}{1+2}\right)G(\omega)\right)}$$

$$\Downarrow$$

$$\frac{1}{\epsilon(\omega)-1} = (\epsilon_e-1)\left(1+\left(\frac{4\pi r^3}{k_B T}\right)\left(\frac{\epsilon_e+2}{3}\right)G(\omega)\right)$$

Ignoring the atomic polarizability,
though it is predominant at high frequencies.

A self consistent macroscopic formulation



$$\frac{\epsilon(\omega)-\epsilon_i}{\epsilon_e-\epsilon_i}=\frac{1}{\left(1+\left(\frac{4\pi r^3}{k_BT}\right)\left(\frac{\epsilon_e+2}{\epsilon_i+2}\right)G_s(\omega)\right)}.$$

A simple prediction

Solving for $G(\omega)$

$$G(\omega) = K\left(\frac{\epsilon_e - \epsilon_i}{\epsilon(\omega) - \epsilon_i}\right) - K, \quad K = \frac{k_B T}{4\pi r^3}\left(\frac{\epsilon_i + 2}{\epsilon_e + 2}\right),$$

and taking the imaginary part

$$G(\omega)'' = \left(\frac{A}{\epsilon(\omega) - \epsilon_i}\right)'', \quad A \text{ real.}$$

$$log\left(G(\omega)''\right) = log\left[\left(\frac{1}{\epsilon(\omega) - \epsilon_i}\right)''\right] + log(A), \quad A \text{ real.}$$

This will hold even if there is an error on the absolute values of $G(\omega)$ and $\epsilon(\omega)$
- but the fitted value of ϵ_i will "inherit" this error.

The local field

Using Clasius Mossotti

$$\frac{\epsilon(\omega)-\epsilon_i}{\epsilon_e-\epsilon_i}=\frac{1}{\left(1+\left(\frac{4\pi r^3}{k_BT}\right)\left(\frac{\epsilon_e+2}{\epsilon_i+2}\right)G(\omega)\right)}.$$

Using Fatuzzo & Mason [1967]

$$\frac{\epsilon_e(\epsilon(\omega)-\epsilon_i)(2\epsilon(\omega)+\epsilon_i)}{\epsilon(\omega)(\epsilon_e-\epsilon_i)(2\epsilon_e+\epsilon_i)}=\left[1+\frac{4\pi r^3}{k_BT}\left(\frac{\epsilon_e+2}{\epsilon_i+2}\right)G(\omega)-\frac{(\epsilon_e-\epsilon_i)(\epsilon(\omega)-\epsilon_i)}{\epsilon_i(2\epsilon(\omega)+\epsilon_i)}\right]^{-1}$$

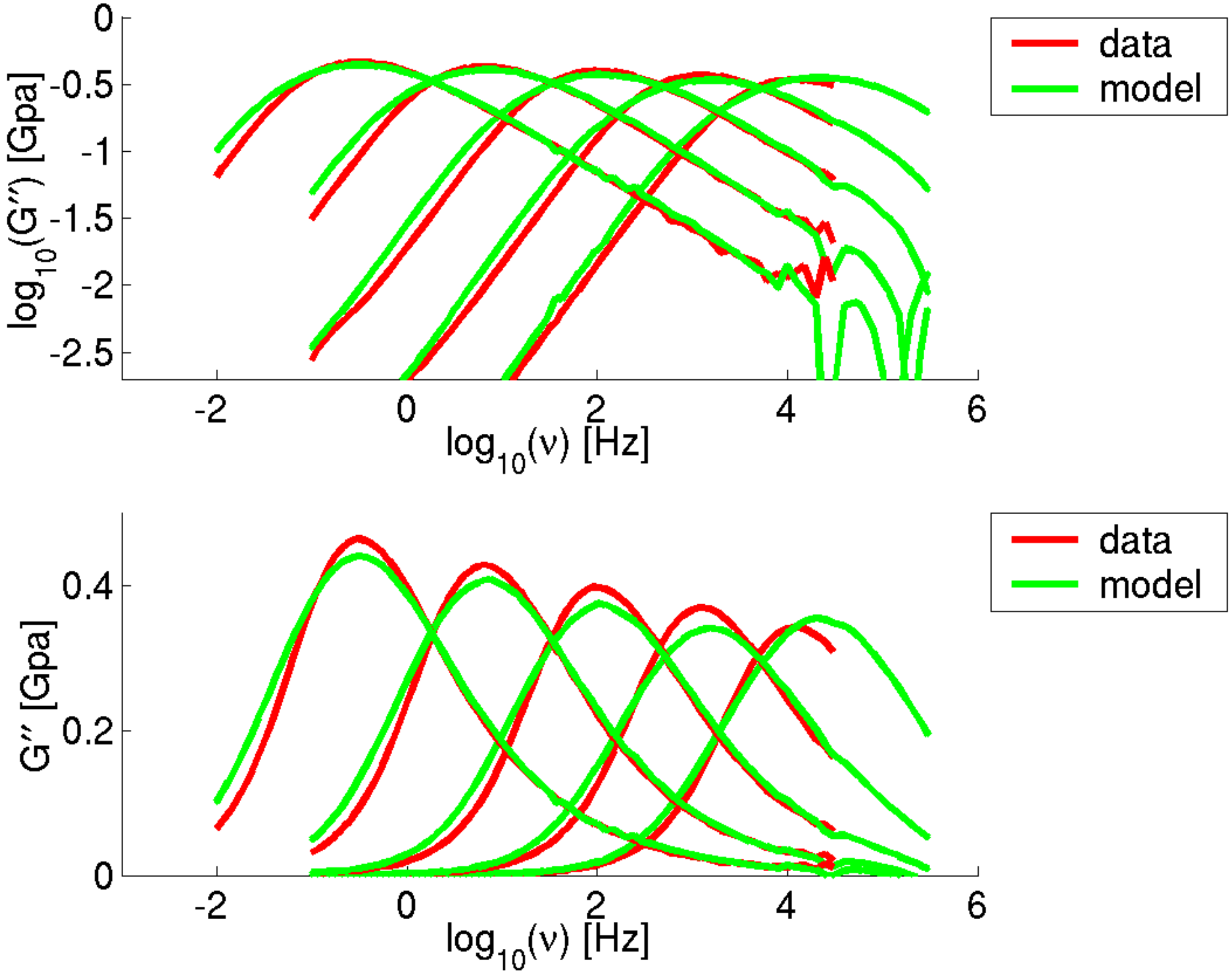
They both reduce to the result obtained using the Maxwell field when $\Delta\epsilon$ is small:

$$\frac{\epsilon(\omega)-\epsilon_i}{\epsilon_e-\epsilon_i}=\frac{1}{\left(1+\left(\frac{4\pi r^3}{k_BT}\right)G(\omega)\right)}.$$

when

$$\epsilon(\omega)=\epsilon_i+\Delta\epsilon(\omega) \text{ and } \epsilon_e=\epsilon_i+\Delta\epsilon_e,\ \ \Delta\epsilon(\omega)\leq\Delta\epsilon_e\ll\epsilon_i$$

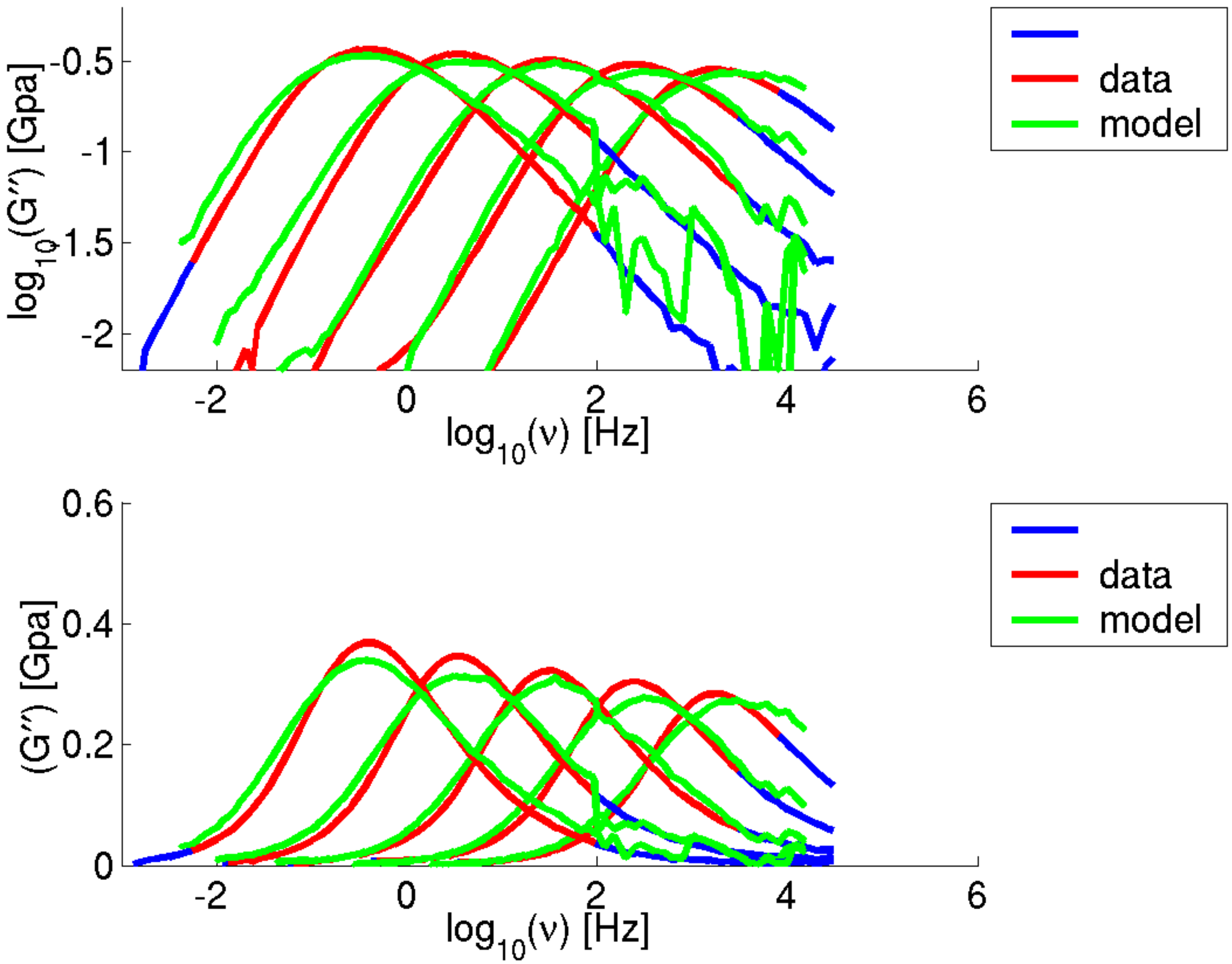
DC704 test of the model



at 215.4K, 219.5K, 223.5K, 227.6K and 231.6K

fitting $\epsilon_i \approx 2.5$

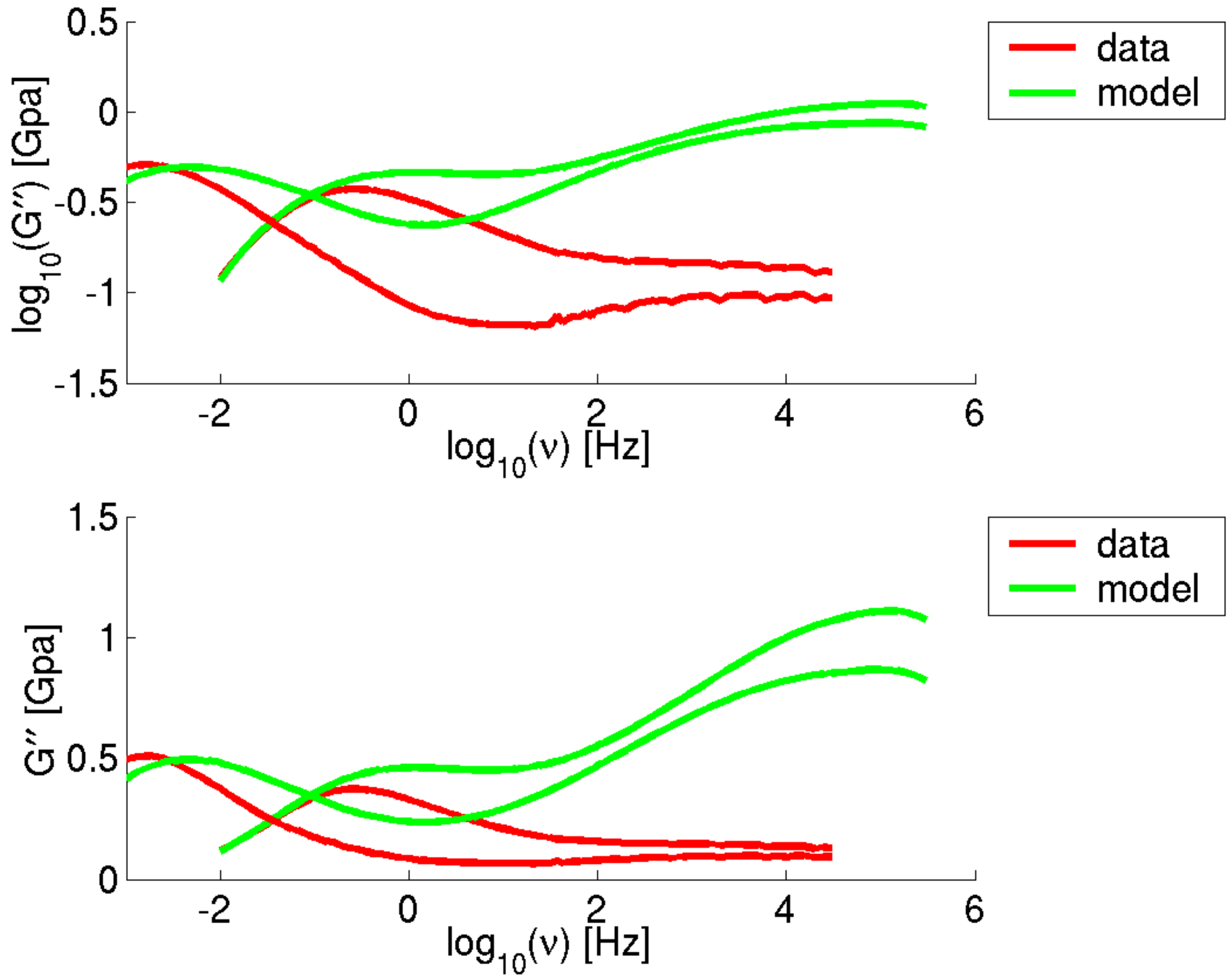
TPE test of the model



at 256K, 260K, 264K, 268K and 272K

fitting $\epsilon_i \approx 2.665$

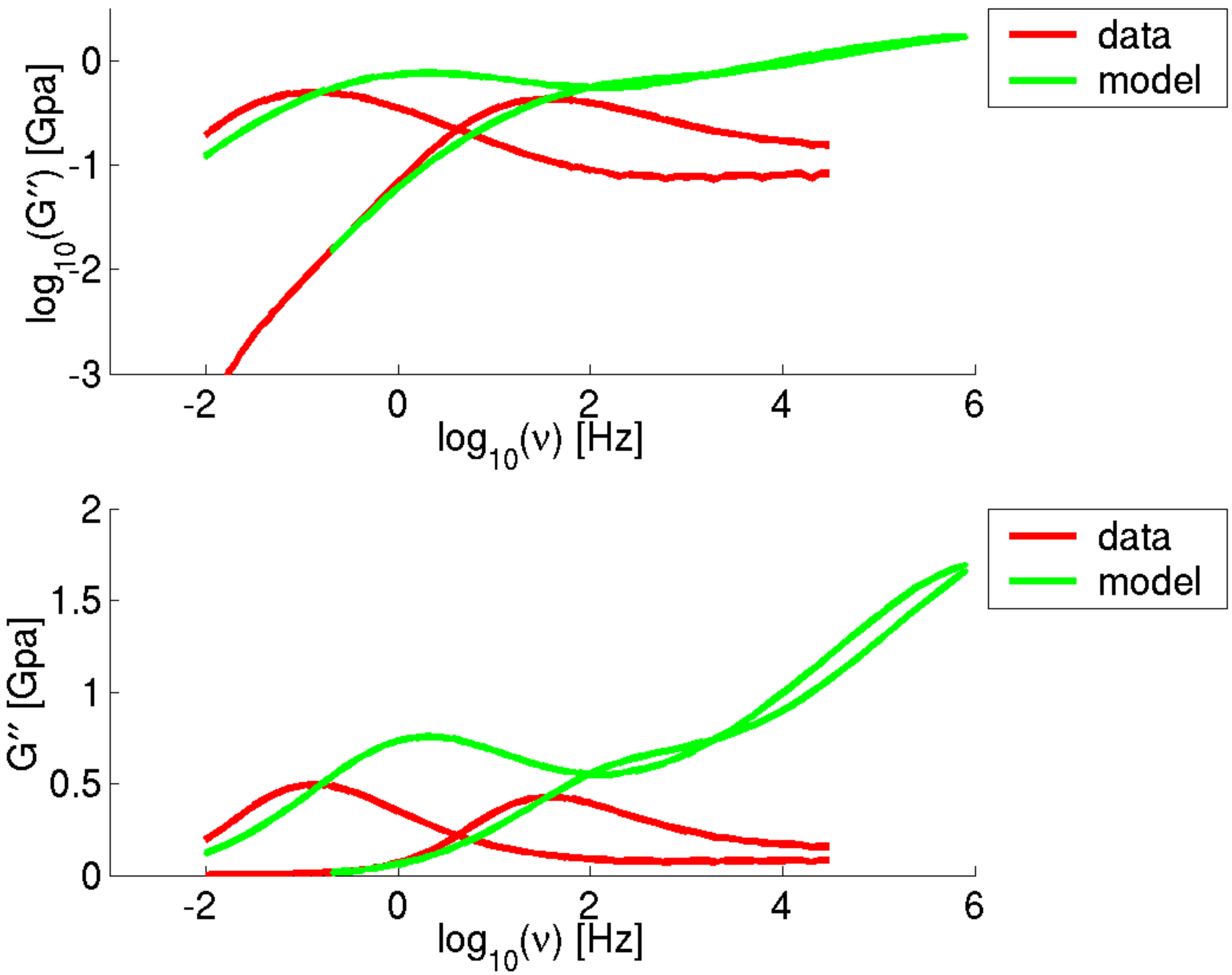
DHIQ test of the model



at 181.5K and 178.5K

using $\epsilon_i = 2$

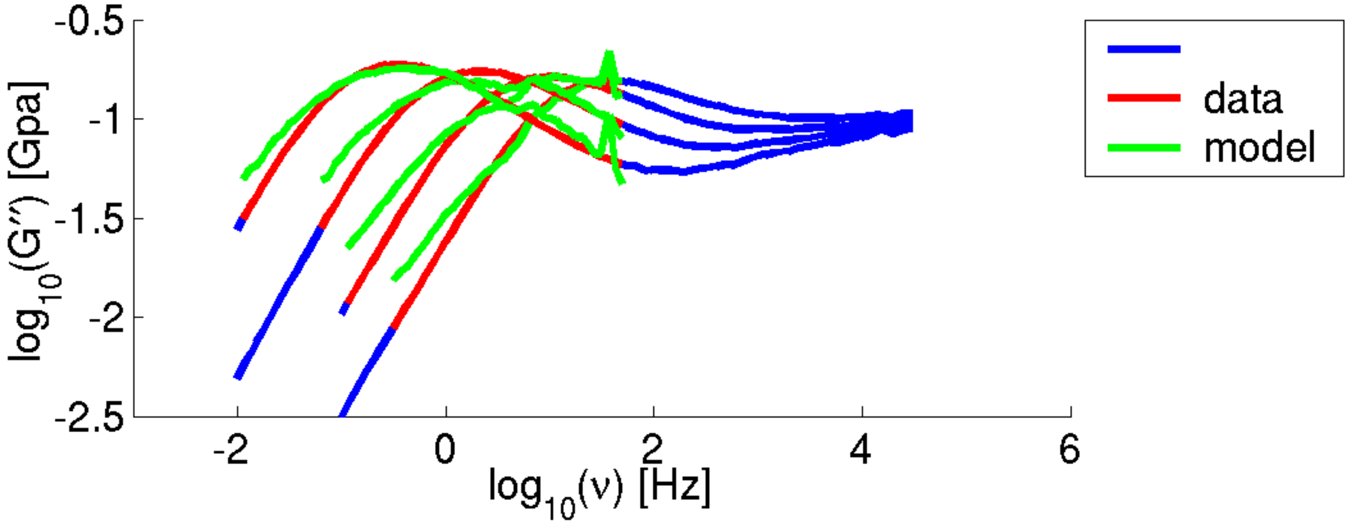
TPG test of the model

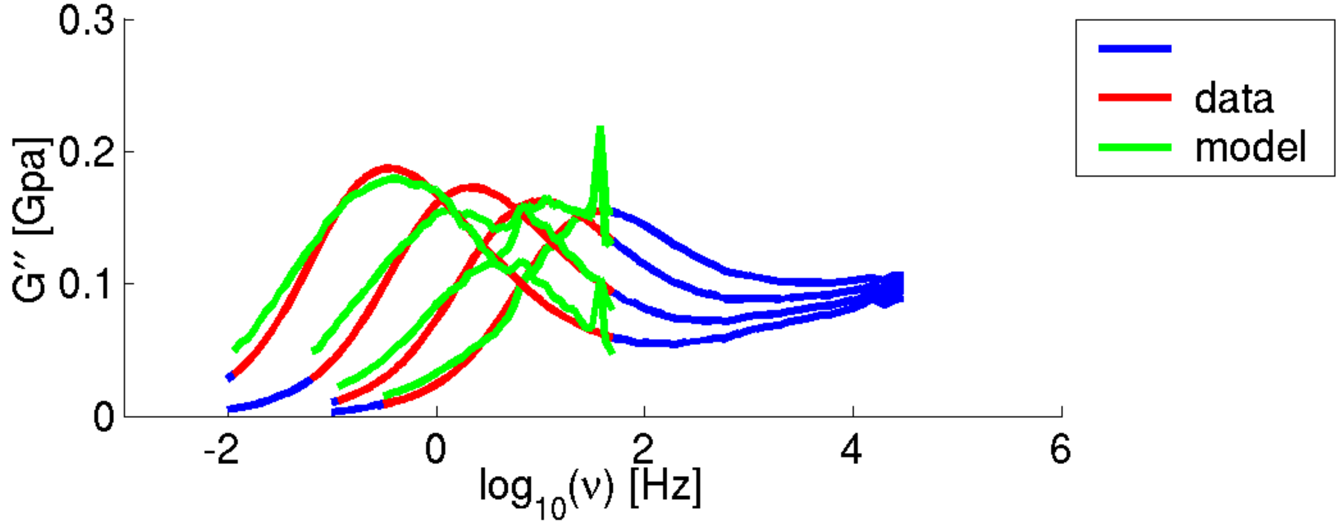


at 192K and 200K

using $\epsilon_i = 2.5$

Squalane test of the model

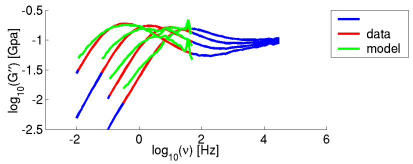




at 172K, 174K, 176K and 178K
fitting $\epsilon_i \approx 2.104$

Summary

- The model can be tested with *one* macroscopic parameter.
- The choice of local field is not significant when the dielectric constant has little frequency dependence.
- The model needs further testing.



Shear Mechanical and Dielectric Relaxation:
Are they Connected?

Other tests of the model

- DiMarzio & Bishop [1974]
  poly-n-octyl methachrylate & poly-n-hexyl methachrylate & polymetyl acrylate

- Días-Calleja et al. [1993]
  poly(cyclohexyl acrylate)
  compares the results using two different local fields

- Christensen & Olsen [1994]
  silicone oil & 1,3-butandiol

- Havrilak & Havrilak [1995]
  poly-n-octyl methachrylate
  compares the model to their own model

- Zorn et al. [1997]
  on a series of 1,2-1,4-polybutadienes, varying 1,2 vinyl content

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