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
  - Visco-elastic properties [DiMarzio & Bishop, 1974, Christensen & Olsen, 1994]
    a different approach [Havrilak & Havrilak, 1995]
## Substances

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

Viscous Liquids and the Glass Transition; Søminestationen 2003
Methods of measurement

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

Shear modulus: Piezoelectric shear modulus gauge (PSG)

\[\text{[Christensen & Olsen, 1995]}\quad 10^{-3} - 10^{4.5}\text{Hz}\]

Measurement: Standard equipment.

\(10^{-3} - 10^2\text{Hz}:\) HP3458A multimeter in conjunction with a Keithley AWFG.

\(10^2 - 10^6\text{Hz}:\) HP 4284A LCR meter

Temperature: Nitrogen cooled cryostat.

Absolute temperature: better than 0.2\text{K}

Temperature stability: better that 20\text{mK}
DC704

shear

TTS shear

dielectric

TTS dielectric

Viscous Liquids and the Glass Transition; Søminestationen 2003
Squalan

Viscous Liquids and the Glass Transition; Søminestationen 2003
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

\[
\alpha_r(\omega) = \frac{\mu^2}{3k_B T \left( 1 + \left( \frac{4\pi r^3}{k_B T} \right) i\omega \eta(\omega) \right)} = \frac{\mu^2}{3k_B T \left( 1 + \left( \frac{4\pi r^3}{k_B T} \right) G(\omega) \right)}
\]

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

Based on unphysical assumptions.

DiMarzio & Bishop [1974]

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

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

Christensen & Olsen [1994]

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

\[ \Downarrow \]

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

Ignoring the atomic polarizability, though it is predominant at high frequencies.
A self consistent macroscopic formulation

\[
\frac{\varepsilon(\omega) - \varepsilon_i}{\varepsilon_e - \varepsilon_i} = \frac{1}{1 + \left(4\pi r^3 k_B T\right) \left(\frac{\varepsilon_e + 2}{\varepsilon_i + 2}\right) G_s(\omega)}.
\]
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

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

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

This will hold even if there is an error on the absolute values of $G(\omega)$ and $\epsilon(\omega)$

- but the fitted value of $\epsilon_i$ will “inherit” this error.
The local field

Using Clasius Mossotti

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

Using Fatuzzo & Mason [1967]

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

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

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

when

\[
\epsilon(\omega) = \epsilon_i + \Delta\epsilon(\omega) \quad \text{and} \quad \epsilon_e = \epsilon_i + \Delta\epsilon_e, \quad \Delta\epsilon(\omega) \leq \Delta\epsilon_e \ll \epsilon_i
\]
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 $\epsilon_i = 2.5$. 

**Diagram:**

- Top graph: Logarithm of the relaxation modulus $G''$ vs. logarithm of frequency $\log_{10}(\nu)$.
- Bottom graph: Logarithm of the loss modulus $G''$ vs. logarithm of frequency $\log_{10}(\nu)$.

**Legend:**
- Red: data
- Green: model

At 192K and 200K using $\epsilon_i = 2.5$. 

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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 & polymethyl 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
References


