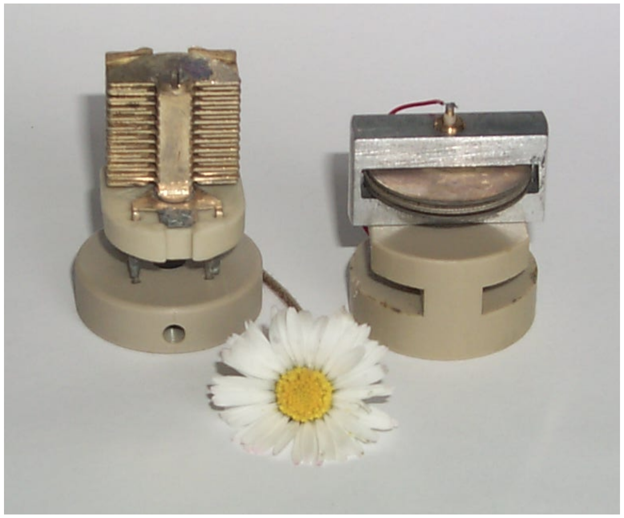
Dielectric and Shear Mechanical Relaxation in Viscous Liquids: Are they Connected?

Kristine Niss[1] and Bo Jakobsen[2]
master students at Roskilde University
supervised by Niels Boye Olsen

http://dirac.ruc.dk/~kniss/masterthesis/

[1]kniss@dirac.ruc.dk
[2]boj@dirac.ruc.dk

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

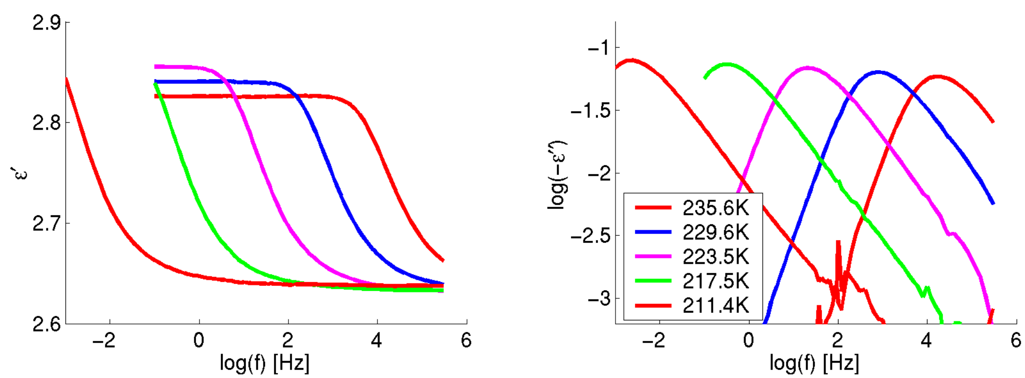
Dielectric relaxation

$$P_z e^{i(\omega t+\phi)} = \epsilon_0 \xi(\omega) E_0 e^{i\omega t} \quad \text{where} \quad \epsilon(\omega) = \xi(\omega) + 1$$

$$C(\omega) = \frac{A\epsilon_0\epsilon(\omega)}{d} = C_0\epsilon(\omega) \quad \text{where} \quad Q_0 e^{i(\omega t+\phi)} = C(\omega) U_0 e^{i\omega t}$$

$$P_z = (\epsilon - 1)\epsilon_0 E_m = N\left(E_i \alpha_i + \langle \mu_z \rangle\right) = N\left(\alpha_i E_i + \alpha_r E_d\right)$$

Typical spectrum (substance: DC704):



Debyes model

- Spherical non-interacting dipoles
- Surroundings can be described as a viscous continuum, with a frequency independent viscosity (η_0)
- No-slip boundary conditions
- Inertial effects are ignored

$$\frac{\partial f}{\partial t} + \nabla \cdot \boldsymbol{J} = 0 \,, \quad \boldsymbol{J} = -D_0 \nabla f + \boldsymbol{v} f$$

$$\zeta_0 = 8\pi r^3 \eta_0 \,, \quad \dot{\theta} = \frac{M}{\zeta_0}$$

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

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

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

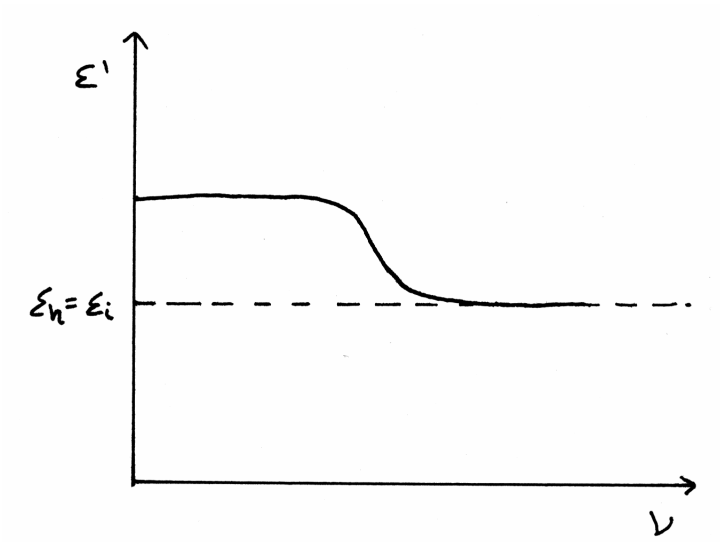
A first order solution is found

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

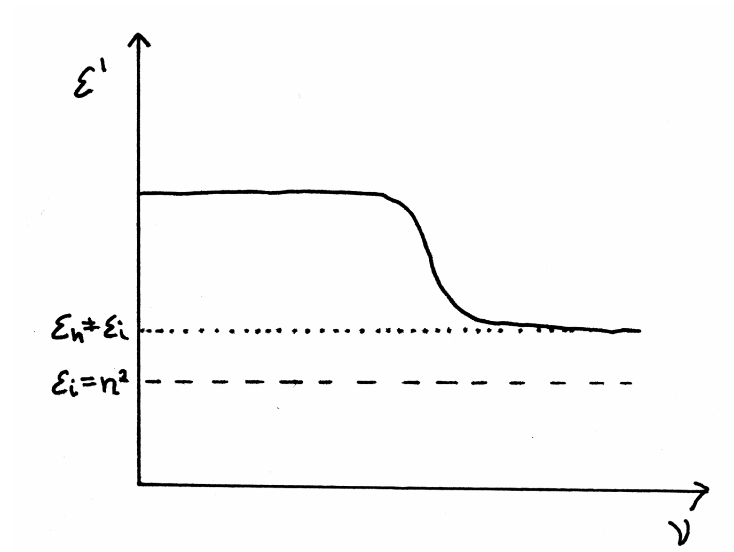
This microscopic polarizability has to be connected to macroscopic measurable quantities.

What controls the high frequency limit

Original Debye model



Generalized Debye model



Original Debye model:

$$\frac{\epsilon-1}{\epsilon+2} = \frac{N}{3\epsilon_0}\left[\alpha_i + \frac{\mu^2}{3k_BT\left(1+\left(\frac{4\pi r^3}{k_BT}\right)i\omega\eta_0\right)}\right]$$

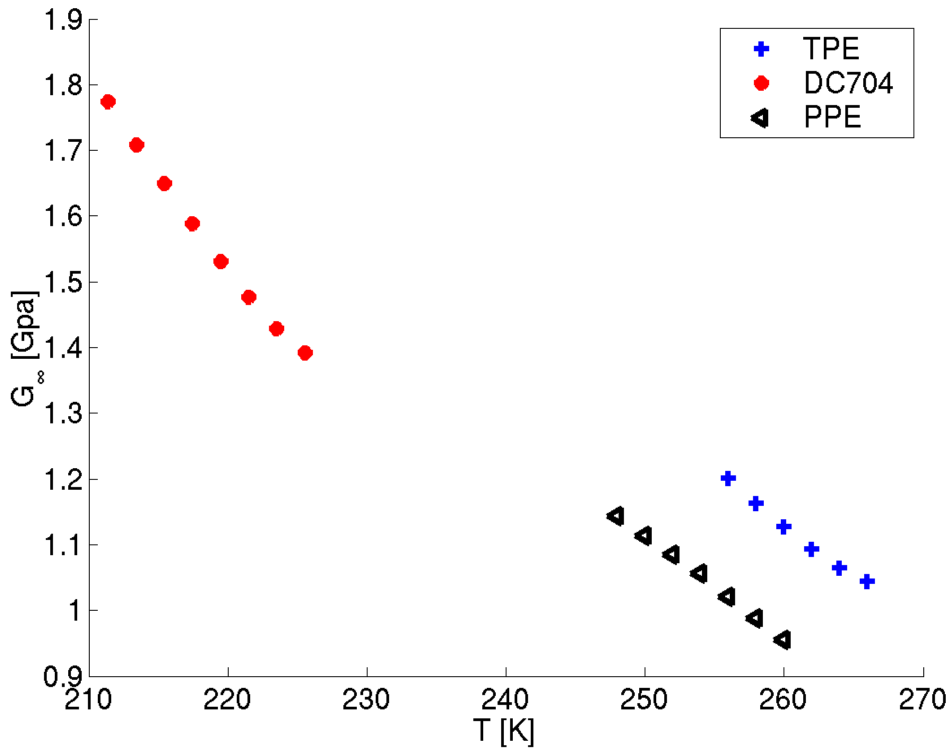
$$\frac{\epsilon_h-1}{\epsilon_h+2} = \frac{N}{3\epsilon_0}\alpha_i$$

Generalized Debye model:

$$\frac{\epsilon-1}{\epsilon+2} = \frac{N}{3\epsilon_0}\left[\alpha_i + \frac{\mu^2}{3k_BT\left(1+\left(\frac{4\pi r^3}{k_BT}\right)G(\omega)\right)}\right]$$

$$\frac{\epsilon_h-1}{\epsilon_h+2} = \frac{N}{3\epsilon_0}\left[\alpha_i + \frac{\mu^2}{3k_BT\left(1+\left(\frac{4\pi r^3}{k_BT}\right)G_\infty\right)}\right]$$

What controls the high frequency limit



Increasing T

Effects giving decreasing C_h

- $k_B T$ increases
- N decreases
- Spacing increases

Effect giving increasing C_h

- G_∞ decreases

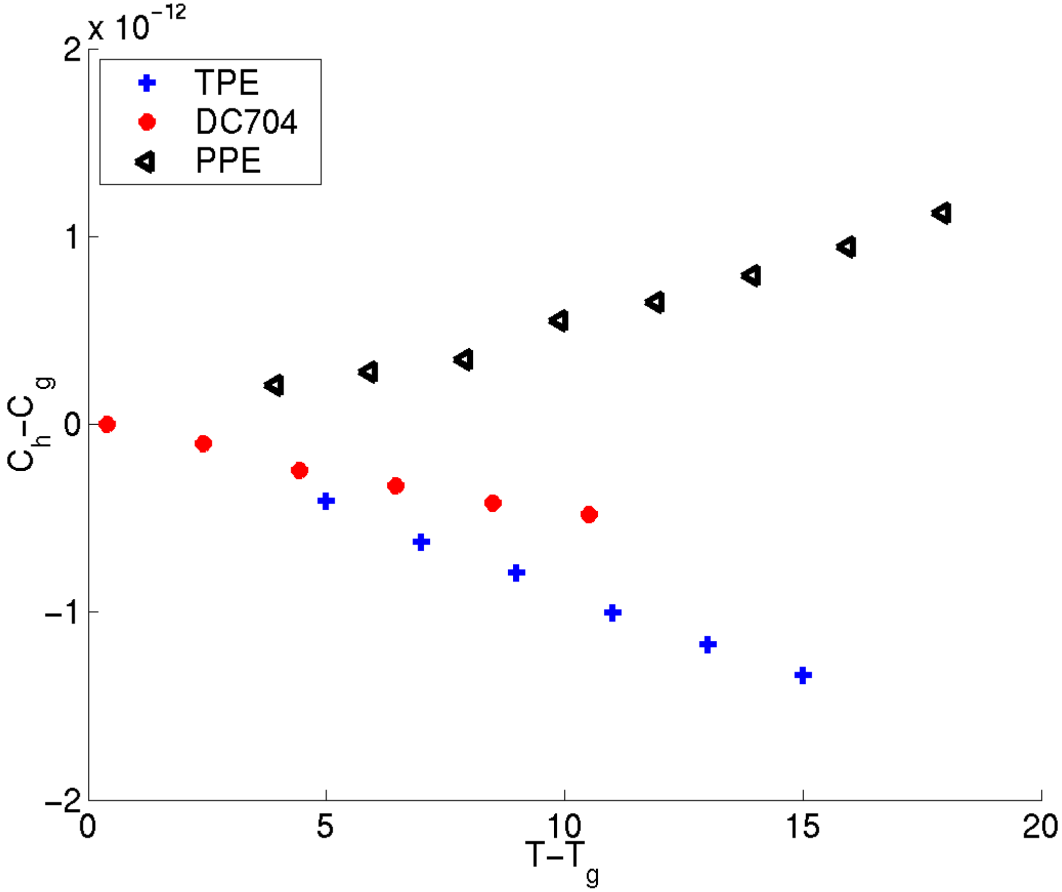
Original Debye model

$$\frac{\epsilon_h - 1}{\epsilon_h + 2} = \frac{N}{3\epsilon_0}\alpha_i$$

Generalized Debye model

$$\frac{\epsilon_h - 1}{\epsilon_h + 2} = \frac{N}{3\epsilon_0}\left[\alpha_i + \frac{\mu^2}{3k_B T\left(1 + \left(\frac{4\pi r^3}{k_B T}\right) G_\infty\right)}\right]$$

Temperature dependence C_h



	T_m	T_g	n^2	$\Delta\epsilon$
TPE Triphenylethylene	343K	249K	–	0.05
DC704 Silicone oil	–	211K	2.42	0.2
PPE Polyphenyl Ether	–	244K	2.66	1.5

Conclusions and questions

- There is an elastic contribution to ϵ_h.
- This is qualitatively in agreement with the generalized Debye model.
- Quantitative testing is difficult
- Other tests
  - The full spectrum, including the loss peak frequency.
  - The temperature dependence of fitted parameters.

Shear Mechanical and Dielectric Relaxation:
Are they Connected?

References

Christensen, T. & Olsen, N. B. [1995]. A rheometer for the measurement of a high shear modulus covering more than seven decades of frequency below 50 kHz, *Review of scientific instruments* **66**(10): 5019.

DiMarzio, E. A. & Bishop, M. [1974]. Connection between the macroscopic electrical and mechanical susceptibilities., *The Journal of Chemical Physics* **60**(10): 3802.