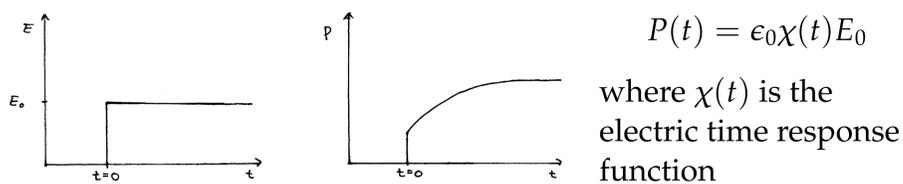


The dielectric and shear mechanical response is studied for viscoelastic molecular liquids. We focus on the high frequency behavior and find qualitative agreement with a generalized Debye-model

General phenomenology

A liquids viscosity increases dramatically when it is supercooled down to approximately $\frac{2}{3}$ of its melting temperature.

The liquids we study have viscosity ranging from 10^8 Pa s to 10^{12} Pa s which means that it flows a billion times slower than shampoo. In such a liquid time dependent behavior is observed in various quantities at experimental time scales. This can be illustrated by a dipolar liquids response to an instantaneously applied electric field.



The simplest models predict exponential/Debye relaxation. This is not found in viscous liquids. The reason for these non-Debye relaxations is not known and it is regarded as one of the main problems in the field of viscous liquids. We attempt to relate two of the relaxation processes which are often considered, namely the shear relaxation and the dielectric relaxation.

Measurements



Dielectric: 22-layer gold platen capacitor with empty capacitance of 68 pF. $10^{-3} - 10^6$ Hz
Shear modulus: Piezoelectric shear modulus gauge (PSG) [1] $10^{-3} - 10^{4.5}$ Hz

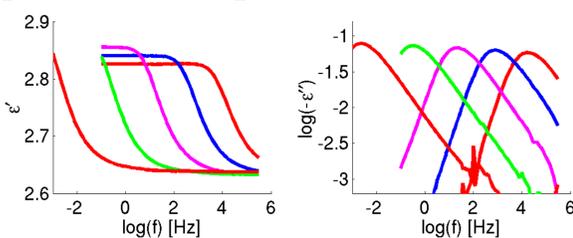
The measurements are performed in the frequency domain.

$$\text{Re} \left(P_z e^{i(\omega t + \phi)} \right) = \text{Re} \left(\epsilon_0 \chi(\omega) E_0 e^{i\omega t} \right)$$

The results are equivalent to the time domain results, the relation between the two domains is general:

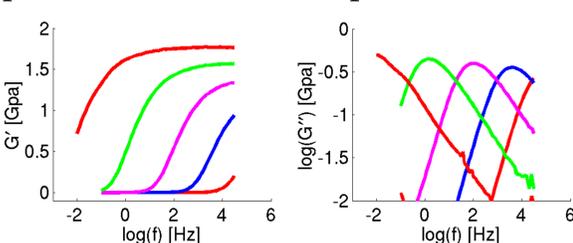
$$\chi(\omega) = i\omega \int_0^\infty \chi(t) e^{-i\omega t} dt$$

Typical dielectric spectrums



Dielectric and shear mechanical spectra on "Dow Corning silicone diffusion pump fluid (DC704)", at the temperatures: 235.6K, 229.6K, 223.5K, 217.5K and 211.4K

Typical shear mechanical spectrums



The maximum in imaginary part moves to higher frequencies as temperature is increased.

The high frequency end corresponds to short times. It is seen that at the high frequencies the liquid responses purely elastic, that is as a solid. At low frequencies the viscoelastic liquid behaves as a normal liquid.

Generalized Debye-model

The idea of understanding the dielectric relaxation by connection it to the frequency independent shear viscosity of the liquid goes back to Debye [2]. We work with a generalized Debye model proposed by DiMarzio and Bishop [3] in 1974, but which has not been thoroughly tested earlier. The lack of testing is partly due to the lack of comparable shear mechanical and dielectric data, and partly due to erroneous analysis of the models high frequency behavior.

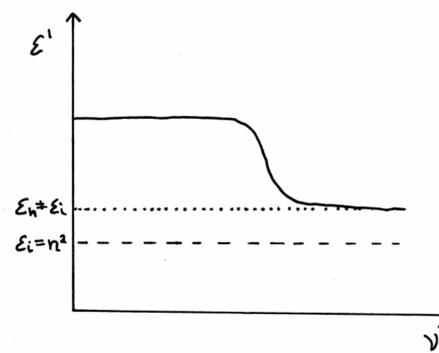
We present a consistent analysis of this high frequency behavior and some of the results from our experimental testing of the model [4].

Assumptions

- Spherical non-interacting dipoles
- Surroundings can be described as a viscous continuum, with a frequency dependent viscosity ($i\omega\eta(\omega) = G(\omega)$)
- Inertial effects can be ignored
- Rotational diffusion controls the dipole orientation

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

N is the dipole density, α_i is the polarizability of the individual molecule due to the induced changes in electron distribution, μ is the size of the permanent dipole moment of the molecules.



The model predicts an elastic contribution to the high frequency value of $\epsilon'(\omega)$ (ϵ_h) because:

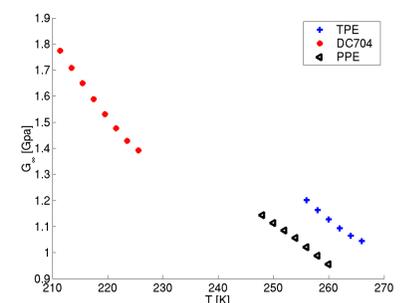
$$\lim_{\omega \rightarrow \infty} G(\omega) \neq \infty$$

This prediction has been ignored in the earlier analysis and tests of the model.

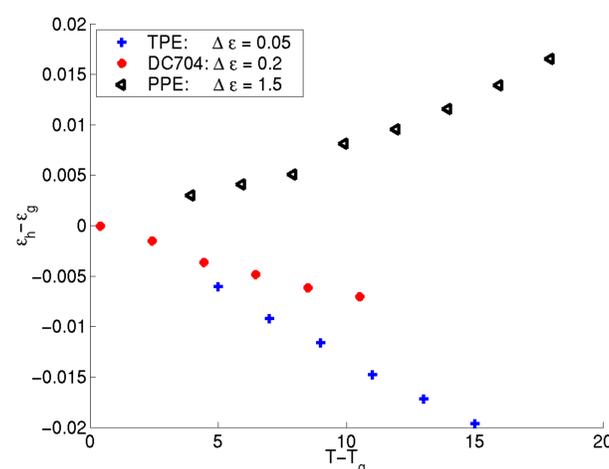
What controls the temperature dependency of ϵ_h ?

Increasing T

- Model predictions
 - Effects giving increasing ϵ_h
 - G_∞ decreases
 - N decreases due to thermal expansion
 - Effects giving decreasing ϵ_h
 - Spacing between capacitor plates increases due to the thermal expansion; giving a decrease in the measured ϵ_h
- Experimental problems



Measured ϵ_h



$\Delta\epsilon$ is directly related to the size of the dipole. For small $\Delta\epsilon$ the expansion of the liquid dominates the measured $\epsilon_h(T)$. As $\Delta\epsilon$ is increased the elastic contribution to $\epsilon_h(T)$ starts to dominate.

Conclusion

- There is an elastic contribution to ϵ_h . This is qualitatively in agreement with the generalized Debye model.

[1] T. Christensen and N. B. Olsen, *Rev. Sci. Instrum.* **66**,5019(1995)
[2] P. Debye, *Polar Liquids*, The Chemical Catalog Company, Inc. (1929)
[3] E. A. DiMarzio and M. Bishop, *J. Chem. Phys.* **60**,3802(1974).
[4] For more results see: <http://dirac.ruc.dk/~kniss/masterthesis/>