Ultraviscous liquids

Prevalence of approximate $\sqrt{t}$ relaxation for the dielectric α process in viscous organic liquids

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What is the philosophy behind the analysis?

A step back and analyze the α relaxation objectively.

- plenty of data - dielectric
- raw data analysis
- no models and data fit
- no subtraction of DC-conductivity

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Data in analysis:

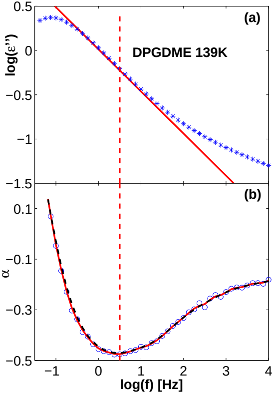
- high quality data
- 4-5 decades above $T_g(\tau_\alpha = 100s)$ (well-defined loss peak and sufficiently broad frequency interval of the high frequency loss)
- high density of measure points
- no simple mono-alcohols, polymers and plastic crystals.

The 52 organic liquids

Some of the data **are measured** and some were kindly **provided** from the Rössler group (Bayreuth, Germany) the Loidl-Lunkenheimer group (Augsburg, Germany) and the Paluch group (Katowice, Polland).

α-phenyl-o-cresol, DC705, trioxatridecane diamine, tricresyl-phosphate, triphenyl phosphite, 2,3-epoxy-proryl-phenylether, polypropylene-glycol, dioctyl phthalate, toluene-pyridine, glycerol, dicyclohecyl-methyl-2-methylsuccinate, 1,3-propane diol, dibuthyl phthalate, diethyl phthalate, 1,2-propanediol (propylene-glycol), sorbitol, salicyl salicylic acid, dipropylene-dimethyl-glycol-dimethyl-ether, di-*iso*-butyl phthalate, methyl-m-toluate, n-ε-methyl-caprolactam, n-propyl-benzene, 2-methyl-tetrahydrofuran, xylitol, polyphenyl-ether, triphenyl-ethylene, tetraphenyl-tetramethyl-trisiloxane, decahydroisoquinoline, propylene carbonate, dibutyl-ammonium-formide, butyronitrile, 2,4,6-trimethyl-heptane, isopropyl-benzene (cumene), 4-methyl-heptane, 2,3-dimethyl-pentane, 3-methyl-heptane, 3-methyl-pentane, sucrose-benzonate, 3-methyl phosphate, 3-fluoroaniline, phenylsalicate (salol), 2-picoline, ethylene glycol, diglycidyl-ether of bisphenol A (epoxy-resin), 4-tertbuthyl-pyridine, carborane, 2-phenyl-5-acetomethyl-5-ethyl-1,3-dioxocyclohexane, dicyclohexyl-2-methyl succinate, biphenyl-2yl-isobutylate, 2-methyl-pentane-2:4-diol, phenolphthalein-dimethylether, benzophenone, isoeugenol.

Model-independent shape parameter



Dielectric scan for ε'' of dipropylene glycol dimethyl ether (DPGDME) $T = 139K$ and the slope of the log-log plot.

The **minimum slope** α_{min} is the minimum value of:

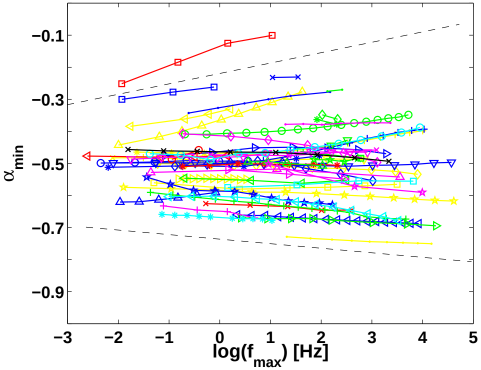
$$\alpha = \frac{d \log \varepsilon''}{d \log f}, \; f > f_{max}$$

Altogether 294 minimum slopes were identified for all the 52 liquids. The number of α_{min} values varies between 2 and 17 for each liquid and $-0.751 < \alpha_{min} < -0.101$.

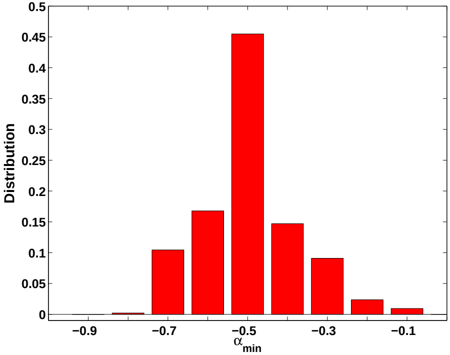
How is α_{min} connected to α relaxation?

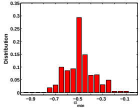
Plot of the minimum slope α_{min} versus loss peak frequency (temperature).

- There is a weak tendency that minimum slopes approach $-1/2$ as temperature is lowered;
- Liquids with well-separated α and β processes exhibit - $\varepsilon''(\omega) \propto \omega^{-\frac{1}{2}}$



The distribution of α_{min} - $\Delta\alpha_{min} = 0.1$

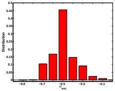


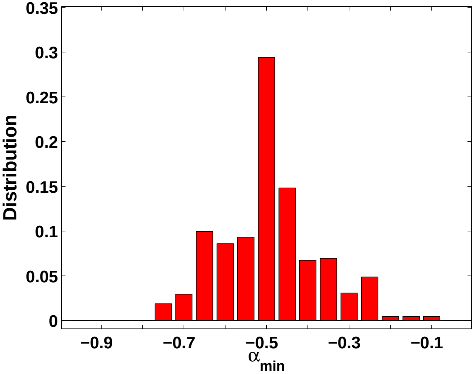


The majority of the investigated liquids have slope close to $-\frac{1}{2}$ or:

$$\varepsilon''(\omega) \propto \omega^{-\frac{1}{2}}, \, \omega > \omega_{max} \, . \tag{1}$$

The distribution of α_{min} - $\Delta\alpha_{min} = 0.05$





The majority of the investigated liquids have slope close to $-\frac{1}{2}$ or:

$$\varepsilon''(\omega) \propto \omega^{-\frac{1}{2}}, \omega > \omega_{max} . \tag{2}$$

...but why are we surprised?

Olsen et al. 2001 stated the conjecture: If the α-process obeys time (frequency) temperature superposition (TTS) $\Longrightarrow$ the frequency dependence of the high-frequency α-relaxations with the universal exponent of $-\frac{1}{2}$, or:

$$\epsilon''(\omega) \propto \omega^{-\frac{1}{2}}, \omega < \omega_{max} . \quad (3)$$

Theoretical results: The idea is almost 40 years old.

- One dimensional diffusion models - S.H. Glarum, J. Chem. Phys. **33** (1960) 639. M.A. Isakovich and I.A. Chaban, Zh. Eksp. Teor. Fiz. **50** (1966) 1343. A.J. Barlow, A. Erginsav, and J. Lamb, Proc. R. Soc. London A **298** (1967) 481. C.J. Montrose and T.A. Litovitz, J. Acoust. Soc. Am. **47**(1970) 1250. C.K. Majumdar, Solid State Commun. **9** (1971) 1087. G. Wyllie, J. Chem. Phys. **76** (1979) 1017.
- BEL model - J.C. Dyre, Erohys. Lett., **71** (2005) 646.
- (Mode coupling theory result)

α_{min} and the deviation from Arrhenius behavior

The "**activation energy temperature index**":

$$I_{\Delta E}(T) = -\frac{d \ln \Delta E(T)}{d \ln T},$$

$f_{max}(T) = f_0 \exp(-\Delta E(T)/k_B T)$ with $f_0 = 10^{14}$ Hz.

Connection to fragility (steepness) index:

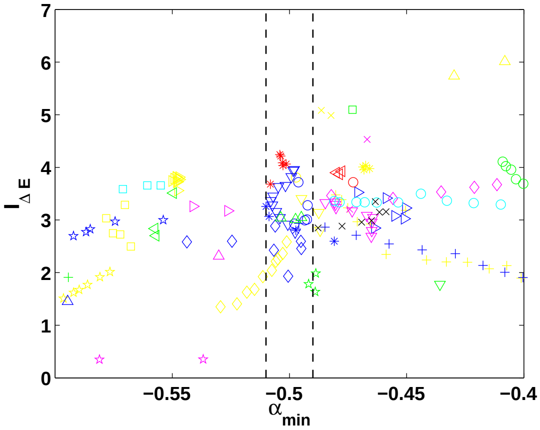
$$\begin{aligned} m &= \log\left(\frac{\tau(T_g)}{\tau_0}\right)(I_{\Delta E}(T_g)+1) \\ &= 16(I_{\Delta E}(T_g)+1), \end{aligned}$$

if $\tau(T_g) = 100$s and $\tau_0 = 10^{-14}$s.

J. C.Dyre, N. B. Olsen, and T.E.Christensen, Phys. Rev. B **53** (1996) 2171.
K. U. Schug, H. E. King, and R. Böhmer, J. Chem. Phys. **109**(1998) 1472 ;
J. C. Dyre and N. B. Olsen, Phys. Rev. E **69** (2004) 042501;

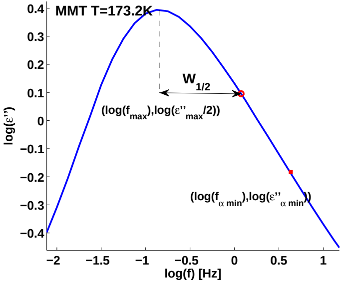
T. Hecksher, A. I. Nielsen, N. B. Olsen, and J. C. Dyre, Nature Physics **4** (2008) 737

Correlation between minimum slope and temperature index?



The “activation energy temperature index” $I_{\Delta E}$ versus minimum slope α_{min}

Another shape parameter - the width

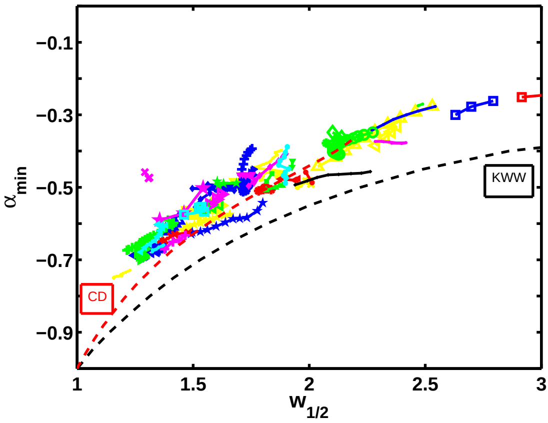


The modified width:

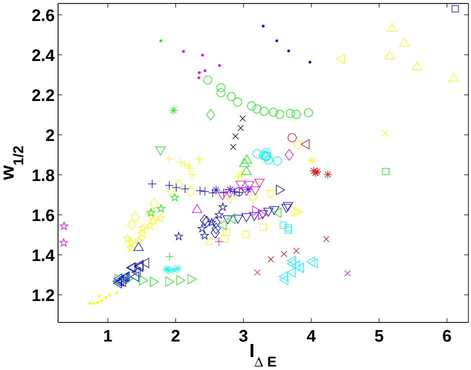
$$w_{\frac{1}{2}} = \frac{W_{\frac{1}{2}}}{W_D/2},$$

where W_D is the Debye width.

Modified width and minimum slope



Correlation $w_{\frac{1}{2}}$ and $I_{\Delta E}$?



The "activation energy temperature index" $I_{\Delta E}$ versus the modified width $w_{\frac{1}{2}}$

Conclusions

- Strong indications that the post-peak dispersion is characterized by $\sqrt{t}$ decay... but more data for different liquids needed=better statistics
- The minimum slope $\alpha_{min} = -\frac{1}{2}$ is a limitting value as α and β processes separate
- The value -0.5 minimum slope and temperature index are not correlated

Thank You for Your attention!

Looking for a post doc. position