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On the non-exponentiality of the Debye-like relaxation of monoalcohols

Dr. Silvia Arrese-Igor

Prof. Angel Alegria

Materials Physics Center
Centro de Física de Materiales
Materialen Fisika Zentroa

Materials Physics Department
Dpto de Física de Materiales
Materialen Fisika Saila

Universidad
del País Vasco
Euskal Herriko
Unibertsitatea

Debye(-like) dielectric relaxation

- Common term to refer “in general” to the particular relaxation shown by some fluids which show:
- **Strong dielectric absorption** (much more than expected on the bases of single molecule dipole)
 - **Slower** and more intense **than structural relaxation** or **α-relaxation**
 - “Generally” **exponential** or nearly exponential (single characteristic time, -almost- no timescale dispersion)

Typically related to hydrogen bond mediated intermolecular association (water, monoalcohols, amides, supramolecular polymers....)

Historicamente con dielectricas pero más recientemente también se ha detectado mediante otras técnicas

Debye(-like) dielectric relaxation in monoalcohols

Object of intense research throughout last century

Seems to be particular to **monoalcohols**

It shows great **variability** (mostly strength) with length and branching of the alkyl chain and with the position of the hydroxyl group on the chain

Many evidence link its origin to **supramolecular structures** resulting from **HB interaction** so that prevailing picture is that Debye-like relaxation originates from the rearrangement of the HB structure

Structure and dynamics of monohydroxy alcohols—Milestones towards their microscopic understanding, 100 years after Debye

Roland Böhmer^a, Catalin Gaiaru^a, Ranko Richert^b

^a *Fakultät Physik, Technische Universität Dortmund, 44221 Dortmund, Germany*

^b *Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA*

detailed mechanism still under debate

Debye(-like): HB structure

Static scattering experimental results: pre-peak denoting supramolecular/cluster structures. On average up to two HB per molecule → -OH groups can aggregate in linear structures

Inelastic scattering experimental results agree with chain-like and ring-like aggregates

Computer Simulations: Chain-like and ring-like aggregates have been identified, the majority forming chain-like aggregates

Average cluster size around 5-10 molecules but broad distributions
variable ring/chain aggregate ratios (OH type and modelling details)

Interpretation of rheological data in terms of short-chain-polymer, size around 9 molecules

Characteristic times distribution of the Debye-like relaxation

“Generally” **exponential** or nearly exponential when pure (single characteristic time, -almost- no timescale dispersion)...

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BUT NOT ALWAYS... some clear examples 2B1O, 2H1D

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Dielectric relaxation of long-chain glass-forming monohydroxy alcohols

Yanqin Gao,^{1,2} Wenkang Tu,¹ Zeming Chen,¹ Yongjun Tian,¹ Riping Liu,¹ and Li-Min Wang^{1,a)}

¹State Key Lab of Metastable Materials Science and Technology, and College of Materials Science and Engineering, Yanshan University, Qinhuangdao, Hebei 066004, China

²Department of Physics, School of Science, North University of China, Taiyuan, Shanxi 030051, China

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The dielectric relaxation of two long-chain glass forming monohydroxy alcohols, 2-butyl-1-octanol and 2-hexyl-1-decanol, is studied at low temperature. Remarkable broadening from the pure Debye relaxation is identified for the slowest dynamics, differing from the dielectric spectra of short-chain alcohols. The broadening of the Debye-like relaxation in the two liquids develops as temperature increases, and the approaching of the Debye-like and structural relaxation widths is shown. Similar results are observed in the dielectric spectra of dilute 2-ethyl-1-hexanol in either 2-hexyl-1-decanol or squalane. The results of the liquids and mixtures reveal a correlation between the broadening and the Debye-like relaxation strength. Molecular associations in monohydroxy alcohols are discussed with the modification of the Debye relaxation. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4825398>]

In the original work "increased broadening at higher T is ascribed to the reduction in chain length of H-bonded associations in Debye liquids"

FIG. 9. Dependence of the relaxation profile parameter, γ_D , of the Debye-like relaxation on the relaxation strength ratio of relaxations I (D) and II (α), $\Delta\epsilon_D/\Delta\epsilon_\alpha$, in various glass-forming liquids. The data of 2E1H is from Ref. 16. Dashed lines are guides to the eye. The inset presents the dependence of γ_D on the Debye-like relaxation strength, $\Delta\epsilon_D$.

Characteristic times distribution of the Debye-like relaxation

2B1O
 $\eta_c=12$

non-exponential

2E1H
 $\eta_c=8$

exponential

37dM1O
 $\eta_c=10$

In the original work "increased broadening at higher T is ascribed to the reduction in chain length of H-bonded associations in Debye liquids"

What can we said about the broadening of Debye-like relaxation?

Only characteristic of long chain monalcohols?

non-exponential

exponential

Characteristic times distribution of the Debye-like relaxation

also in not so long but rather "complex" architectures

exponential

2E1H

non-exponential

5M3H

Characteristic times distribution of the Debye-like relaxation

also in not so long but rather "complex" architectures

- Non exponentiality "hidden" by α -relaxation contribution
- Detailed analysis based on the derivative of ϵ' evidence clear deviations from exponentiality
- The extent of the broadening follows the same trend as in 2B1O or 2H1D, the higher the T the broader the DL relaxation and the lower the $\Delta\epsilon_{\text{Debye}}/\Delta\epsilon_{\alpha}$ ratio.
- Obviation of stretched character implications on the quantification of $\Delta\epsilon_{\text{Debye}}$ (part of the area ascribed to α -relaxation) or τ_{α}

Characteristic times distribution of the Debye-like relaxation

Characteristic times distribution of the Debye-like relaxation

Our approach: Combine BDS and time domain dielectric techniques

Broadband Dielectric Spectroscopy and derivative analysis.

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Thermally Stimulated Depolarization Current (TSDC)

Why?

Partial polarization (PP) methods in **TSDC** allow **detailed study** of relaxations spectral shape or characteristic times distribution.

Starting point was previous experience on the analysis of chain relaxation (normal modes) and slow processes near T_g by TSDC in low molecular weight polymers.

Exercise: We set out to explore to which extent experimental results for different MA are/were compatible with the analogy to polymer chain dynamics.

Thermally Stimulated Depolarization Current (TSDC)

MEASURED QUANTITY: ELECTRIC CURRENT
due to the thermally stimulated release of the polarization during heating

• 1st PART PREPARATION/POLARIZATION:

The experiment starts by **polarizing** the sample (charging the sample capacitor) at a **temperature** where the static value of permittivity is **high** allowing **orientational polarization**.

The polarizing **voltage is maintained during cooling** to low temperature, so that the dipolar entities become frozen and the orientational polarization remains after removing the polarizing voltage.

Thermally Stimulated Depolarization Current (TSDC)

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• 2nd PART MEASUREMENT:

The subsequent heating of the sample capacitor connected to an electrometer allows detecting the depolarization current produced by the randomization of the dipole orientation. The **depolarization current** pass through a **maximum value when the dipolar units become mobile enough** (time scale of the order of the reciprocal of the heating rate) giving rise to a TSDC peak.

TSDC: FULL POLARIZATION

MEASURED QUANTITY: ELECTRIC CURRENT
due to the thermally stimulated release of the polarization during heating

FULL POLARIZATION:
measured current contains contributions from all the dielectrically active relaxations (high T_{on} + low $T_{off} = T_{ini}$)

TSDC: PARTIAL POLARIZATION

MEASURED QUANTITY: ELECTRIC CURRENT
due to the thermally stimulated release of the polarization during heating

PARTIAL POLARIZATION:
variation of T_{on} and/or T_{off} during cooling allows to decrease or even suppress the contribution of slow or fast relaxing entities

EXAMPLE: P182000

variation of T_{off}

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TSDC: Qualitative information

Qualitative PP-TSDC:

- isolate/separate relaxations
- vary/weight contribution of relaxations
- discriminate between exponential and distributed relaxation
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variations of weight with T_{on}

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EXAMPLE: 2E1H

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By definition full or PP of an exponential relaxation provides the same depolarization current except for an intensity factor

Several modes
↓
variations of shape with T_{off}

TSDC: QUANTITATIVE INFORMATION/ANALYSIS

Qualitative PP-TSDC:

- isolate/separate relaxations
- vary/weight contribution of relaxations
- discriminate between exponential and distributed relaxation
-

Quantitative Analysis of TSDC:

- Determination of $\tau(T)$ from MAXima position and variable heating rate experiments
- Determination of $\tau(T)$ from single depolarization curve analysis
- Calculate or construct a model or theoretical of depolarization current curve at equilibrium condition

(i) $\tau(T)$ and shape parameters as inputs

+

(ii) the reduced time formalism

$$\frac{t}{\tau} = \int_{t_{off}}^t \frac{dt'}{\tau(t')}$$

(iii) superposition principle for the calculation currents resulting from PP

+

(iv) general expressions for the depolarization intensity or stored charge of any specific type of relaxation

$$I = \frac{Q_0}{\tau} e^{-(t/\tau)} \quad I = \frac{Q_0}{\tau} \beta(t/\tau)^{\beta-1} e^{-(t/\tau)^\beta} \quad I = \frac{Q_0}{\tau} \frac{1}{\Gamma(b)} (t/\tau)^{b-1} e^{-(t/\tau)}$$

Calculated depolarization curves will reproduce the experiment as long as the system remains in equilibrium i.e. its dynamics follows the equilibrium $\tau(T)$ law used as input !!

PP-TSDC T_{off} variation experiments **Do we observe several Modes?**

2Ethyl1Hexanol (2E1H)

NO indication of several modes

calculated depolarization curve under an exponential model agrees with experimental observation

(no hint of Rouse modes)

PP-TSDC Toff variation experiments **Do we observe several Modes?**

NO variation of shape with Toff

NO variation of shape with Toff

shape variation with Toff

some variation of shape with Toff

PP-TSDC experiments vs calculation **Exponential Debye relaxation?**

Remember: calculated depolarization curves reproduce the response of the system at equilibrium condition

Systems at equilibrium above T_g

Systems at equilibrium above T_g

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Remember: calculated depolarization curves reproduce the response of the system at equilibrium condition

Systems at equilibrium above T_g

Systems at equilibrium above T_g

TSDC vs BDS

Exponential Debye relaxation?

When a Cole-Davidson type relaxation is assumed for the analysis of both **BDS** and **TSDC** data **good agreement** is found for the **width** of the **DL relaxation** between both set of data.

Note that the equivalent τ_s /timescales explored by TSDC are very low/large, explaining why 5M3H is in agreement with an exponential type relaxation when studied by TSDC

PP-TSDC Toff variation experiments **Exponential Debye relaxation?**

When a Cole-Davidson type relaxation is assumed for the analysis of both **BDS** and TSDC data **good agreement** is found for the **width** of the **DL relaxation** between both set of data.

No clear relation between the timescale separation of DL and α -relaxation and b_{CD}

Conclusions

Exponential character of the Debye-like relaxation:

- 2B1O and 2H1D are not unique regarding their non-exponential Debye-like relaxation and shorter MA 5M3H also exhibits non-exponential Debye-like relaxation. The smaller the intensity of the Debye-like relative to the segmental relaxation, the broader the relaxation.
- The former is consistently evidenced by the analysis of: (i) the derivative of the real part of the dielectric permittivity; (ii) Isothermal Depolarization Currents; and Partial Polarization Thermo Stimulated Depolarization Currents.
- A general Cole-Davidson type relaxation gives a good description of BDS, IDC and PP-TSDC the data (at equilibrium). Fitting models in which the extra intensity of a non-exponential Debye-like relaxation is accounted for by a broad symmetric segmental relaxation might underestimate the strength of the Debye-like relaxation.
- No evident relation between b_{CD} and the timescale separation between DL and α -relax

Debye-like relaxation vs Rouse like dynamics:

- Mode analysis by PP-TSDC do not indicate the presence of several Rouse-like modes in the dielectric response of 2E1H. For 2B1O, 37dM1O and 5M3H the occurrence of non-equilibrium effects in the low-T side of the depolarization current prevents from extracting definite conclusions.

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THANK YOU FOR YOUR ATTENTION !

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