“DIELECTRIC SPECTROSCOPY &
Comparison With Other Techniques”
DIELECTRIC SPECTROSCOPY

• measures the dielectric and electric properties of a medium as a function of frequency (time)

• is based on the interaction of an external electric field with the electric dipole moment and charges of the medium
Dielectric properties

Complex dielectric permittivity *relative to vacuum*

\[ \varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \]

Complex conductivity

\[ \sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) \]

Complex electric modulus

\[ M^*(\omega) = M'(\omega) + iM''(\omega) \]

as a function of temperature
Medium in an external electric field

\[ D = \varepsilon_0 E + P \]
\[ P = \varepsilon_0 \chi_s E \]
\[ \varepsilon_s = \chi_s + 1 \]

\[ D = \varepsilon_0 \varepsilon_s E \]
Medium in an external electric field

Relation between macroscopic and microscopic quantities

\[ P = \frac{1}{V} \sum_i p_i \]

Dipole moments can have an induced or a permanent character

Permanent dipole moments, \( \mu \)

Induced polarization, \( P_\infty \)

\[ P = \frac{1}{V} \sum_i \mu_i + P_\infty = \frac{N}{V} \langle \mu \rangle + P_\infty \]

\( \langle \mu \rangle \) is determined by:
- The interaction between the dipoles
- The local electric field at the location of the dipole
Medium in an external electric field

Relation between macroscopic and microscopic quantities

• No interaction between dipoles and local electric field equal to the outer applied field thermal energy $\leftrightarrow$ interaction energy between the dipole and the electric field

$$\langle \mu \rangle = \frac{\mu^2}{3kT} E$$

$$\varepsilon_s - \varepsilon_\infty = \frac{1}{3\varepsilon_0} \frac{\mu^2}{kT} \frac{N}{V}$$  \hspace{1cm} \text{Langevin equation}

• Interactions between molecules, effect of polarization of environment

$$\varepsilon_s - \varepsilon_\infty = \frac{1}{3\varepsilon_0} \frac{\mu^2}{kT} \frac{N}{V}$$  \hspace{1cm} \text{Onsager-Kirkwood-Froehlich equation}

$$F = \frac{\varepsilon_s (\varepsilon_\infty + 2)^2}{3(2\varepsilon_s + \varepsilon_\infty)}$$  \hspace{1cm} \text{“Internal field” Onsager factor}

$$g = \frac{\mu_{\text{int}}^2}{\mu^2} = 1 + z \langle \cos \psi \rangle$$  \hspace{1cm} \text{“Dipole interactions” Kirkwood-Froehlich factor}
Dielectric dispersion in time domain

Perturbation Electric Field $E(t)$

Response Electric Displacement $D(t)$

$\varepsilon(t)$

$D(t) = \varepsilon_0 \varepsilon(t) E_0$

$\varepsilon(t) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \varphi(t)$

$\varphi(0) = 0 \quad \varphi(\infty) = 1$

$\Phi(t) = 1 - \varphi(t)$
Dielectric dispersion in frequency domain

Perturbation
Electric Field
\( E(\omega) \)

Response
Electric Displacement
\( D^*(\omega) \)

\[ E(t) = E_0 \sin(\omega t) \]

\[ D(t) = D_0 \sin(\omega t - \delta) \]

\[ D^*(\omega) = D'(\omega) + iD''(\omega) \]
\[ D'(\omega) = D_0 \cos \delta(\omega) \]
\[ D''(\omega) = D_0 \sin \delta(\omega) \]
\[ \varepsilon'(\omega) = \frac{D_0}{\varepsilon_0 E_0} \cos \delta(\omega) \]
\[ \varepsilon''(\omega) = \frac{D_0}{\varepsilon_0 E_0} \sin \delta(\omega) \]
Time-frequency domain

Time dependent dielectric function  \( \varepsilon(t) \)  

\[
\frac{d\varepsilon(t)}{dt} = \frac{1}{2\pi} \int_0^\infty (\varepsilon^*(\omega) - \varepsilon_\infty) \exp[i\omega t] d\omega
\]

Complex dielectric function  \( \varepsilon^*(\omega) \)  

\[
\varepsilon^*(\omega) = \varepsilon_\infty - \int_0^\infty \frac{d\varepsilon(t)}{dt} \exp[-i\omega t] dt
\]

Relation between dielectric function and correlation function

\[
\varepsilon(t) - \varepsilon_\infty = (\varepsilon_s - \varepsilon_\infty)[1 - \Phi(t)]
\]

\[
\varepsilon^*(\omega) - \varepsilon_\infty = (\varepsilon_s - \varepsilon_\infty) \int_0^\infty \left[-\frac{d\Phi(t)}{dt}\right] \exp[-i\omega t] dt
\]

\[
\Phi(t) = \frac{\sum_i \langle \mu_i(0) \mu_i(t) \rangle + 2 \sum_i \sum_{i < j} \langle \mu_i(0) \mu_j(t) \rangle}{\left\langle \left( \sum_i \mu_i \right)^2 \right\rangle}
\]

\[
\Phi(0) = 1 \quad \Phi(t \to \infty) = 0
\]
Dielectric dispersion in frequency domain

Debye relaxation

\[ \Phi(t) = \exp\left( -\frac{t}{\tau_D} \right) \]

\[ \varepsilon(t) - \varepsilon_\infty = \Delta\varepsilon \left[ 1 - \exp\left( -\frac{t}{\tau_D} \right) \right] \]

\[ \varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon}{1 + i\omega\tau_D} \]
Dielectric dispersion in frequency domain

Kolhrauch-Williams-Watts KWW relaxation

\[ \Phi(t) = \exp \left[ -\frac{t}{\tau_{KWW}} \right]^{\beta_{KWW}} \]

\[ \varepsilon(t) - \varepsilon_{\infty} = \Delta \varepsilon \left[ 1 - \exp \left( -\frac{t}{\tau_{KWW}} \right) \right]^{\beta_{KWW}} \]

Havriliak-Negami relaxation

\[ \Phi_{HN}(\omega) = \frac{1}{\left[ 1 + (i\omega \tau_{HN})^{\alpha} \right]^{\gamma}} \]

\[ \varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta \varepsilon}{\left[ 1 + (i\omega \tau_{HN})^{\alpha} \right]^{\gamma}} \]

\[ \beta_{KWW}^{1.23} \approx \alpha \gamma \quad \gamma = 1 - 0.812(1 - \alpha)^{0.387} \]
Dielectric dispersion in frequency domain
Dipole moments in polymers

A

B

C

-CH₂-CH₂-C≡C-CH₃

-CH₂-C-H

-CH₂-C-H

CH₃

CH₃

CH₃
Molecular motions accommodate dipole reorientation in polymers

Decreasing frequency of external field
Dielectric dispersion in frequency domain
Glassy state (localized motions)

**β, γ relaxations**

Depends on chemical structure and local molecular environment

- Motion of groups present in side chain around the main chain or bonds of the side chain
- Motion of groups in the main chain
- The β relaxation of Johari-Goldstein type

Thermally activated motion between two potential wells separated by a potential barrier
Glassy state (localized motions)

Characteristics of dielectric dispersion

- Temperature dependence of relaxation rate (time) is Arrhenius

\[ f_\beta = f_\infty \beta \exp \left[ -\frac{E_{act}}{kT} \right] \]

- Dielectric strength, \( \Delta \varepsilon \), increases with increasing \( T \), more dipoles contribute

\[ \Delta \varepsilon \propto F_{\text{Onsager}} g \frac{\mu^2 N}{kT V} \]

- Broad (4-6 decades) symmetric dielectric dispersion, becomes narrower with increasing \( T \) as a result of molecular environment homogenization
Glassy state (localized motions)

The graph shows the relationship between the natural logarithm of the maximum frequency ($\log f_{\text{max}}$) and the reciprocal of the temperature in Kelvin ($1000/T[K^{-1}]$) for the glassy state and the liquid/rubbery state. The glassy state is indicated by a red line, while the liquid/rubbery state is indicated by a gray line. The graph highlights the transition between the two states.
Rubbery/liquid state (segmental motions)

α relaxation (dynamic glass transition)

• relaxation time reflects the time involved in the structural rearrangement (glass transition) of the molecules

• $\tau$ changes by many orders of magnitude from the liquid to the glass

• The $\alpha$-relaxation in polymers involves cooperative micro-Brownian segmental motions of the chains

• Segmental motions are associated with conformational transitions taking place about the skeletal bonds
Rubbery/liquid state (segmental motions) II

Characteristics of dielectric dispersion

• Temperature dependence of relaxation rate (time) described by VTF equation

\[ f_\alpha = f_\infty \exp \left[ -\frac{B}{T - T_0} \right] \]

• Dielectric strength, \( \Delta \varepsilon \), decreases with increasing \( T \) more strongly than predicted by

\[ \Delta \varepsilon \propto F_{\text{Onsager}} g \frac{\mu^2 N}{kT V} \]

• Asymmetric dielectric dispersion
• High \( f \) side slope, \( n \): local chain dynamics (\( n \) increases as \( T \) increases)
• Low \( f \) side slope, \( m \): cooperative dynamics of environment (\( m \) increases as \( T \) increases)
Rubbery/liquid state (global motions)
Rubbery/liquid state (global motions)  

**Normal mode relaxation (nm)**

- Observed in polymers containing dipoles type A and AB
- Motions of the whole chain
- Observed at frequencies lower than the $\alpha$ relaxation
- The relaxation time of the process is strongly dependent of the molecular weight
Rubbery/liquid state (global motions) II

Characteristics of dielectric dispersion

- $T$ dependence of relaxation rate (time) same as this of $\alpha$ relaxation

- Dielectric strength proportional to the mean end-to-end vector of chain

\[ \Delta \varepsilon_{nm} = \frac{4\pi N_A \mu_p^2 F_{\text{Onsager}}}{3kTM} \langle r^2 \rangle \]

- $m=1$ and $n=0.7$ predicted by theory, in practice $n$ considerably smaller
Rubbery/liquid state (charge motions)

Conductivity

- Motion of charge carriers

\[
\sigma^*(\omega) = \sigma'(\omega) + i \sigma''(\omega) = i \omega \varepsilon_0 (\varepsilon^*(\omega) - 1)
\]

\[
\sigma'(\omega) = \omega \varepsilon_0 \varepsilon''(\omega)
\]

\[
\sigma''(\omega) = \omega \varepsilon_0 (\varepsilon'(\omega) - 1)
\]

- \(\varepsilon'\) is not affected

- \(\varepsilon''\) increases with decreasing \(f\) (slope of \(\log \varepsilon''\) vs \(\log f\) equal to -1)

- \(\sigma'\) independent of \(f\) equal to dc conductivity, \(\sigma_{dc}\)

- T dependence of \(\sigma_{dc}\) Arrhenius, VTF or other gives information on the conductivity mechanism
Separation of charges at interfaces

Maxwell-Wagner-Sillars relaxation (MWS)
- Blocking of charges at interfaces inside inhomogeneous materials
- Existence of regions with different characteristics ($\sigma, \varepsilon$)
- Relaxation rate (time) depends on:
  - volume fraction, shape, $\sigma$ and $\varepsilon$ values of regions

Electrode Polarization
- Blocking of charges at sample/electrode interfaces
- Observed as a steep increase of $\varepsilon'$
- Magnitude and frequency position of the process depend on the conductivity of the sample (high values of $\sigma$ shift polarization to high f)
- Time of the process depends on the sample thickness (increase of thickness results in an increase of time of process)
Comparison with other techniques

• Understanding the correlation between parameters of the molecular and supermolecular structures and macroscopic properties.

• Contribution to open questions regarding the $\alpha$ relaxation by covering the widest possible time/frequency scale range by different experimental techniques.
Comparison with Mechanical measurements

Material testing method & tool for studying dynamics in polymers

- Material in an external mechanical field
- Insulator $\equiv$ elastic solid, conductor $\equiv$ viscous liquid
- Viscoelastic response is analogous to dielectric dispersion
- Modulus representation is used
- In order dielectric dispersion be compared to mechanical one electric modulus has to be used for data representation

$$M^*(\omega) = \frac{1}{\varepsilon^*(\omega)}$$
Comparison with Mechanical measurements

Extension in broad $f$ range by constructing master plots
Comparison with Mechanical measurements

Comparison of relaxation time temperature dependence
Comparison with Mechanical measurements

Selectivity of dielectric spectroscopy (block copolymers)
Comparison with Quasielastic Neutron Scattering

- Observation of the dynamics on a microscopic length and time scale ($10^{-7}$-$10^{-11}$s)

- $S(Q, \omega)$ contains not only temporal information but also spatial information of the particle correlation function
Comparison with Quasielastic Neutron Scattering

Different T

![Graph showing S(Q,\omega) (a.u.) vs. E(\mu eV) for different Q values at different temperatures](graph1.png)

![Graph showing S(Q,t)/S(Q,0) vs. t for different Q values at different temperatures](graph2.png)
Comparison with Quasielastic Neutron Scattering

\[ S(Q, \omega) = -\frac{1}{\omega} \text{Im}(\Phi^*(\omega)) \]

\[ \tau(Q, T) = \alpha(T)\tau(Q) \]

\[ \tau\left(Q = 1\text{Å}^{-1}, T \right) \]

Comparable to

\[ \tau_{\text{dielectric}}(T) \]
References

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