University of Potsdam, Institute of Physics
Advanced lab experiments
May 31, 2001

M6 Dielectric spectroscopy

Tutor: Dr. Peter Frübing [1]

Contents

The computer programs were written by Mirko Krumpe, stud. phys.

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[1] Tel.: (0331) 977-1456, Email: fruebing@rz.uni-potsdam.de, Raum 1.19.2.16.

1 Introduction

1.1 Motivation

Dielectric spectroscopy measures the dielectric permittivity as a function of frequency and temperature. It can be applied to all non-conducting materials. The frequency range extends over nearly 18 orders in magnitude: from the μHz to the THz range close to the infrared region. Dielectric spectroscopy is sensitive to dipolar species as well as localised charges in a material, it determines their strength, their kinetics and their interactions. Thus, dielectric spectroscopy is a powerful tool for the electrical characterisation of non-conducting or semiconducting materials in relation to their structure and also of electronic or sensor devices. The lab experiment is an introduction into basic concepts and measurement practise of this widely used technique.

It is highly recommended to study this manual in detail. It is already rather concise. There is no textbook which can be alternatively recommended for an introduction.
In the text, there are a few **Checkpoints**. They test your understanding of the basic concepts; you should be prepared to answer the questions in the discussion with the tutor prior to the experiment. Selected topics will be included in the lab report.

1.2 Physical and mathematical concepts

- Electric polarisation
- Debye's theory of dielectric relaxation
- Equivalent-circuit analysis
- Dielectric relaxation in condensed matter, particularly in polymers

1.3 Equipment

- Hewlett Packard model 4284A precision impedance meter (ac bridge)
- Dielectric-sample holder
- Novocontrol QUATRO cryosystem

1.4 Tasks

1. Impedance spectrum of a $R-C$ model circuit
   Measure the frequency dependence of the capacitance of a $R-C$ unit representing a homogeneous dielectric specimen with a finite dc conductivity and with a Debye relaxation supplied with ideal contacts. Discuss the response function by use of an appropriate representation of data. Determine the characteristic quantities which

describe the dielectrical properties of the specimen. Neglecting the dc conductivity, calculate the maximum frequency of the dissipation factor and compare it with the experimental value.

2. Dielectric spectrum of ice
   Measure the dielectric spectrum of ice at three fixed temperatures between -50 °C and -5 °C . Discuss the frequency and temperature dependence of the permittivity by use of the Cole-Cole representation and by comparison with the Debye response.

3. Dielectric spectroscopy on a polymer film
   Measure the temperature dependence of the dielectric permittivity of an amorphous polymer film containing one kind of strong molecular dipoles at three fixed frequencies. Explain the result qualitatively by use of structural and thermal data which will be given below. Calculate the effective dipole moment of the molecular dipoles.

2 Theoretical background

2.1 Electric polarisation

When a metal body is exposed to an electric field, free electrons are displaced by electric forces until the field in the body vanishes. In an ideal dielectric (dc conductivity is zero) there exist only bound charges (electrons, ions) which can be displaced from their equilibrium positions until the field force and the oppositely acting elastic force are equal. This phenomenon is called *displacement polarisation (electronic or ionic polarisation)*. A dipole moment is induced in every atom or between ion pairs. In molecular dielectrics, bound charges can also form permanent dipoles. The molecular dipoles can only be rotated by an electric field. Usually, their dipole moments are randomly oriented. In an external field, however, an orientation parallel to the field direction is preferred, so that a dipole moment is induced. This process is called *orientational polarisation.*

Now consider an arbitrarily shaped dielectric sample with two metal electrodes partially covering the surface at opposite faces. The *polarisation* $\vec{P}$ is defined as *dipole moment per unit volume*:

$$\vec{P} = \frac{\mathrm{d}\vec{m}_{el}}{\mathrm{d}V}\,, \tag{1}$$

where $\vec{m}_{el}$ is the dipole moment, defined by

$$\vec{m}_{el} = \sum_{i=1}^{N} q_i \vec{r}_i\,. \tag{2}$$

Here, q_i and r_i are the charges and their coordinates, respectively, and N is the number of dipoles. It follows that for homogeneous, isotropic materials the static polarisation is given by

$$\vec{P} = N_D \vec{m}_{el}\,, \tag{3}$$

where N_D is the dipole density, defined as $N_D = N/V$.

The induced dipole moments create an internal field, which lowers the external field. Therefore, the polarisation saturates at higher field strengths. The resulting mean internal field is called the *macroscopic electric field* $\vec{E}$. This field is also considered in the Maxwell equations. At small fields the polarisation is proportional to $\vec{E}$:

$$\vec{P} = \epsilon_0 \chi \vec{E} \,, \tag{4}$$

where ϵ_0 is the *permittivity of free space* and χ is the *electric susceptibility* of the material. In real dielectrics non-linearities occur if space charges or dipolar domains exist.

Due to the polarisation process, an image charge Q occurs on the metal electrodes adding to the displacement charge which is present in vacuum. The charge per unit area deposited on the electrodes is called the *electric displacement* $\vec{D}$:

$$\vec{D} = \frac{\mathrm{d}Q}{\mathrm{d}A} \cdot \frac{\vec{A}}{A} \,, \tag{5}$$

where $\vec{A}$ is the vector normal to electrode area and A is its absolute value. In linear dielectrics (no space charges and no domain formation) and for low electric fields (far below saturation), the electric displacement is proportional to the macroscopic electric field. Then $\vec{D}$ can be separated into the vacuum contribution and the contribution of the material:

$$\vec{D} = \epsilon_0 \epsilon_r \vec{E} = \epsilon_0 \vec{E} + \vec{P} = \epsilon_0 \vec{E} + \epsilon_0 (\epsilon_r - 1) \vec{E} \,. \tag{6}$$

ϵ_r is the *relative permittivity* of the material. With Eq. (4) it follows that $\epsilon_r = \chi + 1$.

The macroscopic field has to be distinguished from the *local field* E_{loc} acting on an atomic or molecular unit which involves the fields of its electrically charged environment. It was shown by Lorentz that in cubic crystals as well as amorphous solids (including polymers) the local field is given by

$$\vec{E}_{loc} = \frac{\epsilon_r + 2}{3} \vec{E} \,. \tag{7}$$

The field dependence of the orientational polarisation is given by *Langevin's equation*:

$$\vec{P} = N_D \vec{\mu} L(x) \,. \tag{8}$$

N_D is the density of the permanent dipoles, $\vec{\mu}$ their dipole moment and $L(x)$ the *Langevin function*, given by

$$L(x) = \overline{\cos\theta} = \coth x - \frac{1}{x} \tag{9}$$

with

$$x = \frac{\vec{\mu} \vec{E}_{loc}}{kT} \,. \tag{10}$$

$\overline{\cos\theta}$ is the mean value of the cosine of the tilt angles of all dipole moments with respect to the field direction, k is Boltzmann's constant and T the temperature.
For small field strengths (far from saturation) L is approximately given by

$$L(x) = \frac{x}{3}\,. \tag{11}$$

With Eq. (4) and Eq. (7) and $\epsilon_r = \chi + 1$, it follows that for cubic crystals as well as amorphous materials

$$\chi = \frac{\chi+3}{3} \cdot \frac{N_D\vec{\mu}^2}{3\epsilon_0 kT} = \frac{\chi+3}{3} \cdot \frac{C_{el}}{T}\,. \tag{12}$$

C_{el} is the *electrical Curie constant*, and Eq. (12) is *Curie's law.* It relates the macroscopic quantity "susceptibility" to the microscopic quantities "dipole concentration" and "dipole moment". If the dipole concentration is known then the dipole moment can be calculated by this expression.

In an alternating electric field, the displacement polarisation leads to electric oscillations. This is a resonant process with resonant frequencies of 10^{15} to 10^{14} Hz for the electronic and 10^{13} to 10^{12} Hz for the ionic polarisation.
The orientational polarisation is not a resonant process, because the molecular dipoles have inertia. The response of the orientational polarisation to a change of the electric field strength is therefore always retarded. This process is called *dielectric relaxation.* The characteristic time constant of such a relaxation process - this is the time for reaching new equilibrium after changing the excitation - is called the *relaxation time* τ. It is strongly temperature dependent, because it is closely related to the viscosity of the material. At room temperature, the relaxation times of the orientational polarisation in crystals are 10^{-11} to 10^{-9} s. In amorphous solids and polymers, however, they can reach a few seconds or even hours, days and years, depending on temperature.

Real dielectrics also contain charge carriers which can be moved by electric forces between potential walls, formed by non-ohmic or blocking contacts or internal boundaries, e. g. between crystalline and amorphous phases in a semicrystalline material. This leads to a space charge polarisation (*electrode polarisation* or *Maxwell-Wagner polarisation*, respectively), which on the other hand is limited by diffusion. These processes are also relaxation processes, and are called *charge-carrier relaxations.* Because these processes are closely related to the conductivity, they are sometimes also named *conductivity relaxations.* The relaxation time τ_c of a conductivity relaxation is given by

$$\tau_c = \frac{\epsilon_0\epsilon_r}{\sigma_{dc}}\,, \tag{13}$$

where σ_{dc} is the dc conductivity of the material. It reaches about one hour for $\sigma = 10^{-15}(\Omega\text{cm})^{-1}$.
As long as the polarisation is linear with respect to the electric field it is not possible to distinguish whether a molecular dipole is rotating or a unipolar charge carrier is hopping between two equilibrium positions. However, due to this relation, the relaxation time of

a charge-carrier relaxation is generally larger than the relaxation times of the dipolar relaxations in the same material and for a given temperature. Furthermore, charge-carrier relaxations are generally more efficient in dielectric measurements because the charges are displaced for longer distances than in the case of rotating dipoles.

The displacement polarisation is always present. Therefore, Eq. (6) has to be modified:

$$\vec{D} = \epsilon_0 \epsilon_r \vec{E} = \epsilon_0 \vec{E} + \epsilon_0(\epsilon_\infty - 1)\vec{E} + \epsilon_0(\epsilon_r - \epsilon_\infty)\vec{E} = \vec{D}_{Vac} + \vec{P}_{Res} + \vec{P}_{Rel}\ . \tag{14}$$

ϵ_∞ is the so-called *unrelaxed permittivity*, because it is also present nearly immediately after switching on the field or at very high frequencies (infra-red and optical), where all relaxation processes cannot follow the field changes. $\vec{D}_{Vac}$, $\vec{P}_{Res}$ and $\vec{P}_{Rel}$ are the vacuum contribution, the resonance contribution and the relaxation contribution to the electric displacement, respectively.
The limit $\epsilon_r(t \to \infty)$ is called the *static permittivity* ϵ_s. Thus, the static polarisation is

$$\vec{P}_{\text{Rel,s}} = \epsilon_0(\epsilon_s - \epsilon_\infty)\vec{E} = \epsilon_0 \Delta\epsilon \vec{E}\ . \tag{15}$$

$\Delta\epsilon$ is called the *relaxation strength.* Note that ϵ_s, ϵ_∞ and $\Delta\epsilon$ are defined for a single relaxation process. Generally, more than one relaxation process exist in a given material. In this case these quantities have to be specified separately for each process.

The build-up and decay of the polarisation can be studied by connecting the electrodes with an ammeter and measuring the *displacement current density* $\vec{J} = \dot{\vec{D}}$ after or during a well-defined change of the applied field. Usually, $E(t)$ is a step function or a sinusoidal function. These measuring regimes are called the *time domain* and the *frequency domain*, respectively.

In the following passages we restrict ourselves to a *parallel-plate capacitor* filled with a homogeneous and isotropic dielectric. Then the matrixes ϵ, χ and σ become scalars and the vectors $\vec{E}$, $\vec{D}$ and $\vec{P}$ have only components perpendicular to the area of the plates. We further restrict ourselves to small field strengths where the polarisation is proportional to the electric field. Finally, we restrict ourselves to a spatially uniform polarisation.

2.2 Debye relaxation

The time dependence of the polarisation after a step in the applied field is assumed to be given by the simple first-order kinetics

$$\dot{P}_{\text{Rel}}(t) = \tau^{-1}[(P_{\text{Rel,s}} - P_{\text{Rel}}(t)]\ . \tag{16}$$

Now consider a system consisting of a certain number of one kind of spherical and non-interacting molecular dipoles rotating in a non-polar viscous environment. Its relaxation time is

$$\tau = \frac{4\pi\eta R_d^3}{kT}\ , \tag{17}$$

where η and R_d are the dynamic viscousity of the material and the radius of the dipoles, respectively.
The temperature dependence of the relaxation time follows that of the viscousity which is determined by the *Arrhenius equation*

$$\tau(T) = \tau_0 \exp \frac{E_a}{kT} . \tag{18}$$

τ_0 is the *reciprocal frequency factor* and E_a is the *activation energy.* A relaxation process with these properties is called a *Debye relaxation.* By viewing Eq. (15) it is obvious that at a given temperature the Debye process is completely determined by the quantities τ and $\Delta\epsilon$.

Checkpoint *Calculate the explicit time dependence of P_{Rel} and of the displacement current density $J = \dot{P}_{Rel}$ after applying a voltage step by solving Eq. (16)! Determine the quantities τ and $\Delta\epsilon$ from this solution.*

Now the sinusoidal excitation will be considered in more detail. If the applied field is given by

$$E(t) = E_m \exp(i\omega t) , \tag{19}$$

then the stationary polarisation oscillates with the same angular frequency ω. However, it is retarded by the angle ϕ:

$$P_{\mathrm{Rel}}(t) = P_{\mathrm{Rel,m}} \exp[i(\omega t + \phi)] . \tag{20}$$

The resonant part of the polarisation and the vacuum contribution to the electric displacement are always in phase with the electric field. By considering this, the electric displacement is

$$D(t) = P_{\mathrm{Rel,m}} \exp[i(\omega t + \phi)] + (P_{\mathrm{Res,m}} + D_{\mathrm{Vac,m}}) \exp(i\omega t) . \tag{21}$$

with

$$(P_{\mathrm{Res,m}} + D_{\mathrm{Vac,m}}) = \epsilon_0 \epsilon_\infty E_m \tag{22}$$

Finally, the current density is

$$J(t) = \frac{\mathrm{d}D(t)}{\mathrm{d}t} = i\omega[P_{rel}(t) + \epsilon_0\epsilon_\infty E(t)] \tag{23}$$

However, we are more interested in the dielectric spectrum, where ω is the independent quantity. Fourier transform of Eq. (20) gives

$$P_{\mathrm{Rel}}(\omega) = \frac{P_{\mathrm{Rel,s}}}{1 + i\omega\tau} . \tag{24}$$

With Eq. (15) it follows that

$$D(\omega) = \frac{\epsilon_0(\epsilon_s - \epsilon_\infty)}{1 + i\omega\tau} E(\omega) + \epsilon_0\epsilon_\infty E(\omega) \tag{25}$$

and with Eq. (6),

$$\epsilon_r = \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau} + \epsilon_\infty \, . \tag{26}$$

ϵ_r is a complex number defined as $\epsilon_r = \epsilon' - i\epsilon''$. By separating ϵ_r into its real and imaginary part, the *Debye equations* are obtained:

$$\epsilon' = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} + \epsilon_\infty \, , \quad \epsilon'' = \frac{\epsilon_s - \epsilon_\infty}{1 + \omega^2\tau^2} \, \omega\tau \, . \tag{27}$$

Though ϵ' is only the real part of the relative permittivity it is usually called the *permittivity.* ϵ' is a measure of the energy stored in the oscillations of the dipolar units. ϵ'' is called the *dielectric loss*, because it is related to the energy dissipation in the material due to internal friction. The Debye equations describe the dielectric spectrum of a *single Debye relaxation.*

With $J = \dot{D}$ the alternating current density follows as

$$J(\omega) = i\omega\epsilon_0\epsilon_r E(\omega) = i\omega D(\omega) \, . \tag{28}$$

The term $i\omega\epsilon_0\epsilon_r$ defines the ac conductivity σ_{ac}. Equation (28) is *Ohm's law.*

If we measure the time dependence of the polarisation after a voltage step then we work in the *time domain.* We measure the *response function* $P_{rel}(t)$ directly, however, to obtain the dielectric spectrum we have to deconvolute the response function. In contradiction, the measurement of $J(\omega)$ gives the *dielectric spectrum* $\epsilon_r(\omega)$ directly. We are in the *frequency domain.* The response function follows by convolution. These considerations remain valid also for more complicated systems such as multiple relaxations or non-Debye dielectrics.

In practise, there is no ideal dielectric. The dc conductivity is always present and has to be taken into account. Then with Eq. (28)

$$J(\omega) = i\omega D(\omega) + \sigma_{dc}E(\omega) = i\omega\epsilon_0\tilde{\epsilon}_r E(\omega) \tag{29}$$

with

$$\tilde{\epsilon}_r = \epsilon' - i(\epsilon'' + \frac{\sigma_{dc}}{\omega\epsilon_0}) \tag{30}$$

Checkpoint *Discuss the frequency dependence of the complex permittivity for a single Debye relaxation in an ideal dielectric as well as by considering an additional dc conductivity! What follows for* $\omega \to 0, \omega \to \infty$ *and* $\omega = 1/\tau$*? How does the result have to be modified in case of two Debye relaxations with different relaxation times as well as by considering a charge carrier relaxation and the displacement polarisation!*
Finally, discuss the Debye response on a logarithmic frequency scale! Calculate the half width of the Debye peak on a double-logarithmic scale!

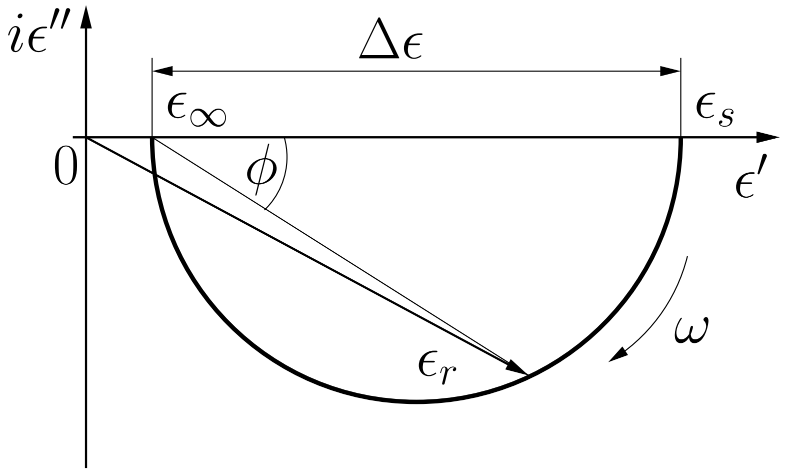

Figure 1: The locus of the complex permittivity in the Gaussian plane (Cole-Cole representation)

Determination of the relaxation parameters $\Delta\epsilon$ and τ of a single Debye relaxation

The characteristic parameters $\Delta\epsilon$ and τ of a single Debye relaxation can be determined from both quantities, ϵ' and ϵ''. The physical background is that in the time domain there is of course exactly one response function, consequently, both quantities contain the full information. They are related to each other through the *Kramers-Kronig transformation*. The relaxation time τ can be determined from the position of the loss maximum or the turning point of the permittivity curve, respectively. The relaxation strength is the difference between the limits of $\epsilon'(\omega)$ for $\omega \to 0$ and $\omega \to \infty$ or twice of the maximum value of $\epsilon''(\omega)$. In practice, however, it is often difficult to determine $\Delta\epsilon$ and τ because real dielectric spectra are generally broader than the Debye spectrum and their shape is not pre-defined. Furthermore, the frequency range is often limited for technical reasons. Then, the measurement of both parts of the permittivity gives more reliable information for a proper determination of the relaxation parameters. Particularly, a useful way to obtain these quantities is the so-called *Cole-Cole representation*. The locus of the complex number ϵ_r in the complex plane is a semicircle in the fourth quadrant (Fig. 1):

$$(\epsilon' - \frac{\epsilon_s + \epsilon_\infty}{2})^2 + \epsilon''^2 = (\frac{\epsilon_s - \epsilon_\infty}{2})^2 \ . \tag{31}$$

From Eq. (31) and Fig. 1 follows

$$\tan\phi = \frac{\epsilon''}{\epsilon' - \epsilon_\infty} = \omega\tau \ . \tag{32}$$

In practice, ϵ' and ϵ'' are measured in a middle frequency range and plotted in the complex plane. Then the semicircle is extrapolated to ϵ_s and ϵ_∞. The relaxation time follows from Eq. (32).

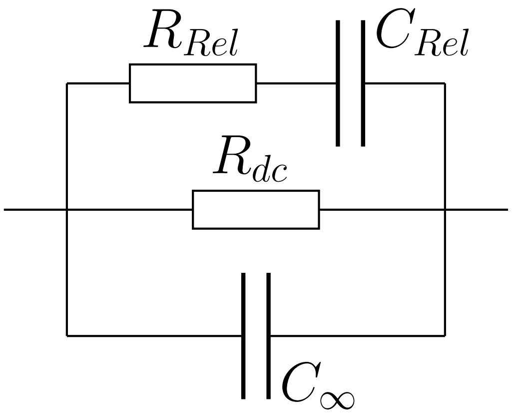

Figure 2: $R - C$ model of a homogeneous dielectric sample supplied with ideal electrical contacts

Modelling of a dielectric sample

A real dielectric always contains bound charges as well as free charges. The former determine the displacement polarisation whereas the latter causes the dc conductivity. Now it is assumed that additionally a Debye relaxation is present, that means, the dielectric contains one kind of non-interacting dipoles which rotate in its non-polar viscous environment. If it is further assumed that the dielectric is homogeneous then these three processes run spatially parallel. This situation can be modelled with ideal resistors and ideal capacitors (Fig. 2). R_{dc} represents the dc conductivity. C_∞ represents the vacuum contribution and the displacement contribution to the electric displacement, they follow the external field nearly immediately. The series connection of R_{Rel} and C_{Rel} models the Debye relaxation.

Checkpoint *Show that the current through the series connection of R_{Rel} and C_{Rel} after applying a voltage step shows exactly the same time dependence like $J = \dot{P}_{Rel}$ (cf. Eq.(16)).*

2.3 Eqivalent-circuit analysis

An arbitrarily shaped dielectric body with two metallic electrodes partially covering the surface at opposite faces is connected to a voltage supply. Due to polarisation in the material a change of the voltage dV induces a change of the charge dQ on the electrodes. We define the *capacitance* of this device as

$$C = \mathrm{d}Q/\mathrm{d}V \,. \tag{33}$$

This definition is quite general. It is valid e. g. for an interdigitated capacitor with planar comb-like electrodes covered by a thin dielectric layer, or for an electrolytic capacitor, where the dielectric is a thin oxide film on the surfaces of a sponge-like metallic body, or for a p-n-junction in a semi-conducting material, where a dielectric region is formed by a depletion zone, depending on the applied voltage. However, if we focus on the properties of the dielectric material, it is advisable to use a well-defined geometry such as a parallel-plate capacitor. Assuming a linear and homogeneous dielectric, an intimate contact between the electrodes and the material, and a homogeneous electric field, it can be easily derived that the capacitance of the parallel-plate capacitor is

$$C = \epsilon_0 \epsilon_r \frac{A}{d} \, , \tag{34}$$

where A and d are the electrode area and the sample thickness, respectively. Note, that homogeneity of the field is only given for $A \gg d^2$, so that fringing effects can be neglected.

Consider now an electrical circuit consisting of a generator $V = V_m \sin(i\omega t)$, a parallel-plate capacitor and an ac ammeter connected in series. With Eq. (29), $J = I/A$ and $E = V/d$ the current $I = I_m \sin i(\omega t + \phi)$ flowing through the ammeter is

$$I(\omega) = i\omega \tilde{C}(\omega) V(\omega) \tag{35}$$

with the (complex) *capacitance*

$$\tilde{C} = C' - iC'' \tag{36}$$

$\tilde{C}$ also contains the dc conductivity (cf. Eq. (30)). Eq. (35) is again *Ohm's law* (cf. Eq. (28)). The quantity $Y(\omega) = i\omega\tilde{C}(\omega)$ is called *admittance*, its reciprocal value $Z(\omega) = 1/Y(\omega)$ is the *impedance*. The phase shift between I and V is usually expressed by the *loss angle* $\delta = \pi/2 - \phi$. Another useful quantity is the *loss factor*

$$\tan\delta = \frac{C''}{C'} = \frac{\epsilon''}{\epsilon'} = \frac{Z''}{Z'} = \frac{Y'}{Y''} \, . \tag{37}$$

ϵ' is a measure of the energy *stored* whereas ϵ'' is a measure of the energy *dissipated* in the dielectric. Therefore, $\tan\delta$ is also called the *dissipation factor*[2]. It contains no more information than ϵ' or ϵ'', but it is independent of the capacitor geometry. This is particularly important if the capacitor geometry is not well defined. Furthermore, $\tan\delta$ is used as a measure of the sensitivity of a dielectric equipment. Recently, dielectric equipment with $\tan\delta \approx 10^{-5}$ has become available, corresponding to a resolution of $\phi = 6 \cdot 10^{-4\,\circ}$.

$Y(\omega)$ and $Z(\omega)$ are complex numbers. Actually, we measure the absolute value together with the phase angle ϕ or the real and imaginary parts.
Using the admittance it follows from Eqs. (35) and (36)

$$I(\omega) = [G(\omega) + iB(\omega)]V(\omega) \, , \tag{38}$$

with the *conductance* $G = Y' = \omega C''$ and the *susceptance* $B = Y'' = \omega C'$. Eq. (38) corresponds to a situation with a fixed voltage V driving a current I which may be represented by a component I' *in phase with* V and a component I'' *preceding* V *by* $\pi/2$. Technically,

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[2] The dissipation factor is frequently denoted with the symbol D, and $Q = 1/D$ is called the *quality factor*. However, we do not use these symbols here to avoid confusion with D used for the electric displacement and Q used for the charge.

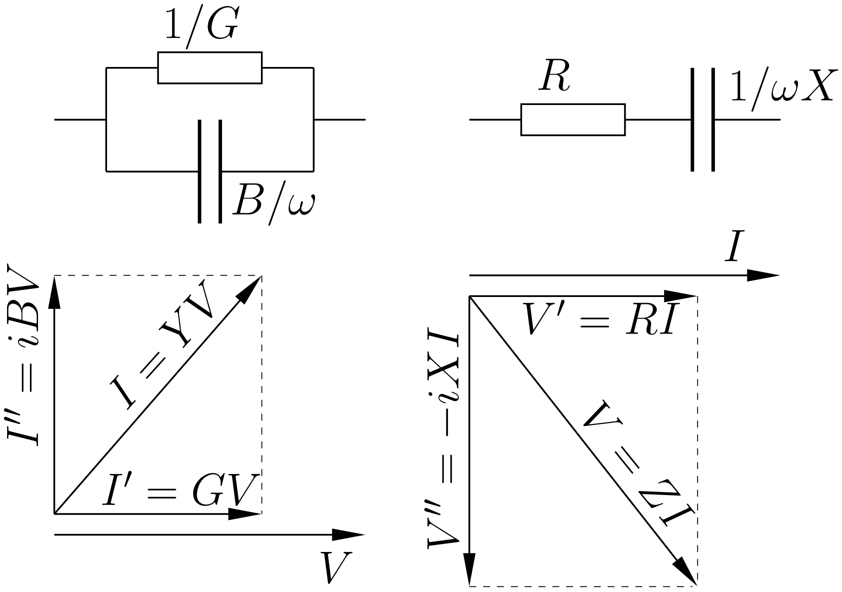

Figure 3: Parallel and series equivalent circuits with the corresponding phasor diagrams

this situation is given by an *equivalent circuit* consisting of an ideal capacitor (without loss) $B(\omega)/\omega$ in parallel to an ideal resistor (representing the loss in the capacitor) $1/G(\omega)$ (Fig. 3).

Alternatively, using the impedance we may write

$$V(\omega) = [R(\omega) - iX(\omega)]I(\omega)\,, \tag{39}$$

with the *resistance* $R = Z' = C''/(\omega C^2)$ and the *reactance* $X = Z'' = C'/(\omega C^2)$. Eq. (39) corresponds to a situation given by a constant current I in an equivalent circuit consisting of an ideal resistor $R(\omega)$ with a voltage drop V' *in phase with* I in series with an ideal capacitor $1/(\omega X(\omega))$ with a voltage drop V'' *delayed by* $\pi/2$ (Fig. 3).

The background of this contemplation is that both equivalent circuits correspond to different physical situations. The parallel equivalent circuit (corresponding to the *admittance representation*) is the *natural representation* of a situation where two or more physical phenomena exist in parallel, such as conductivity and polarisation in a “leaky” capacitor. The series equivalent circuit (corresponding to the *impedance representation*) is the natural representation of a situation where processes occur in series, as in a capacitor with barrier regions adjacent to a bulk with different conductivities and/or permittivities. Using the expression $Y = 1/Z$ it is of course possible to express Z by G and B or to express Y by R and X. However, this leads to more complex expressions (*wrong representations*) and should therefore be avoided.

These considerations are particularly important for a proper calculation of the permittivity. Obviously, this is possible only if the admittance representation can be used because only this representation corresponds to a homogeneous dielectric with a unique permittivity.

Then, with Eq. (34), Eq. (36) and Eq. (38) it follows that

$$\epsilon' = \frac{d}{\epsilon_0 A} \frac{B}{\omega} \,, \quad \epsilon'' = \frac{d}{\epsilon_0 A} \frac{G}{\omega} \,. \tag{40}$$

Checkpoint *Determine the capacitance $\tilde{C}(\omega)$ of the $R-C$ model of a dielectric sample (Fig. 2) and calculate the model parameters R_{dc}, C_∞, R_{Rel} and C_{Rel}. Which representation do you prefer, admittance or impedance?*

Equivalent circuit analysis is the *first step* of the dielectric analysis. It can be particularly helpful in recognizing and separating in-series processes. The *second step* is the determination of the relaxation parameters. Each process has to be considered separately because the Debye equations hold only for a "single" relaxation. The *third step* is the physical interpretation of the experimentally determined dielectric function. This includes its relation to processes occuring on the molecular scale, such as movements of certain molecular species, dipole orientation and its stability, phase transitions or phase separation as well as chemical reactions. Furthermore, the physical interpretation involves the calculation of quantities which are related to these processes: e. g. effective dipole moments, such as pyroelectric and piezoelectric coefficients or the glass transition temperature. Of course, the third step requires additional information from other experiments, particularly thermal analysis and X-ray structural analysis.

Unfortunately, the dielectric response of liquids and solids generally deviates considerably from the Debye type. The loss maxima are broader and generally asymmetric. The reason is obvious: the Debye model does not include particle interactions; therefore it applies only to gases and dilute solutions. In condensed matter dipole-dipole interactions lead to a distribution of relaxation times around a most probable value. For the presentation and comparison of experimental data it is appropriate to modify Debye's equations in such a way that on the one hand the parameters $\Delta\epsilon$ and τ retain their original meaning and on the other hand the width and asymmetry of the loss peak are taken into account. Such an empirical relaxation function is the *Havriliak-Negami* (HN) function:

$$\epsilon_r = \frac{\epsilon_s - \epsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\beta} + \epsilon_\infty \,. \tag{41}$$

$0 < \alpha \leq 1$ and $0 < \beta \leq 1$ are shape parameters describing the width and the asymmetry of the loss peak, respectively. They have no physical meaning. Note that generally $1/\tau \neq \omega_{max}$ where ω_{max} is the maximum position of a non-Debye peak. Thus, the complete description of a relaxation process includes the calculation of *four parameters*: relaxation strength, relaxation time and two shape parameters. Usually, this is performed by use of a least squares fit of the HN function to the experimental loss function. This so-called *HN analysis* is particularly useful for separating two superimposing relaxation processes as well as for separating a concuctivity term from the low-frequency end of the overall spectrum.

2.4 Temperature dependence of the relaxation time

Real loss peaks shift to higher maximum frequencies with increasing temperature because the relaxation time decreases. This property is often used as a powerful tool to extend the frequency range of dielectric spectroscopy indirectly by orders of magnitude. It can be easily recognised particularly for the Debye relaxation. Inserting Eq. (18) into Eq. (26) gives

$$\epsilon_r = \frac{\epsilon_s - \epsilon_\infty}{1 + i\omega\tau_0 \exp[E_a/(kT)]} + \epsilon_\infty \,. \tag{42}$$

This temperature dependence is much stronger than that of Curie's law which can be neglected. From Eq. (42) it is clear that for the Debye relaxation one obtains the same graph whether one is plotting $\log \epsilon_r$ versus $\log f$ at fixed T or $\log \epsilon_r$ versus $1/T$ at fixed f. This property is also called the *time-temperature superposition principle*. If the response is not of the Debye type, then this is generally not true, and there is no unambiguous way to relate the temperature dependence to the frequency dependence according to a theoretical model. Thus, $\tau(T)$ can only be determined from the frequency dependence. Nevertheless, for an overview and for a more qualitative analysis it is frequently appropriate to plot the real loss maxima versus temperature because they appear better resolved in this representation.

2.5 Dielectric relaxation in polymers

Polymers are generally characterised by the presence of various dipolar units in different environments. This leads to a broad distribution of relaxation times. The corresponding loss peaks are usually extended over several frequency decades.

Starting isothermally at low frequencies generally the *α relaxation* is found which accompanies the glass transition in the amorphous part of the material, that is the onset of segmental movements of the polymer chains. The loss peak of the α relaxation has an asymmetric shape. Its temperature dependence obeys the *Vogel-Fulcher-Tammann law* (VFT law) which can be derived from the theory of the glass transition:

$$\tau(T) = \tau_0 \exp \frac{T_a}{T - T_V} \,. \tag{43}$$

τ_0 and the activation temperature T_a are fit parameters and T_V is the *Vogel temperature* which is related to the dynamic glass-transition temperature. The asymmetric shape and the VFT behaviour are typical features of a co-operative process. Generally, the α relaxation has the highest strength, therefore it is often called the *primary or main relaxation*
At higher frequencies the *β relaxation* is present which involves local intra-molecular movements. It is sometimes followed by the *γ relaxation* of even smaller molecular units. Consequently, they are called *secondary relaxations.* Finally, a δ relaxation due to isolated molecules of impurities can be present at the high-frequency end of the spectrum. The loss peaks of these processes are symmetric, and they show an Arrhenius temperature dependence. These are typical features of a non-cooperative process.

Dielectric spectroscopy can only determine the relaxation parameters of these processes. A relation to movements of certain molecular species has to be found with the help of detailed knowledge about the chemical synthesis and by additional non-dielectric investigations. As an example, for partially crystalline polymers separate α and so-called α_c relaxations have to be distinguished, the latter originating from polymer chains in amorphous regions which are partly immobilized by pinning on crystals.

On the low-frequency end of the spectrum frequently a charge carrier relaxation appears, particularly in the presence of ionic impurities. It was already pointed out that the movement of charged particles between boundaries (electrodes or phase boundaries) is very efficient because it generates a large effective dipole moment due to larger charge displacements than in case of rotating dipoles, and huge losses due to strong internal friction. It can obscure the dipolar processes, and it is not typical for a special polymer. Therefore, it should be avoided by carefully purifying the substance and carefully preparing the electrical contacts. The charge carrier relaxations exhibit an Arrhenius temperature dependence because they are closely related to the exponential temperature dependence of the conductivity.

3 Experiment

3.1 Setup

The experimental setup is shown in Fig. 4. The device under test (DUT) is mounted in a special sample holder for dielectric measurements which is directly connected to the input terminals of the impedance analyser. The sample holder is part of a cryostat which belongs to the QUATRO cryosystem. The DUT is heated and cooled with dry nitrogen gas. The ac bridge as well as the cryosystem are fully remote controlled by a personal computer.
The measuring circuit is presented in Fig. 5 in simplified form. The DUT is part of an auto-balancing bridge. The generator supplies the potential V_1 at the high terminal of the DUT. The zero-voltage detector detects the potential at the DUT's low terminal and controls magnitude and phase of the output V_2 of the variable amplitude-phase generator until the range-resistor current I_2 and the DUT current I_1 balance, and the potential at the DUT's low terminal becomes zero. With $I_1 = V_1/Z$, $I_2 = V_2/R$ and the condition $I_1 = -I_2$ the impedance of the DUT is

$$Z = -\frac{V_1}{V_2} R \,. \tag{44}$$

The balancing operation is performed automatically over the full frequency range.

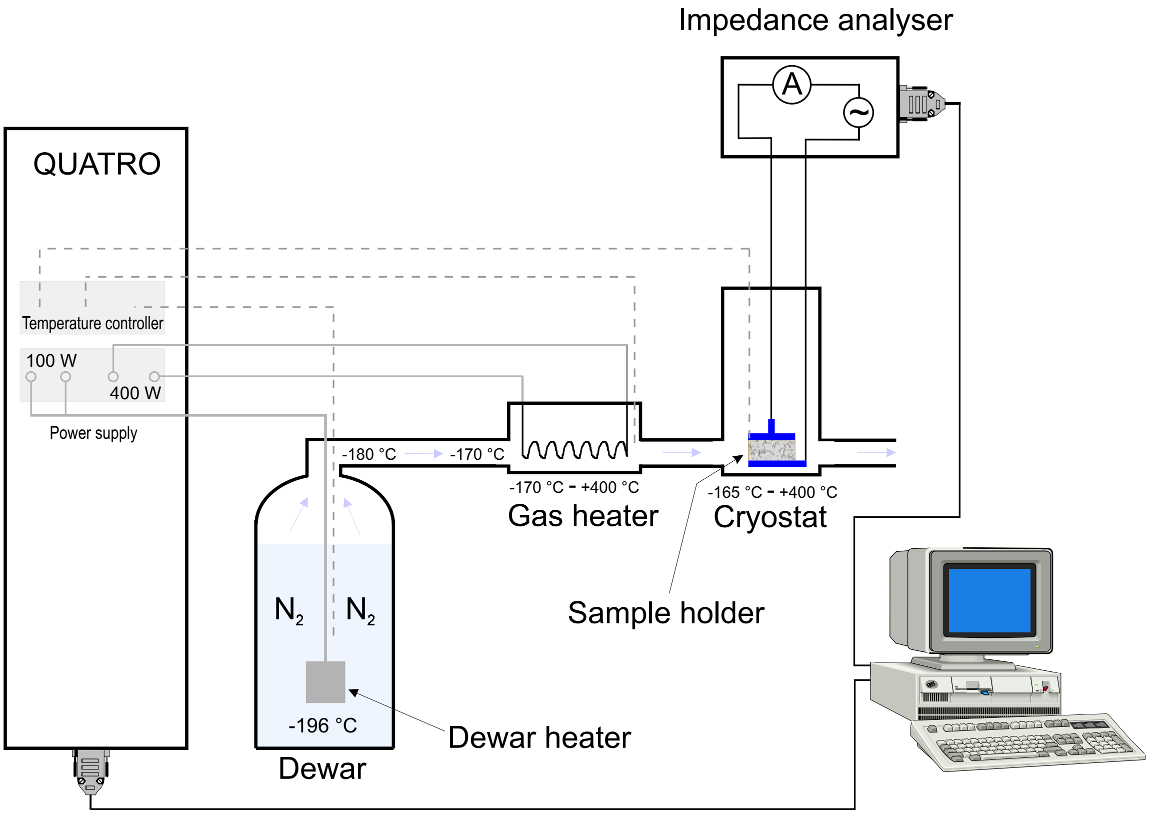

Figure 4: The experimental setup

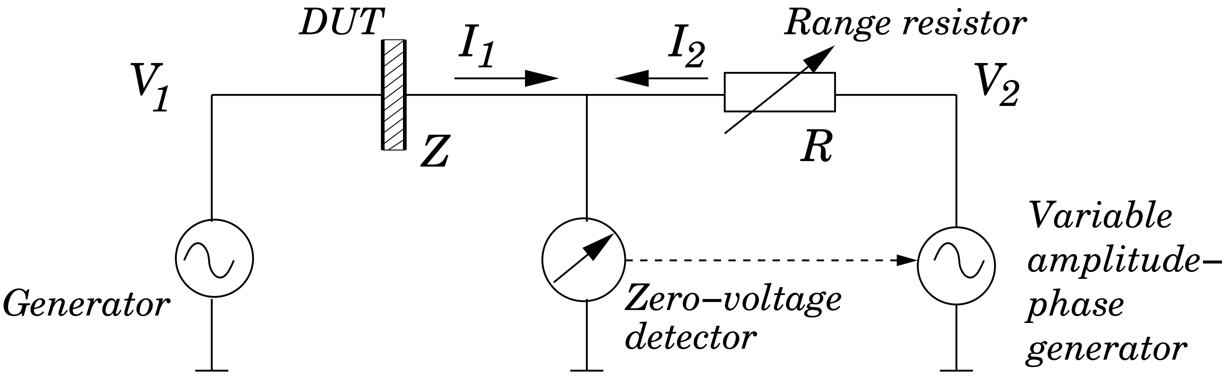

Figure 5: Simplified measuring circuit illustrating the operation of the auto-balancing bridge

Technical parameters of the setup:

- Generator $V_1 = 0 \ldots 30$ V_{pp}
- Frequency range 20 Hz. . . 1 MHz
- Sensitivity $\tan\delta = 10^{-5}$
- Temperature range $-170 \ldots + 400$ °C
- Accuracy of temperature adjustment $\Delta T = 0.01$ K
- Maximum heating rate about 10 K/min

3.2 Samples

The RC circuit for the first task is mounted in a "black box" which can be easily placed between the plates of the sample holder.

For the second task double-destilled and de-ionised water is used.

Checkpoint *Liquid water is a near-Debye dielectric; it shows only slight but significant deviations from the Debye equations. It would be well suited to verify the Debye model. Unfortunately, this is not possible here for experimental reasons. Estimate the loss-peak frequency of water at 20 °C ! The gas-kinetic radius of the* H_2O *molecule is* $R_d = 230$ *pm and the dynamic viscousity is* $\eta = 1.003 \cdot 10^{-3}$ Nsm^{-2}. *(Dielectric spectra of water are presented in [1] or [2])*

Checkpoint *Estimate the maximum possible dc conductivity of ice so that no loss peak caused by a conductivity relaxation appears in the frequency range of our investigation! Assume a Debye response for your calculation. The static dielectric constant of water is about* $\epsilon_s = 80$ *at room temperature.*

The polymer for the third task is made of a thermoplastic polyurethane (TPU) where certain non-polar chemical units are exchanged by a nitroaniline dye which forms strong molecular dipoles.

Thermoplastic polyurethanes are prepared by a two-step polymerisation method in an organic solvent: (1) preparation of an isocyanate-terminated prepolymer obtained by reaction of an excess amount of an aromatic isocyanate with an oligomeric glycol in bulk or in solution and (2) a diffusion-limited reaction of the prepolymer with a diamine. Polyurethanes are two-phase systems consisting of *soft and hard segments*. The latter have a crystal-like structure where the polyurethane chains lie parallel and which is stabilized by hydrogen-bonds between the urethane groups. The hard segments (HS) are embedded in the soft phase (Fig. 6). This structure shows only weak dielectric losses, particularly above room temperature.

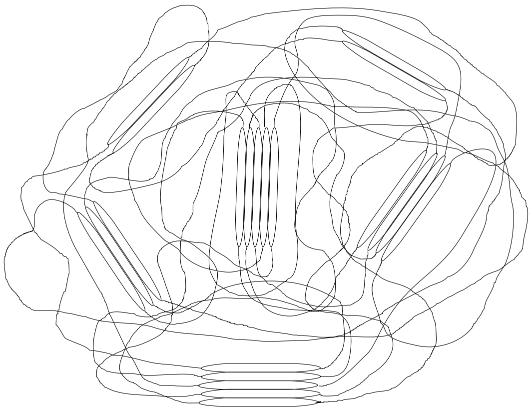

Figure 6: Supramolecular structure of a polyurethane: hard segments embedded in the soft phase

The incorporation of nitroaniline dipoles prevents the formation of hard segments and produces a nearly amorphous structure. This can be recognised with differential-scanning calorimetry (DSC). The DSC thermograms of dipole-free and dipole-containing films are presented in Fig. 7. Instead of endothermal and exothermal peaks due to hard-segment melting and crystallisation, respectively, in the film-material without dipoles, a glass transition at about 90 °C is observed in the dipole-containing film. It is accompanied by a strong dielectric relaxation (α relaxation). It is assumed that its relaxation strength is mainly determined by the dipole moment and the dipole concentration of the nitroaniline dipoles.

All chemical components are shown in Fig. 8. The chemical components of the dipole-free polymer are:

- Soft segments: polyoxytetramethylene, molecular weight about 1000 g/mol (PTHF 1000)
- Hard segments composed of:
  - $4,4'$-methylene bis(phenylisocyanate) (MDI) as diisocyanate component
  - butane-$1,4$-diol (BD 1.4) as so-called chain extender

In the dipole containing polymer the BD 1.4 is partly substituted by the nitroaniline compound bis-(2-hydroxyethyl)amino-4-nitrobenzene (BHEANB).

The BHEANB is a so-called $A - \pi - D$ *dipole*. It consists of the amino group as electron donor and the nitro group as electron acceptor that are linked by the delocalized π-electron system of the benzene ring. Due to donor-acceptor interaction the π-electron system is asymmetrically deformed and a dipole moment is induced. Its value is 8.5 D

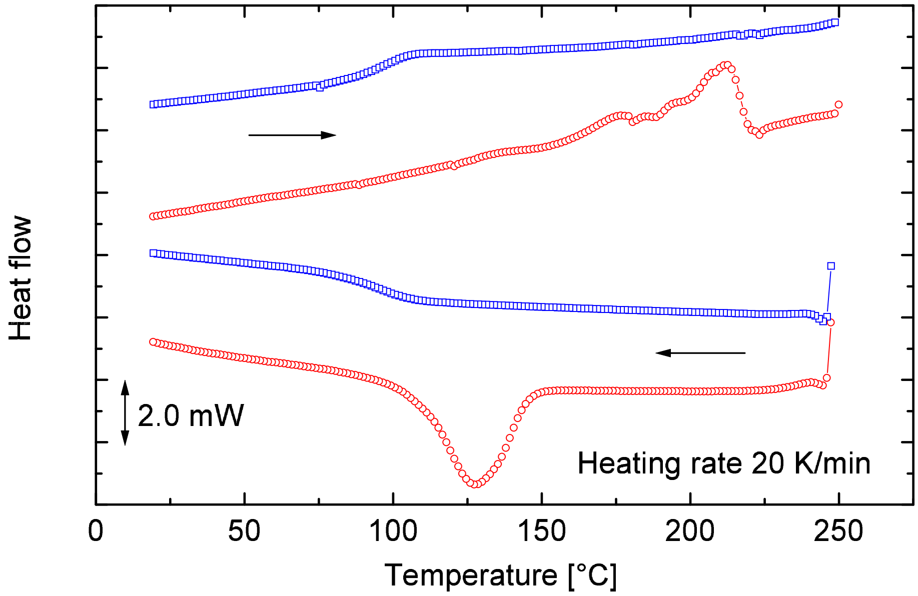

Figure 7: DSC thermograms of the dipole-free (circles) and the dipole-containing (squares) polyurethane films. Hard-segment melting and crystallisation on the dipole-free film as well as the glass transition at about 90 °C on the dipole-containing film are clearly visible.

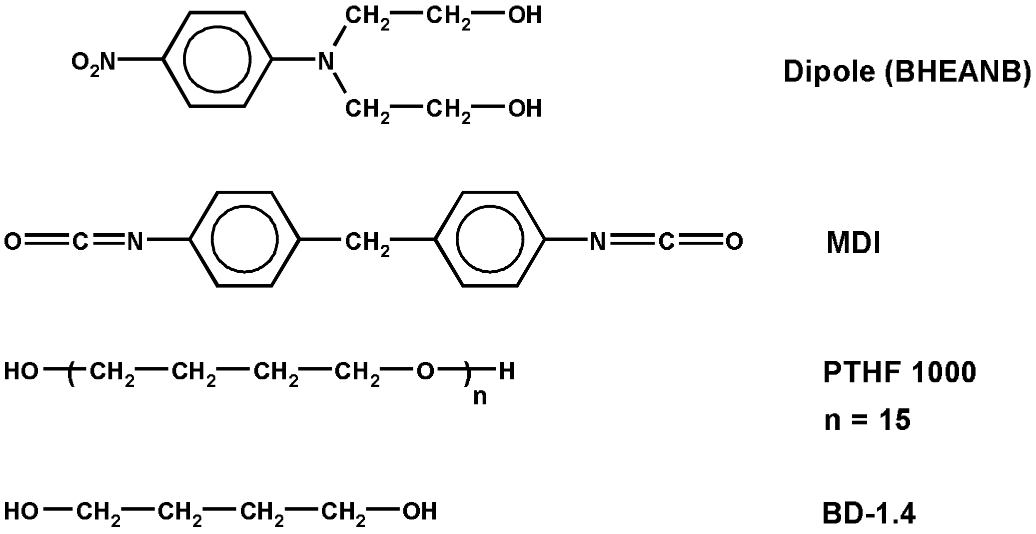

Figure 8: Chemical components of the thermoplastic polyurethane

(1 D $= 3.34 \cdot 10^{-30}$ Cm) determined by means of a quantum-chemical calculation (Spartan program package with Austin model Hamiltonian).

The chemical composition of the dye-containing polymer used in the experiment is: 1 mol PTHF1000, 17.34 mol MDI, 8 mol BD 1.4, 8 mol BHEANB. The chemical reaction is a polyaddition, there are no reaction products which go out.

Free standing films were made by coating with a doctor blade onto glass from N,N-dimethylformamide (DMF) solution. The density of the films is $\rho = 1.0$ g/cm^{-3}. The reference substance is colourless whereas the dipole-containing film is yellow coloured due to its nitroaniline-dye content. The films are thermally stable up to about 200 °C as determined by thermogravimetric analysis.

3.3 Running the experiment

1. Turn on the cryosystem, the rotary pump and the vacuum gauge (vacuum is necessary for thermal insulation) as well as the impedance meter. A vacuum of 0.01 mbar is sufficient.
   Turn on the computer, start *Testpoint*, click on mode *run*, go to the directory `DielSpec`.
2. **First task:** The DUT is simply placed between the plates of the sample holder. Be careful, the bottom electrode of the sample holder is not fastened! Do not overtighten the precision screw! Put the sample holder into the cryostat and fasten the flange with clamps. There are five terminals on the sample holder: 4× BNC, numbered 1-4, 1× LEMO. Connect the BNC sockets to the input terminals of the impedance meter as follows:
   BNC socket 1 to terminal Hcurr (High current),
   BNC socket 2 to terminal Hpot (High potential),
   BNC socket 3 to terminal Lcurr (Low current),
   BNC socket 4 to terminal Lpot (Low potential).
   Connect the LEMO socket with the QUATRO channel 4.
   Run `Spectrum`. This program measures the spectrum at constant temperatures. Choose an appropriate measuring quantity (impedance function). Run a single scan from 20 Hz to 1 MHz at room temperature (without temperature control).
3. **Second task**: Fill double-distilled water into a special chamber for the investigation of liquids. The electrodes are separated by a fused-silica spacer ring which determines the electrode diameter l and the electrode distance d. They are $l = 16$ mm and $d = 0.21$ mm, respectively. The contribution of the spacer to the capacitance can be neglected. Be careful particularly when handling the liquid-sample chamber; the fused-silica spacer is mechanically extremly sensitive. Clean all electrodes with alcohol before use. Avoid touching the electrode surfaces. After running the experiment, remove the water and dry the chamber.

Run `Spectrum_ice`. This program measures the spectrum (the conductance G and the susceptance B) at constant temperatures and calculates the real and imaginary part of the permittivity. Enter the electrode distance and the electrode diameter.
The following parameters are recommended: temperatures -5 °C , -20 °C , -35 °C ; frequency range 20 Hz to 1 MHz.

4. **Third task**: Two kinds of samples are used: first, the colour-less dipole-free reference film; second, the yellow-coloured dipole-containing film. The films have already been provided with evaporated aluminium contacts of about 50 nm thickness and 1.00 cm^2 area. Measure the film thickness by use of a micrometer screw. Then mount the film carefully between two polished stainless-steel plates of 1.00 cm^2 area into the sample holder.
   Run `Admittance`. This program measures G and B at three fixed frequencies during a slow linear temperature rise and calculates the real and imaginary part of the permittivity. Enter the film thickness and the electrode diameter.
   Recommended parameters: start temperature 20 ° C, end temperature 150 ° C, heating rate 3.0 K/min, frequencies: $f_1 = 100$ Hz, $f_2 = 500$ Hz, $f_3 = 1$ kHz.

5. After finishing the measurements power off the heaters, then turn off the impedance meter, vacuum gauge, rotary pump and cryosystem. Vent the vacuum system by opening the vacuum valve. Finally, close the vacuum valve.

4 Bibliography

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3. A. K. Jonscher, Dielectric relaxation in solids, Chelsea Dielectric Press Limited, London 1983 (available from the tutor)

References

[1] Literature 1, p. 70 (data from W. Hackel and M. Wien, Phys. Z., vol. 38 (1937) p. 767)

[2] Literature 3, Fig. 5.3, p. 167 (data from P. R. Mason et al., Adv. Mol. Rel. Proc., vol. 6 (1974) p. 217)