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A NONLINEAR DIELECTRIC MEASUREMENT METHOD FOR THE STUDY OF COMPLEX LIQUIDS

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A measurement system for the study of nonlinear dielectric effect (NDE) of complex liquids is constructed. The method is based on the determination of a change in frequency of an LC oscillator. The fluid is contained in a dielectric cell, which is the capacitive component of the oscillator. A rectangular electric pulse with variable amplitude and width is applied to the liquid, and the frequency of the oscillator is continuously sampled under the duration of the pulse with a modulation domain analyzer. The magnitude of NDE for diethyl ether and carbon tetrachloride was measured with the apparatus and compared to corresponding reference data. The NDE value of silicone oil used as a carrier liquid of electrorheological (ER) fluids was also determined.

Keywords: nonlinear dielectric effect, dielectric permittivity, electrorheological fluids

Introduction

In many cases the dielectric permittivity of molecular and complex fluids (electrorheological liquids) depends on the electric field strength, E inside the dielectric [1]:

$$\varepsilon_E = \varepsilon_0 + \varepsilon_2 E^2 + \ldots \,, \tag{1}$$

where ε_0 is the linear dielectric permittivity. The change in dielectric permittivity caused by a strong electric field is called the nonlinear dielectric effect (NDE). The magnitude of this effect can be described by the ε_2 coefficient in Eq. (1) [1]:

$$\varepsilon_2 = \lim_{E\to 0} \frac{\varepsilon_E - \varepsilon_0}{E^2} = \lim_{E\to 0} \frac{\Delta\varepsilon_E}{E^2} \,. \tag{2}$$

Only the ε_0 linear dielectric permittivity can be measured by the conventional linear measurement techniques. The nonlinear measurement methods are suitable to determine the ε_2 parameter.

In the study of electrorheological (ER) fluids, the complementary linear and nonlinear dielectric measurements yield valuable information about chain formation induced by the external electric field.

The nonlinear dielectric measurement system

Fig. 1 illustrates the schematic block diagram of the NDE apparatus. The concept [3, 5, 6] of the measurement setup is based on the determination of the frequency change of an LC oscillator. The sample under investigation is contained in a dielectric cell, which acts as a parallel plate capacitor. This capacitance C_c combined with the inductance L forms the LC oscillator, which has a resonance frequency f.

A high voltage power supply and a high voltage switch makes up the pulse generator system, which is used to impose rectangular pulses to the cell. A high voltage decoupling capacitor (C_b) connected in series with the dielectric cell blocks the pulse from the active elements of the oscillator. The applied high voltage creates a strong electrical field between the plates of the measuring cell.

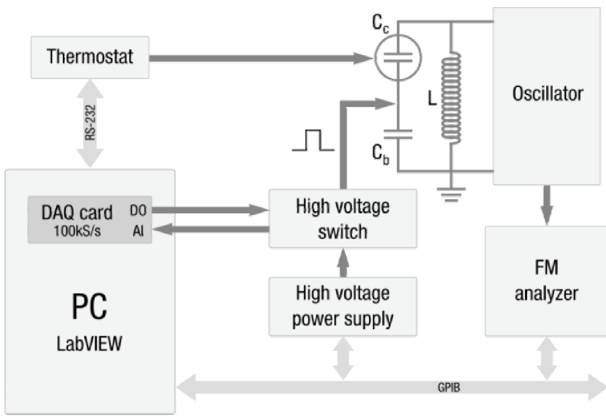

Figure 1: Block diagram of the nonlinear dielectric equipment

The dielectric permittivity of the fluid changes under the influence of the electric field, which causes a change in capacitance of the dielectric cell. Because the value of C_c is the decisive capacitive element of the LC oscillator, the nonlinear dielectric effect manifests as a change in frequency (Δf). A modulation domain analyzer is responsible for the accurate measurement of this frequency change.

The trigger signal initiating the frequency measurement is supplied by the counter unit of a data acquisition (DAQ) card. The same card is responsible for the generation of the rectangular TTL level pulses controlling the system switching the high voltage pulse. The analogue input of this DAQ system is used for registering the divided output of the high voltage pulse generator.

The control software is developed in LabVIEW programming environment. The most important functions of the software are the programming of the DAQ system and the communication with the modulation domain analyzer. The program is used to set up the temperature-controlling equipment. After the measurement is complete, the control software processes the raw measurement data.

Dielectric cell

The construction of the measuring cell is critical, because large forces can act between the plates when a strong electric field is switched on. The schematic structure of the cell is shown in *Fig. 2*.

The cylindrical electrodes are made of stainless steel and have diameters of 43 mm. Each electrode has a vertically oriented inlet for the convenient, bubble free filling of the cell. In order to avoid measuring errors, the exclusion of air bubbles is crucial. Between the two electrodes a quartz ring ensures the fixed distance. The height of this ring is 10 mm, which sets the distance between the electrodes to 0.3 mm. In this configuration the empty cell has a capacitance of 41.71 pF. The quartz spacer can be replaced by rings with different height, so the electrode gap is variable. To prevent leakage, Teflon gaskets provide proper sealing on both side of the quartz ring.

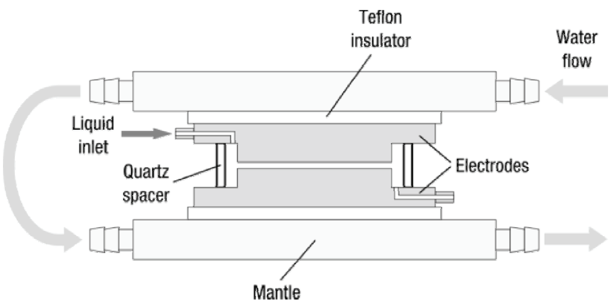

Figure 2: Schematic cross section view of the dielectric cell

Each of the two electrodes is surrounded by a hollow copper mantle through which a water flow is passed. The temperature of the water is controlled by a Medingen E20B6 thermostat. The mantle is electrically insulated from the electrode by a Teflon disk. One of the electrodes has a bore containing a resistance thermometer (Pt100). The whole structure of the cell is held together by four brass screws firmly.

Oscillator

The extremely small magnitude of $\Delta\varepsilon_E$ results in a small frequency change, typically in *ppm* order. The detection of such small changes in frequency requires a high stability oscillator.

A double triode oscillator of type ECC88 valve was chosen. This type has been used previously by various authors [3, 6]. *Fig. 3* shows the circuit diagram of the used LC oscillator.

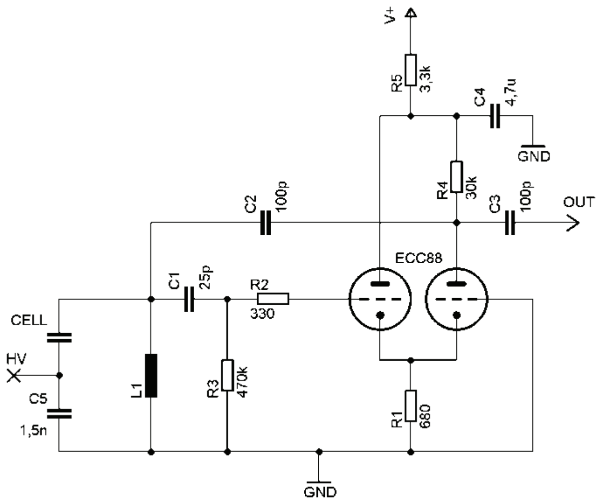

Figure 3: Circuit layout of the oscillator

An advantage of the valve oscillator is its ability to oscillate even when the cell is filled with moderately conducting liquid. In order to maximize the frequency stability of the oscillator, the anode voltage and the cathode heating current are carefully chosen. The source of the heating current is a custom built power supply unit, while a Voltcraft PPS-12008 PSU provides the anode voltage for the valve.

The printed circuit board is designed so that different inductors can be inserted into the circuit. Three air core solenoids were made of enamelled copper wires of various sizes wind around ceramic cylinders. The inductances of the coils are: $L_1 = 19.57$ μH, $L_2 = 10.58$ μH, and $L_3 = 3.53$ μH. When the dielectric cell is empty, the resonant frequency of the oscillator is around $f_1 = 3.48$ MHz, $f_2 = 4.70$ MHz, and $f_3 = 8.32$ MHz for the three solenoids.

The blocking capacitor is another critical component of the oscillator. Its function is to decouple the high-voltage pulse from the active elements of the circuit. It is connected in series with the measuring cell, so it has to have a high capacitance giving small contribution to the capacitance of the cell. Another requirement for the C_b bypass capacitor is the ability to withstand the peak amplitude of the high voltage pulse. Besides these demands, its capacitance must be stable as voltage changes. To meet all these requirements, a cluster of four silvered mica capacitor is used as the decoupling capacitor. The total capacitance of the cluster is 1500 pF, and the rated peak voltage is 2000 V.

The high voltage pulse generator is connected to the oscillator through a decoupling resistor, whose resistance is 21 kΩ. The function of this element is to surpass the change in Ohmic resistance connected to the oscillator circuit when the pulse generator system is active.

Because the valve is sensitive to mechanical vibrations, which can cause unwanted changes in frequency of the oscillator, the whole circuit board and the dielectric cell is rigidly mounted on an aluminium plate. Further precaution is taken to minimize the transmission of vibration to the aluminium mounting plate.

Modulation domain analyzer

A Hewlett-Packard 53310A modulation domain analyzer is used to measure the change in frequency of the oscillator before, during, and after the high voltage pulse. The time interval of the frequency measurement before and after the pulse equals to forty percent of the pulse width. The typical total duration of the measurement is in the range of 5–100 ms. The main time base is set according to the total measurement time. The analyzer has the option to adjust the time base between 10 μs and 10 s.

The signal from the oscillator is routed to the analyzer, which has a measurement range of 10 Hz to 200 MHz. The sampling rate of the input frequency is managed automatically by the instrument, based on the time base setting. Under a typical measurement lasting for 20 ms the sampling interval is 0.1 ms.

The internal trigger system of the analyzer is switched off, so it is operating in a triggered mode instead of auto one. An external TTL level signal is connected to the external arm input. The measurement is initiated at the falling edge of the trigger signal, so the occurrence of the trigger is assigned to the zero position of the horizontal time axis. All measurement data is collected after this reference point.

Before the frequency measurement commences, the analyzer searches for the input signal, and determines the base frequency. The centre of the vertical axis is adjusted to this frequency value, and the span value is given manually.

The GPIB (IEEE-488) port of the instrument is used for communication purposes. All the above mentioned parameters and settings are sent through this interface. The analyzer is armed by a software command after which it is ready to take measurements. The instrument is waiting in this armed state for the trigger to initiate the sampling of the input signal.

The results are queried by the control computer, and the raw measurement data is sent through the GPIB port. The raw data is composed of ASCII characters of screen coordinates. The actual frequency-time point pairs can be computed according to the scale and offset values read from the instrument. The accuracy of the Δf measurement is improved by repeating the data acquisition N times, and averaging the results. The N parameter is adjustable: typically an $N = 5$ value is sufficient.

High voltage pulse generator

A PS350 DC high voltage power supply made by Stanford Research System serves as the base of the pulse generator. The output voltage of this programmable precision power supply ranges from 50 V to 5000 V. The maximum output current is 5 mA. The output voltage can be set with a resolution of 1 V, and the voltage set accuracy is 0.01%.

The instrument has a GPIB port, which is connected to the IEEE-488 communication bus. So both the output voltage value and the state of the output are under computer control.

A custom built high voltage switch is responsible for the generation of the rectangular high voltage pulses. The device is switched by a TTL level rectangular signal, which is generated by the counter unit of a data acquisition card. The high voltage is reduced 5000-fold and routed to the monitor output of the switch.

Solid polyethylene insulated RG-59 type coaxial cables lead the voltage to the switch and to the dielectric cell. The cables are fitted with SHV connectors.

Trigger and rectangular pulse generator

Two signals need to be generated. This function is handled by a PCI-6052E multifunction data acquisition card made by National Instruments. The DAQ card occupies a PCI slot inside the control computer. The device has two counter units which are used to generate the signals. One trigger is necessary for the modulation domain analyzer to initiate the frequency measurement. This signal is outputted by *Counter0* and has TTL voltage level, and a logical high idle state.

Counter1 is the source of the rectangular pulse, which is controlling the high voltage pulse generator. The voltage level of this signal is also TTL, with a logical low idle state. The pulse width and the delay before the rising edge of the pulse are settable by the program. The initial delay is forty percent of the pulse width, so the start of the frequency measurement is synchronized to the generation of the rectangular pulse.

The signal generated by *Counter0* is internally routed to *Counter1* and initiates it with the pre-programmed parameters.

An additional function of the DAQ card is the registration of the divided voltage monitor output. For this purpose the analogue input of the card is used. The analogue input channel has 16 bit resolution. The maximum sampling rate of the card is 333 kS/s. The actual sampling rate is set to 100 kS/s. The DAQ device is configured in differential input mode. The data acquisition is triggered by the internally routed signal generated by *Counter0*. This ensures that all functions of the card are started at the same time.

A National Instruments BNC-2090A shielded rack mountable terminal block connects the DAQ card to the high voltage pulse generator and to the modulation domain analyzer.

Temperature control system

The temperature of the water circulating in the outer mantle of the dielectric cell is controlled by a Medingen E20B6 thermostat. Heat losses of the cell are reduced by insulating the tubes connecting the cell to the thermostat.

The thermostat controls the temperature of the dielectric cell by the external Pt100 resistance thermometer placed inside a hole bored into one of the electrodes. Through an RS-232 serial interface the thermostat is communicating with the control PC. This enables the setting of the desired cell temperature by software, and, on the other hand, the actual cell temperature can be monitored. The accuracy of the temperature control system is 0.01 °C

Control software

The LabVIEW program provides a graphical user interface, with controls to set the essential parameters of the nonlinear measurement apparatus. The desired cell temperature can be adjusted, and the actual temperature is also shown and updated once per second. Additional adjustable parameters are the following: the amplitude and the width of the rectangular high voltage pulse, the span of the vertical display in hertz, and the number of frequency measurements to average.

The first task of the software is to switch on the high voltage power supply, and wait until the voltage output is stabilized. The initialization command string sent to the analyzer leaves the instrument in an armed state. The following step programs the two counter units of the data acquisition device and configures the analogue input. After *Counter0* generates the signal, all the events mentioned in the description of the trigger and pulse generator system are timed by hardware.

The control software reads out the raw frequency vs. time data, and the scaling and offset factors from the analyzer. At the same time the voltage values measured on the analogue input channel are requested from the DAQ device. The aforementioned events are repeated *N* times and the averaged and scaled frequency vs. time and high voltage vs. time results are displayed as stacked plots with a common horizontal time axis.

Calibration

To calculate the ε_2 magnitude of the nonlinear dielectric effect defined by Eq. (2) the value of $\Delta\varepsilon_E$ has to be calculated from the measured $\Delta f/f$ ratio. The two values are related through the following equation [4]:

$$\Delta\varepsilon_E = \frac{2\Delta f}{f}\left(\varepsilon_0 + \frac{C_s}{C_0}\right) , \tag{3}$$

where C_0 is the capacitance of the empty dielectric cell and C_s is the total stray capacitance. Using two materials of relative permittivity $(\varepsilon_0)_1$ and $(\varepsilon_0)_2$ and measuring the corresponding f_1 and f_2 oscillator base frequencies the C_s/C_0 value can be determined from the equation [4]:

$$\frac{C_s}{C_0} = \frac{(\varepsilon_0)_2 - (\varepsilon_0)_1\left(\dfrac{f_1}{f_2}\right)^2}{\left(\dfrac{f_1}{f_2}\right)^2 - 1} . \tag{4}$$

For the calibration measurements, diethyl ether and carbon tetrachloride was used. The linear dielectric permittivity of both materials was measured with the linear measurement method outlined in the following section.

The linear dielectric measurement system

For the determination of the linear dielectric permittivity an Agilent measurement apparatus is employed. The components of the system are the 16452A dielectric cell for liquids and the 4284A precision LCR meter. The apparatus has a 20 Hz to 1 MHz measurement frequency range and a 0.05% basic accuracy. The equipment is controlled over GPIB with a custom developed LabVIEW program.

The dielectric cell employs the parallel plate method, similar to the method used by the nonlinear measurements. The liquid under test is between two circular shaped electrodes, separated by a spacer to form a capacitor. The 4284A LCR meter is used to measure the capacitance of the cell. On the basis of the measured capacitance value and the known geometry (area of the electrode and electrode separation) of the cell the linear dielectric permittivity is easily calculated.

To control the temperature of the dielectric cell it is immersed in a silicone oil bath which is placed inside the tank of a Medingen E20B12 thermostat. The temperature of the cell is controlled with an accuracy of 0.01 °C.

Results

The nonlinear measurement apparatus was tested with diethyl ether and carbon tetrachloride at 25.0 °C. These two materials were chosen because nonlinear measurement data have been published by various authors for both dielectrics.

Fig. 4 shows the measured $\Delta\varepsilon_E$ values for diethyl ether as a function of the electric field strength for 25.0 °C. The plot shows that $\Delta\varepsilon_E$ is a quadratic function of E. The width of the rectangular pulse was 20 ms and the base frequency of the oscillator was 2.58 MHz.

Table 1 summarizes our NDE measurement results for diethyl ether and carbon tetrachloride in comparison with reference data. The results are in good agreement with values published by other authors [2, 4].

The nonlinear dielectric effect of silicone oil (polydimethylsiloxane) which is used as a carrier liquid in the preparation of electrorheological fluids was also measured. The kinematic viscosity of the silicone oil was 350 mm^2s^{-1}. The material was supplied by Sigma-Aldrich. For the measurement a 30 ms wide rectangular pulse was applied, and the base frequency of the oscillator equalled to 2.89 MHz. The measured NDE value for silicone oil is also shown in *Table 1*.

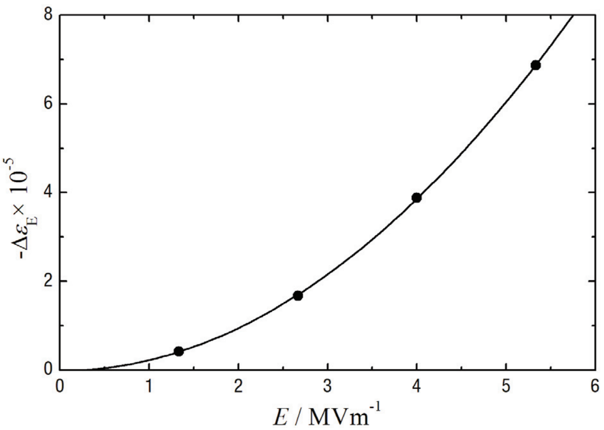

Figure 4: The change in relative permittivity of diethyl ether as a function of electric field at 25.0 °C.

Table 1: NDE measurement results compared to reference data.

Material	$\Delta\varepsilon_E/E^2$ (10^{-19} m^2V^{-2})	
	Our result	Reference
Diethyl ether	-26.46±1.11	-(20–36.5)[a]
Carbon tetrachloride	1.93±0.08	1.61–1.93[b]
Silicone oil	3.56±0.15	–

[a] [2].
[b] [4].

Conclusions

An LC oscillator based measurement equipment for the study of nonlinear dielectric effect of liquids is proposed. The system is tested by the measurement of ε_2 for carbon tetrachloride and diethyl ether.

In the next future we are going to use the equipment to measure the nonlinear dielectric effect of electrorheological fluids. The chain-formation of ER fluids can be described by the linear and nonlinear dielectric measurements using an association theory[7].

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