

## Dielectric-spectroscopy approach to ferrofluid nanoparticle clustering induced by an external electric field

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An experimental study of magnetic colloidal particles cluster formation induced by an external electric field in a ferrofluid based on transformer oil is presented. Using frequency domain isothermal dielectric spectroscopy, we study the influence of a test cell electrode separation distance on a low-frequency relaxation process. We consider the relaxation process to be associated with an electric double layer polarization taking place on the particle surface. It has been found that the relaxation maximum considerably shifts towards lower frequencies when conducting the measurements in the test cells with greater electrode separation distances. As the electric field intensity was always kept at a constant value, we propose that the particle cluster formation induced by the external ac electric field accounts for that phenomenon. The increase in the relaxation time is in accordance with the Schwarz theory of electric double layer polarization. In addition, we analyze the influence of a static electric field generated by dc bias voltage on a similar shift in the relaxation maximum position. The variation of the dc electric field for the hysteresis measurements purpose provides understanding of the development of the particle clusters and their decay. Following our results, we emphasize the utility of dielectric spectroscopy as a simple, complementary method for detection and study of clusters of colloidal particles induced by external electric field.

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### I. INTRODUCTION

Colloids consisting of magnetic nanoparticles coated with surfactants and suspended in a liquid carrier are known as ferrofluids or magnetic fluids [1]. Constituting unique properties they have been used for diverse applications in nanotechnology [2–5]. One of the fundamental requirements for a ferrofluid is the stability of the magnetic particles against aggregations. In this research field, a variety of experimental, theoretical, and computational approaches have been applied towards studies of aggregation and the microstructure formation process of magnetic nanoparticles in ferrofluids. In particular, the particle aggregation and chain formation in external magnetic field have been intensively studied for different ferrofluids [6–8]. Magnetic field induced chainlike assemblies of magnetic particles and the effect of shear in microchannels were analyzed in [9]. Recently, fluctuations of orientation order and clustering in a two-dimensional superparamagnetic colloidal system under quenched disorder were observed [10]. The current interest has been also focused on dynamics of cluster formation in monolayers of paramagnetic particles subjected to an oscillating magnetic field [11]. It was shown that the effective oscillating magnetic field enhances the aggregation process in magnetorheological fluids, when simultaneously applied with a static magnetic field; the two fields are transverse to each other [12]. For ferrofluids based on dielectric liquids, the magnetic field induced particle cluster formation exerts considerable influence on the ferrofluids' relative permittivity. This well-known phenomenon is called

the magnetodielectric effect [13–15]. However, among the experimental investigations of magnetic nanoparticles cluster formation, there has been little research into the potential external electric field induced nanoparticle clustering.

It is well known that electrical forces can act both on particles and on the suspending fluid. The major consequences of electrical forces acting on nanoparticles suspended in a fluid are electrophoresis and/or dielectrophoresis. While the earlier phenomenon occurs due to the action of the electric field on the fixed, net charge of the particle, the latter only occurs when there are induced charges and only results in motion in a nonuniform dc or ac electric field [16]. In ferrofluids based on insulating liquids and magnetite nanoparticles, the polarizability and permittivity of the nanoparticles is much greater than that of the liquid medium. The resulting difference in the charge density on either side of the nanoparticle gives rise to an induced dipole across the nanoparticle, aligned with the applied electric field. According to the electrostatic theory, the close particles with induced electric dipoles can form long chains aligned along the applied field lines when the electrical forces are greater than thermal, and gravitational forces which act on the particles [17]. Moreover, in ferrofluids, this electrostatic attractive force may support van der Waals forces and the magnetic dipole-dipole interactions against which the nanoparticles are stabilized by surfactants. This effect was proved by dynamic light scattering carried out on a diluted magnetite ferrofluid based on kerosene (with oleic acid as surfactant) with volume fraction from 0.01% to 0.1%, exposed to an electric field of 0.5 MV/m [18,19]. Considering the aforementioned facts, the effect of such a clustering should be pronounced in thin layers of ferrofluids confined between two parallel plane electrodes. Since the

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magnetite nanoparticles are rapidly polarized in the insulating medium [19], the cluster formation process, depending on the viscosity of the surrounding medium, may be expected even in ac electric fields of frequencies higher than those in electrical power systems.

Most studies on dielectric properties of ferrofluids have been devoted to insulating fluids-based ferrofluids. Lately, transformer oil-based ferrofluids are of great scientific interest due to the enhanced heat transfer (thermomagnetic convection) [20–22] and higher breakdown voltage when compared with pure oils [23,24]. The latter phenomenon is still not sufficiently understood. Regarding this peculiarity, the electric field induced particle cluster formation can play a significant role.

In this study we focus on dielectric spectroscopy of a transformer oil-based ferrofluid with magnetite nanoparticles coated with oleic acid molecules. In a limited frequency range (from 20 Hz to 2 MHz) we investigate the electrode spacing influence on the low-frequency dielectric dispersion, while keeping the electric field intensity at a constant value. We assumed that by increasing the electrode separation distance of a few micrometers, one can allow the formation of larger clusters induced by the electric field between the two electrodes. Then, the relaxation times of the processes dependent on the particle (cluster) size should be also dependent on the electrode separation distance. This is expected to be clearly seen by different positions of the corresponding relaxation maximum in the measured frequency scale. We also demonstrate changes in the observed relaxation process by applying dc bias voltage and the resulting strong dc electric field. The aim of the present study is to point out the changes in the low-frequency dielectric dispersion in ferrofluids, which are considered to stem from the cluster formation of magnetic particles induced by the external electric field.

**II. EXPERIMENTAL METHODS**

The assumed electric field induced particle cluster formation was studied on a ferrofluid synthesized according to the basic procedure developed by Bica [25,26]. The magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles were coprecipitated from an aqueous solution of Fe<sup>2+</sup> and Fe<sup>3+</sup> ions in the presence of NH<sub>4</sub>OH at 80 °C–82 °C. After the coprecipitation, the magnetite nanoparticles were sterically stabilized with a single vegetal oleic acid layer (C<sub>18</sub>H<sub>34</sub>O<sub>2</sub>, 65%–88%, Merck), chemisorbed on the particles’ surfaces. The chemisorption was followed by washing with distilled water with magnetic decantation to remove residual unreacted salts. Then, the flocculation redispersion procedure was repeated several times to ensure a negligible presence of free surfactant in the final solution. The purified magnetite nanoparticles were dispersed in the inhibited mineral oil (Mogul Trafo CZ-A, Paramo) with viscosity value of 14.59 mPa·s, pH of 3.459, and relative permittivity of 2.1 in the whole investigated frequency range. The listed values were measured at room temperature (296 K).

The saturation magnetization  $M_S$  of the originally prepared ferrofluid sample is 23.15 A m<sup>2</sup> kg<sup>-1</sup>, and the estimated dc magnetic susceptibility is 0.75. These values were obtained by a superconducting quantum interference device (SQUID) magnetometer and an ac susceptometer, respectively, with the uncertainty less than 1%. The corresponding magnetic

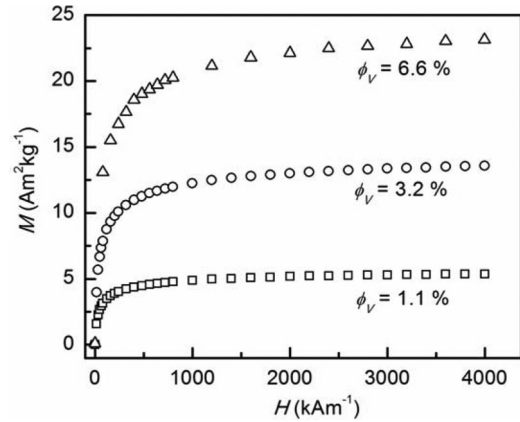


FIG. 1. Magnetization curves of the investigated ferrofluid samples with different magnetic volume fractions.

volume fraction  $\phi_V$  is 6.6%, calculated as  $\phi_V = M_S/M_d$ , where  $M_d$  is the domain magnetization of the bulk magnetic particle ( $M_d = 446 \text{ kA m}^{-1}$  for magnetite [1]). Dynamic light scattering measurements yielded the average hydrodynamic particle diameter of 33.28 nm with the standard deviation of 0.64. Following the basic ferrofluid characterization, two diluted ferrofluid samples were prepared in addition, whose respective magnetic volume fractions and magnetization values are depicted in Fig. 1.

In order to verify the presence, or absence, of the unreacted salts and hydrated ions, the original ferrofluid sample, as well as all diluted samples and the pure transformer oil, were characterized by infrared spectroscopy. The Fourier transformed infrared (FTIR) spectra were obtained using FTIR spectrometer Vertex 80v (Bruker) by attenuated total reflectance (ATR) measurements with diamond or ZnSe windows, with 256 scans and resolution 4 cm<sup>-1</sup>. Figure 2 shows the FTIR spectra of two samples with magnetic volume fraction of 3.2% and 6.6%, as well as the pure transformer oil. The absorption peaks at 2953, 2921, 2852, 1458, and 1377 cm<sup>-1</sup> correspond to C-H bonds in the transformer oil. The peak at 580 cm<sup>-1</sup> is attributed to the magnetite. In addition to these peaks, two

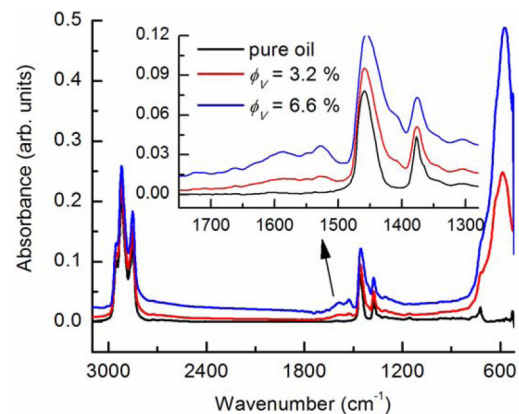


FIG. 2. (Color online) FTIR spectra of the transformer oil and two ferrofluid samples. The magnified region points out the absorption peaks corresponding to N-H bonds and confirming so the presence of NH<sub>4</sub><sup>+</sup> ions on the particles.

TABLE I. The values of electrode separation distances  $d$ , adjusted ac test signal voltages  $V$ , and resulting electric field intensities  $E$ , employed during the dielectric-spectroscopy measurements.

$d$ ( $\mu\text{m}$ )	1.6	3.2	5.1	9.8	20	50	75
$V_{\text{rms}}$ (mV)	32	64	102	196	400	1000	1500
$E$ (kV/m)	20	20	20	20	20	20	20

weak absorption peaks at 1573 and 1530  $\text{cm}^{-1}$  have been observed in the ferrofluid samples only, not in the oil. Both these peaks are attributed to N-H bonds from the amide group. The intensity of both peaks increases with increasing volume fraction of magnetic particles. Consequently, the obtained results clearly confirm the presence of hydrated  $\text{NH}_4^+$  ions bonded to the negatively charged particle surfaces, so forming an electric double layer around the particles. The significance of the ammonium ions can be understood also from the recent study [27].

The dielectric-spectroscopy experiments were performed on the LCR meter (Agilent E4980A) in the frequency range from 20 Hz up to 2 MHz. As sample holders we employed small capacitors, commercially available as liquid crystal (LC) cells, with the active electrode area  $A = 25 \text{ mm}^2$ . Their composition of two flat glass pieces coated with indium tin oxide (ITO) electrodes, separated in distance  $d$  of a few micrometers, constitutes favorable conditions for precise permittivity measurements of dielectric liquids in the low-frequency range. Errors due to edge effects of the capacitor border are minimized by keeping the ratio  $d/A$  at small values. The ferrofluid samples were drawn into the cells by capillary action. After the filling process we allowed the sample to stabilize for a few minutes. Then, the capacitance and dissipation factor were measured in the whole frequency range. In order to investigate the assumed particle clustering induced by the external electric field, we measured the ferrofluid samples in the cells with different electrode separation distances. However, in each of the cases, the ac electric field intensity was maintained at the constant value 20 kV/m by the accurate ac test signal voltage adjustment. Table I presents the values of the chosen electrode separation distances, applied voltages, and resulting electric field intensities. The measurements were carried out at room temperature in an electromagnetically shielded, anechoic chamber, whereby the experimental setup was free of external electromagnetic interferences from dc up to 18 GHz. The uncertainty of the acquired data is less than 0.3%.

### III. RESULTS AND DISCUSSION

#### A. Basic consideration

The assumed electric field induced magnetic particles clustering in the ferrofluid originate from the fact that the uniform electric field  $\mathbf{E}$  induces electric dipole moments in the particles. The effective dipole moment  $\mathbf{P}$  of the spherical particle can be expressed as follows [17,28]:

$$\mathbf{P} = 4\pi\epsilon_m K R^3 \mathbf{E}, \quad (1)$$

where  $R$  is the radius of solid particles and  $K$  is known as the Clausius-Mossotti factor, which gives the measure of

the effective polarization as a function of permittivity of the particle  $\epsilon_p$  and the surrounding medium  $\epsilon_m$ :

$$K = \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m}. \quad (2)$$

In ac electric fields, the particle dipole moment also depends on the angular frequency of the applied field:  $\mathbf{P} = 4\pi\epsilon_m K R^3 \mathbf{E} e^{i\omega t}$ . If particles are close each to other, then the electrostatic dipole-dipole interactions appear, and together with van der Waals and magnetic dipole-dipole forces contribute to the total particle-particle interaction force. Hence, it is expected that the resulting particle cluster formation will have a substantial impact on dielectric relaxation processes which take place on the particle-medium interface. This effect can be proven by frequency dependent complex dielectric permittivity measurements.

The complex dielectric permittivity of a material placed in a plate capacitor is defined as [29]

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \frac{C^*(\omega)}{C_0}, \quad (3)$$

where  $C^*(\omega)$  is the complex capacitance and  $C_0$  is the capacitance of the air filled capacitor. In our experiment, the real part of the complex permittivity  $\epsilon'(\omega)$  was calculated by dividing the measured real capacitance  $C'(\omega)$  of the sample filled capacitor by the corresponding  $C_0$ . The imaginary permittivity  $\epsilon''(\omega)$ , also known as the loss factor, was determined from the measured dissipation factor  $\tan \delta(\omega)$  according to the following relation:

$$\epsilon''(\omega) = \epsilon'(\omega) \tan \delta(\omega). \quad (4)$$

#### B. Low-frequency dielectric spectrum

The obtained permittivity spectra for the three investigated ferrofluid samples are summarized in Fig. 3. As can be seen, the low-frequency dielectric dispersion that occurred in all the cases is considerably dependent on the electrode separation distance  $d$ . Since the investigated ferrofluid sample is a nonpolar insulating complex liquid, one can exclude the association of the permittivity slope with the electrode polarization, which is a frequently encountered phenomenon when measuring conductive systems [30]. Owing to the high conductivity of magnetite (25 kS/m), and the low conductivity of the transformer oil (10 pS/m), the Maxwell-Wagner relaxation process in the studied ferrofluid should appear close to the terahertz frequency region. The relaxation time of this process was determined according to the general Maxwell-Wagner formula [31], whereas any effects of internal magnetism of the particles have been neglected. As the spherical magnetite particles are nonpolar and dielectrically isotropic, orientation polarization is also excluded from the consideration. In our previous work [32], as well as in some other earlier studies on transformer oil-based ferrofluids [33–35], the low-frequency relaxation process was assigned to the electric double layer (EDL) polarization taking place on the particle surfaces. Although the nanoparticles are sterically stabilized by a single oleic acid layer, the above-mentioned fabrication procedure gives rise to the EDL formation. Becoming negatively charged by the adsorbed  $\text{OH}^-$  and oleate ions on the surface, each magnetite nanoparticle is surrounded by the hydrated  $\text{NH}_4^+$



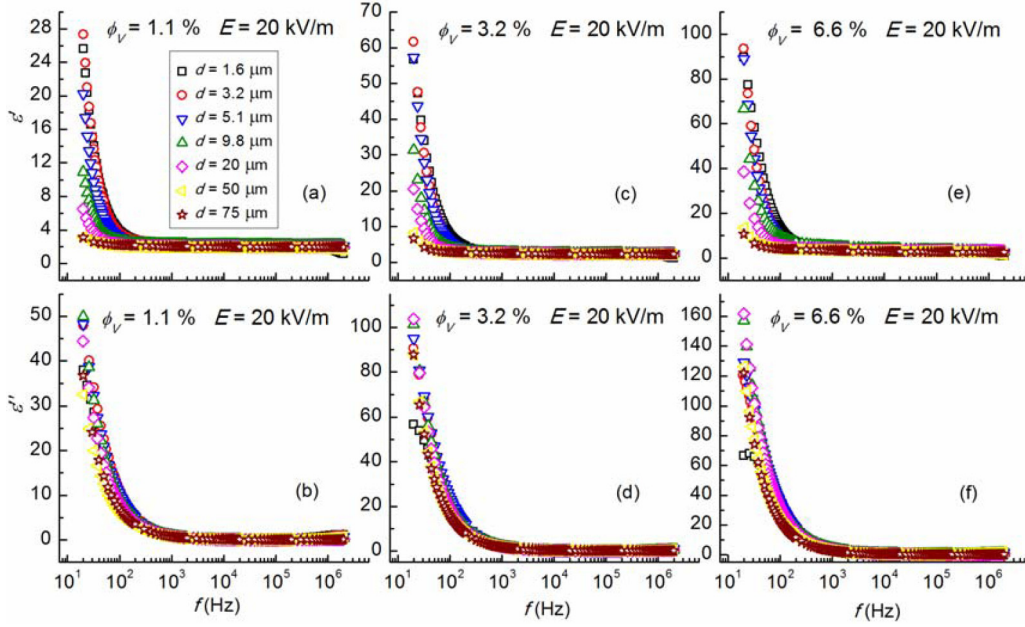


FIG. 3. (Color online) The real and imaginary permittivity spectra dependent on the electrode separation distance. The legend is valid for the all depicted graphs (a)–(f).

ions, so forming the EDL [36]. Current thinking about the EDL is that the polarization mechanism arises from a combination of diffuse and bound layer contributions [16]. However, in the case of nonpolar carrier liquids, such as transformer oils, one should consider only fixed (adsorbed  $\text{OH}^-$ ) and bound layer ( $\text{NH}_4^+$ ). This condition allows the low-frequency relaxation process to be described by the original Schwarz theory [37], where the exchange between the suspending electrolyte and the charged layer is neglected. In this theory, the corresponding relaxation time is given by

$$\tau = \frac{R^2}{2ukT} = \frac{R^2}{2u_0kT} \exp\left(\frac{E_a}{kT}\right), \quad (5)$$

where  $R$  is the radius of the colloidal particle,  $k$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $u$  is the mechanical mobility of the ions on the particle’s surface, dependent on the activation energy  $E_a$  and the mobility in free solution  $u_0$ . Since the polarization of the EDL is a purely local effect related to the particle, the movement of the counterions along the particle surfaces can be viewed as virtual dipoles in the insulating liquid. Then, this process should be characterized by the famous Debye-like dielectric behavior, which in our case is deduced from the Cole-Cole representation plotted for all the investigated samples measured in the cell with the electrode separation distance  $d = 1.6 \mu\text{m}$  (Fig. 4). That distance has been chosen due to the partially appeared relaxation maximum in the imaginary permittivity spectra, which is a significant indication of a dielectric relaxation process. The experimental data tend to create a semicircle with its center on the horizontal axis, which is demonstrated by a supplemented radius  $r$ . In general, the semicircle character is considered as the main characteristic of a Debye relaxation process [16]. Explicit investigation of that relaxation process in a broad frequency and temperature range will be reported elsewhere in a future study.

### C. Electrode spacing effect

To analyze the electrode spacing effect, let us focus on the dielectric loss spectra. Seeing that the investigated frequency range did not allow revealing of the entire relaxation maximum in  $\epsilon''(\omega)$  for the applied spacing and temperature conditions, a more preferable way of data presentation should be chosen. In dielectric spectroscopy, besides the loss factor  $\epsilon''(\omega)$ , the dissipation factor  $\tan \delta(\omega)$  and imaginary part  $M''(\omega)$  of the dielectric modulus  $M^*(\omega)$  are often analyzed [38]. The latter is the reciprocal permittivity  $1/\epsilon^*(\omega)$  that can be measured directly, or calculated from the following relation:

$$M^*(\omega) = M'(\omega) + iM''(\omega) = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + i \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2}. \quad (6)$$

Figure 5 illustrates the comparison of the three dielectric loss representations for the most concentrated ferrofluid

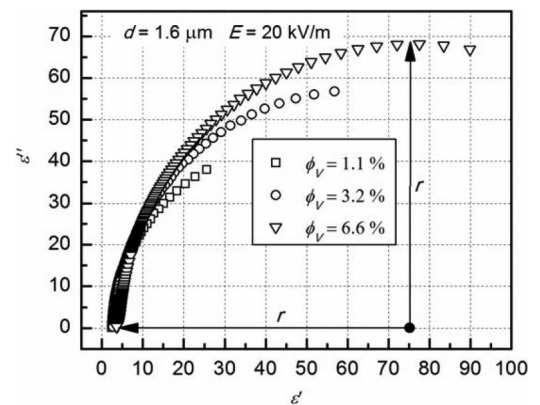


FIG. 4. Cole-Cole graph consisting of the available experimental data and the depicted radius of the semicircle pointing out the Debye relaxation behavior.

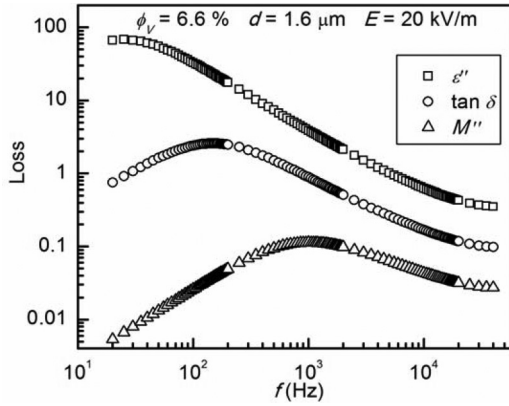


FIG. 5. The low-frequency relaxation maximum presented in the three ways of dielectric loss spectra.

sample measured at the smallest electrode separation distance. Whereas the  $\varepsilon''$  peak arises from the low-frequency limit, the  $\tan \delta$  and  $M''$  peaks are expectedly shifted towards higher frequencies. The shift of the  $M''$  peak is twice that of  $\tan \delta$ , which is in accordance with the Debye relaxation depicted on a log-log scale, as discussed in [38]. Since transformer oil-based ferrofluids are potential insulating media for power and distribution transformers, we prefer to plot  $\tan \delta$ , as it is frequently used to characterize liquids for electrical and engineering applications. Then, the relaxation time determined from  $\tan \delta$  maximum frequency position is related to the real relaxation time as follows:

$$\tau_{\tan \delta} = \frac{\tau}{2\pi} \left( \frac{\varepsilon_s}{\varepsilon_\infty} \right)^{1/2}, \quad (7)$$

where  $\varepsilon_s$  and  $\varepsilon_\infty$  are the low- and high-frequency limits of the dielectric permittivity, respectively.

The electrode spacing effect on the investigated ferrofluid samples'  $\tan \delta$  spectra is shown in Fig. 6. The shift of the maxima position towards higher frequencies, caused by higher magnetic volume fraction, is analyzed in our previous work [32]. However, the increasing electrode separation distance causes the remarkable broadening of the relaxation maximum towards lower frequencies. The average relaxation time is therefore increasing. As the electric field intensity and temperature were constant, the increase in the relaxation time can be caused only by the increased particle size; see Eq. (5). This broadening of the relaxation maximum is then associated with the formation of larger particle clusters when the space between the two electrodes is increased. Since the right-hand side of the maximum remains at almost constant frequency position, the broadening indicates the increase in the particle cluster size distribution. In the ferrofluid sample exposed to the low-ac electric field it is therefore probable to find individual particles and their clusters with the size distribution dependent on the micro-electrode-gap dimension. If the particles aggregate in terms of touching each other, then the  $\text{NH}_4^+$  ion atmosphere around the individual particles can be disrupted and finally form an envelope around the whole aggregate. Consequently, the polarization of the EDL takes place on a larger object (aggregate). The resulting relaxation time is increased according to Eq. (5), and that leads to the

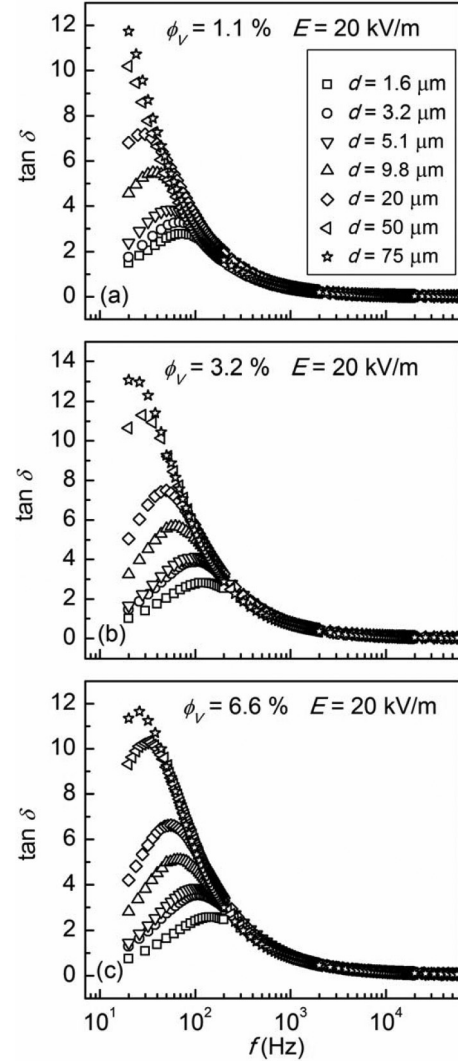


FIG. 6. The dependence of the  $\tan \delta$  loss spectrum on the electrode separation distance. The legend is valid for the all depicted graphs (a)–(c).

shift of  $\tan \delta$  maximum position towards lower frequencies. If the electric field does not force the particles to stick together, then the particles can form chainlike clusters with the original EDL around the individual particles. Nevertheless, the ionic mobility in such a configuration and the related relaxation time is slower.

The observed changes in the amplitude of  $\tan \delta$  maximum with increasing electrode separation distance are related to the cluster size. The increase in the cluster size produces an increase in the dipole moment which correlates with the permittivity growth [39]. That can be also read from Figs. 3(e) and 3(f), where the loss peak with the smallest amplitude has appeared in the case of the smallest electrode separation distance, and the real permittivity (static permittivity) increases with the increase in that distance as well. In other words, the counterion charges in the EDL are free to move along the larger aggregates in response to the ac electric field, whereby more energy is dissipated at the relaxation frequency. When plotting the frequency position of the maxima in  $\tan \delta$  spectra

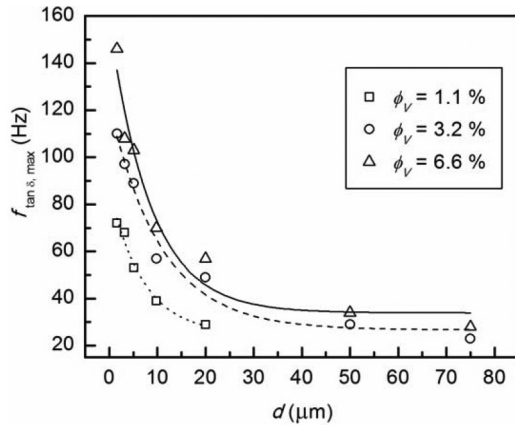


FIG. 7. The exponential dependence of the detected  $\tan \delta$  maxima frequency position on the electrode separation distance. The solid, dashed and dotted lines represent the exponential fit of the data obtained on the samples with the magnetic volume fractions of 6.6%, 3.2%, and 1.1%, respectively.

versus the electrode separation distance, one can obtain an exponential dependence (Fig. 7). Accordingly, the cluster size and the relaxation time of the EDL polarization are exponentially proportional to the electrode separation distance. Following this observation, the position of the  $\tan \delta$  maximum related to the frequency is particularly sensitive at the small range of electrode separation distances. Then, one would predict a critical electrode separation distance inherent to certain constant electric field intensity, where the size of the created clusters is saturated, and behind that distance the maxima position would be frequency stable. Unfortunately, the numerical estimation of the cluster size according to the Schwarz theory faces difficulties with the determination of the counterion mechanical mobility in transformer oil-based ferrofluids.

**D. Direct current bias electric field effect**

The dc electric field induced particle cluster formation can be also detected by applying the dc bias voltage dependent dielectric spectroscopy, which in this study has been carried out on one ferrofluid sample ( $\phi_V = 6.6\%$ ) measured at a constant electrode separation distance ( $d = 1.6 \mu\text{m}$ ). Several  $\tan \delta$  spectra have been obtained with the applied dc bias voltage of different values, which is summarized in Fig. 8. In these experiments, the effective value of testing ac voltage was 32 mV. The first measurement was undertaken at zero dc bias voltage. Then, the dc voltage of 1 V was applied to the sample capacitor and the second spectroscopic measurement started. Immediately after this measurement, the dc voltage was increased to 2 V and the third spectrum was measured. In this way, the dc bias voltage was increasing up to 4 V and the acquired spectra of these five particular measurements are presented in Fig. 8(a). In order to reveal the induced cluster behavior, the experimental procedure continued in hysteresislike measurement sequence. It means that when the measurement with dc bias voltage of 4 V was completed, the dc voltage was decreased back to 3 V and the dielectric spectroscopy was performed again. The  $\tan \delta$  spectra, which

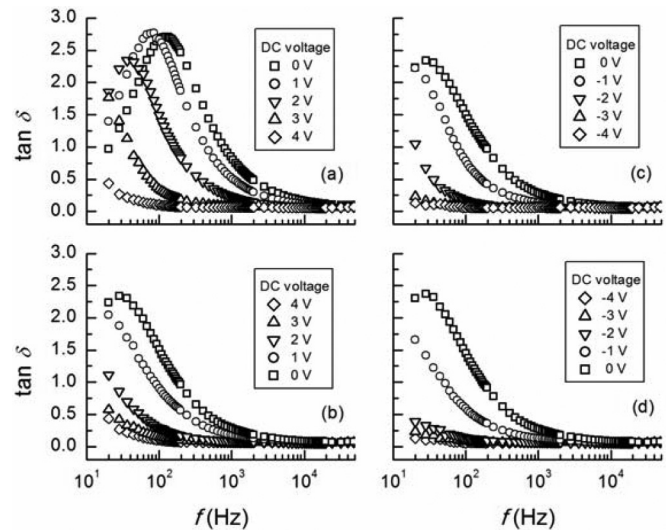


FIG. 8. The dependence of the  $\tan \delta$  loss spectrum on the applied dc bias voltage. The measurements were conducted one after the other with the following sequence: from 0 V up to 4 V (a), from 4 V down to 0 V (b), from 0 V down to  $-4$  V (c), from  $-4$  V up to 0 V (d). The investigated ferrofluid sample with magnetic volume fraction  $\phi_V = 6.6\%$  was measured in the LC cell with electrode separation distance  $d = 1.6 \mu\text{m}$  and the applied test signal level of 32 mV (20 kV/m). The intensity of dc electric field was 0.625, 1.25, 1.875, and 2.5 MV/m corresponding to the applied dc bias voltages of 1, 2, 3, and 4 V, respectively.

were gradually obtained at the applied dc bias voltages from 4 V down to 0 V in 1 V decreasing steps, are depicted in Fig. 8(b). Subsequently, the measurement at zero dc bias voltage was followed by the measurements with the changed bias voltage polarity from  $-1$  V down to  $-4$  V [Fig. 8(c)], and back up to 0 V again [Fig. 8(d)]. Each particular measurement took approximately 6 min.

In Fig. 8(a), one can see the increase in the relaxation maximum amplitude only for the applied dc bias voltage of 1 V. The relaxation maximum obtained at this condition is also shifted to lower frequencies as in the previous experiment. This is associated with the initial formation of particle clusters driven by the applied dc electric field. However, when the dc field was gradually amplifying, the relaxation maximum was shifting to lower frequencies, whereas its amplitude was greatly decreasing. This is the consequence of the dominant polarization force of the dc electric field. In this case, the strong dc electric field induces the dipoles in the particles, resulting in the formation of larger clusters, while at the same time this field polarizes and keeps the counterions on the opposite cluster sides so strongly that their ability to respond to the ac field decreases markedly. Thereby the dc electric field raises an energy barrier on the polarization axis, so reducing both mobility and the moving range of the counterions, which is reflected in the lower-frequency position of the loss peak and its decreased amplitude, respectively. From the reverse measurements [Fig. 8(b)], one can notice a certain kind of remanence in the induced cluster size when the relaxation time and the amplitude of the loss peak achieve the initial values with the noticeable lag. This can be clearly seen



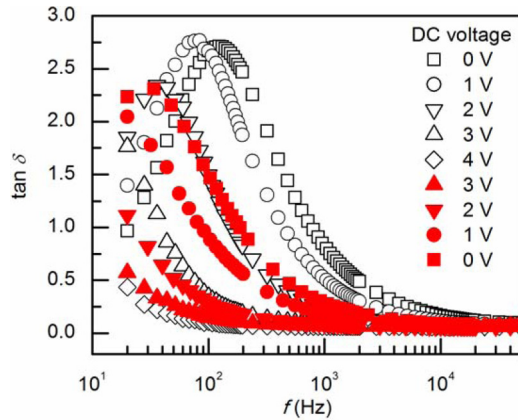


FIG. 9. (Color online) Remanence in the induced particle clusters presented by the superimposed  $\tan \delta$  loss spectra from Figs. 8(a) and 8(b). The empty symbols represent the data acquired in measurement sequence with the applied dc bias voltage  $U_B$  from 0 V up to 4 V, whereas the full symbols belong to the data measured back from 3 V down to 0 V dc bias voltages.

by plotting all the spectra in one graph depicted in Fig. 9. A greater degree of that lag is observed in the frequency position of the relaxation maxima, while their reincrease in amplitude seems to have a faster response to the decreasing dc voltage. The former can be related to the cluster structure inertia when the total attractive forces are still able to resist the disrupting thermal energy effect. The latter is related to the decreasing energy barrier, whereby the counterions surrounding the cluster acquire greater freedom in response to the ac electric field. The above-described behavior accounts for the fact that the relaxation maxima do not match at zero dc bias voltages. Then, starting the dielectric-spectroscopy measurements with the dc bias voltage from 0 V down to  $-4$  V [Fig. 8(c)], the amplitude of the loss peak and its position in frequency scale were suppressed again. This means that the quick electronic repolarization of the particle clusters allowed them to interact further with the near clusters, so forming even larger objects. Consequently, this led to the similar counterions' relaxation dynamics as in the previous case. The tendency to achieve the initial state can be again seen from the reverse measurement results [Fig. 8(d)]. Finally, in comparison to Fig. 6, the relaxation maxima in these graphs are not just widened, but shifted with the whole shape. This difference can be associated with the formation of particle clusters with a different degree of size distribution. While the low ac electric field allows one to find individual particles and different sizes of induced clusters in the sample volume, the strong dc electric field reduces that distribution eminently.

The analyzed hysteresis behavior can be graphically presented also by plotting the dissipation factor values taken at a constant frequency versus the applied dc bias voltage. For that purpose we chose the values acquired at the frequency of 120 Hz which is the relaxation frequency of the considered process measured in the absence of dc bias field. Figure 10 shows the decreasing character in  $\tan \delta$  values when the dc bias voltage increases (from 0 to 4 V). This is associated with the growing particle clusters and the resulting shift of the relaxation maximum. Owing to that shift, the decreasing

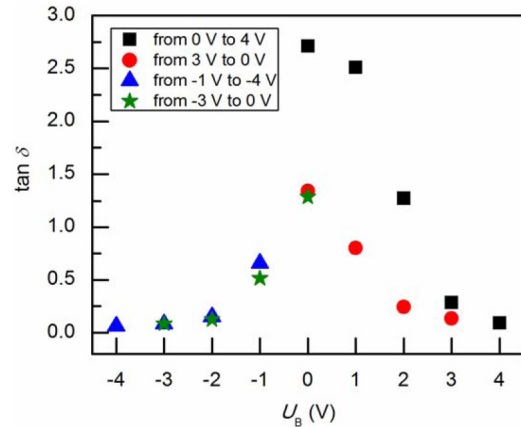


FIG. 10. (Color online) Hysteresis in the electric field induced particle clustering presented by plotting  $\tan \delta$  values taken at 120 Hz frequency as function of the applied dc bias voltage  $U_B$ . The rectangular data points form the initial curve.

values in the right maximum tail are scanned at 120 Hz, not the maximal value anymore. Afterwards,  $\tan \delta$  increases in response to the decreasing dc voltage (from 4 to 0 V). However, the data do not follow the original values, but acquire lower magnitudes instead. This reflects the low effect of decaying clusters and their remanence even when the dc bias voltage is set to zero again. Therefore, the curve obtained from the initial measurements with the applied dc voltage from 0 V up to 4 V can be called the initial or virgin curve, as during these measurements the clusters were induced by the applied dc voltage. The increasing dc voltage with opposite polarity causes the repeated decrease in  $\tan \delta$ , whereby a quasisymmetry has been found in the related (from 0 to  $-4$  V) and previous curve (from 4 to 0 V). Finally, the  $\tan \delta$  values, measured with the decreasing dc bias voltage back to zero, nearly match with the previous data. The similar trend in these two curves (measured under the negative dc voltage) originates in the fact that before the measurement from 0 to  $-4$  V the preformed (remanent) clusters, induced by the previous measurement, had been presented in the sample. This is contrary to the initial curve starting from zero dc bias voltage when no clusters affected the  $\tan \delta$  values.

To get a better understanding of the cluster formation process, we let the sample relax for a day, and then conducted several dielectric-spectroscopy measurements in time periods during which the dc bias voltage was kept at a constant value. In Fig. 11, we present the experimental results of eleven dielectric-spectroscopy measurements. The first measurement was carried out in the absence of any dc bias voltage. Then, the dc bias voltage of 1 V was applied to the sample cell for 40 min. During this time period we conducted five measurements in 7-min intervals. In the presented graph, one can see that the increased loss peak amplitude due to the applied dc bias voltage appeared only in the first measurement. Then, this amplitude diminishes with the passing time that is seen from the other four  $\tan \delta$  spectra. A slight shift to the lower frequencies can also be noticed. Both these effects are supposed to stem from the growth of the clusters and their stabilization in time. These time dependent changes in the loss spectra were more pronounced

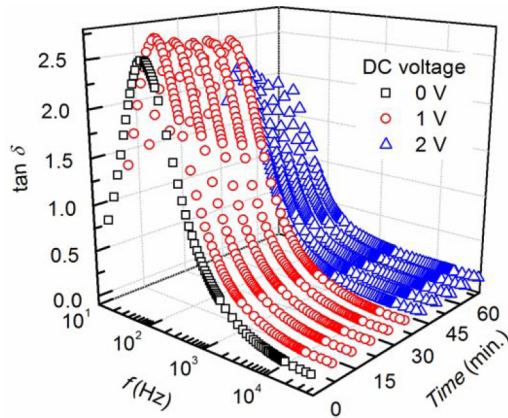


FIG. 11. (Color online) The time development of the dc bias voltage dependent  $\tan \delta$  loss spectra measured for the ferrofluid sample with  $\phi_v = 6.6\%$ .

when the dc bias voltage was increased to 2 V. In accordance with Eq. (1), the effective dipole moments of the clusters increase with increase in the electric field intensity and the cluster size. This results in stronger cluster-cluster interactions and growth of the clusters during the time period when the dc voltage was applied. Hence, the counterion relaxation dynamics is greatly influenced.

The decay of the created clusters after turning the dc bias voltage off can be understood from Fig. 12. This picture shows the result of the following experimental protocol which was carried out on the same sample after the second day of rest. The  $\tan \delta$  spectrum of the investigated ferrofluid sample in

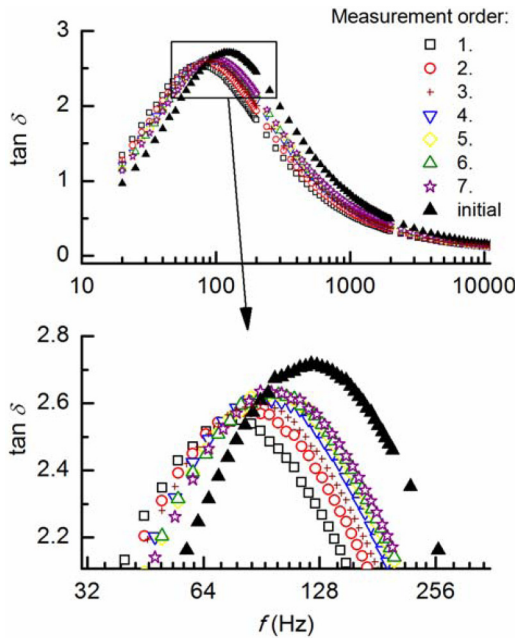


FIG. 12. (Color online) Time decaying particle clusters reflected in  $\tan \delta$  loss spectra measured at zero dc bias voltage after a 50-min exposure of the sample to the dc electric field of 0.625 MV/m. The measurements were conducted in 12-min intervals. The obtained spectra are compared with the initial spectrum measured before the application of the dc electric field to the sample.

the LC cell was firstly measured in the initial state before the exposure to the dc electric field. The sample was then exposed to the dc electric field of 625 kV/m generated by the applied dc bias voltage of 1 V, with the duration of 50 min. When this voltage was turned off, we started to record several measurements of  $\tan \delta$  spectra. In Fig. 12 we have depicted seven relaxation maxima which were gradually measured in approximately 12-min intervals. The distinct increase in the relaxation maximum height and the shift of the maximum to the higher frequencies is related to the decreasing size of the created particle clusters and relative decrease in the EDL relaxation time. In this way we therefore point out the decay process which is driven by the thermal energy of the bulk sample. Following the observed shifts towards the initial state, one can deduce that the decay of the biggest clusters progresses more quickly than that of smaller clusters. This has become evident by nearly overlapping loss spectra measured in 12-min intervals after 55 min of the dc electric field absence (from measurement number 5). After 90 min of intensive experimental observation, the initial state had still not been achieved.

Finally, let us remark that the particle clusters induced by the external electric field can contribute to the process of the electric breakdown field strength enhancement in transformer oils. The clustering should be taken into account especially in connection with the charged nanoparticle model, where the nanoparticles act as electron scavengers [40]. This model considers charging of nanoparticles by free electrons from the field ionization, to convert fast electrons to slow negatively charged nanoparticle charge carriers with effective mobility reduction. A consequence of that converting is the reduced speed of the streamer development formed by the charged nanoparticles. Based on the analysis in this paper, low electric fields can induce formation of particle clusters before the ionization takes place. In this regard, the slow particle clusters may constitute suitable free electron scavengers. However, further study and computer simulations of that process with polarized particles, surfactants, and EDL are requested.

#### IV. CONCLUSION

In this study, the isothermal dielectric spectroscopy of a transformer oil-based ferrofluid was employed to detect the predicted electric field induced particle cluster formation. The low-frequency relaxation process was assigned to the electric double layer polarization. We investigated the role of electrode separation distance at constant electric field intensity on the relaxation maxima. The broadening of the relaxation maximum towards lower frequencies was observed as the response to the increased electrode separation distance. On the basis of the particle size dependent relaxation time, we associate the broadening with the cluster formation induced by the applied ac electric field. The broader relaxation maximum therefore indicates the increase in the magnetic solid fraction size distribution. A similar indication of the cluster formation was observed when the dc bias voltage was applied. The observed temporal hysteresis in the relaxation time reflects the particle cluster formation and decay behavior. In our next investigation we will therefore focus on the apparent magnetic particle cluster formation in external electric field studied by



*in situ* Small Angle X-ray Scattering (SAXS), Small Angle Neutron Scattering (SANS), and electrorheology experiments. If the clustering process is sufficiently proved and a static or dynamic cluster structure is understood, its impact on the electric breakdown in ferrofluids should be taken into account.

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