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# Frequency dependence of dielectric anisotropy in ferrofluids

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## Abstract

We have conducted broadband, temperature-dependent dielectric spectroscopy on ferrofluids of various concentrations. We study the change of the permittivity on application of a homogeneous magnetic field ($\approx 0.5\,\mathrm{T}$, parallel or orthogonal). The results reveal that the field-induced magnetodielectric effect is markedly frequency dependent and should be attributed to two different mechanisms: The structural anisotropy affects not only the interfacial polarisation of the nanoparticles, but also the strength of the hopping process observed in the samples. Both these effects influence the low-frequency permittivity values. High-frequency measurements should be used to derive information on the microstructure by means of effective media analysis.

*Keywords:* Ferrofluids; Dielectric spectroscopy; Magnetodielectric anisotropy; Hopping; Relaxation; Frequency dependence

## 1. Introduction

The magnetodielectric anisotropy (MDA) effect is one of the interesting phenomena observed in ferrofluids. In the past it has been attributed to an orientation of ellipsoidal magnetic particles parallel to the imposed magnetic field. The most accepted explanation, however, is the formation of chain-like structures. Dielectric spectroscopy is a direct way to study ferrofluids [1–3]. Here we discuss measurements covering a broad range of frequencies, temperatures and concentrations.

## 2. Experimental set-up, samples

The complex dielectric function was measured using a broadband method [4]. The sample was placed in a plane capacitor and the transmission was measured in a single sweep (5–$10^9$ Hz). The temperature was varied between 93 and 293 K with an accuracy of 0.2 K. An electromagnet allowed to apply fields between 0 and 0.5 T, parallel or perpendicular to the electric field of the capacitor. The sample dimensions (diameter 11 mm, thickness 1 mm) were small compared to the poles of the magnet (diameter 120 mm, distance 100 mm) providing a fairly good local field homogeneity.

The samples (EMG series, Ferrofluidics GmbH) consisted of magnetite particles in organic oil (Isopar) with oleic acid as surfactant. Density measurements were carried out to determine the volume filling factor $f$ of magnetite, which varied from 1% to 19% approximately.

## 3. The dielectric spectrum

In Fig. 1 the imaginary part of the permittivity of a sample with $f = 19\%$ is shown at selected temperatures. At temperatures above the freezing point of Isopar (about 208 K) the DC-conductivity dominates the spectrum. It is accompanied by a polarisation mechanism in the kHz range. The latter shows the same thermal activation and can be attributed to conductivity relaxation (see e.g. Ref. [5]). With decreasing temperature a pronounced relaxation with a characteristic frequency $\nu_h(T)$ enters our frequency window (in the GHz range at room temperature). A detailed analysis shows that this

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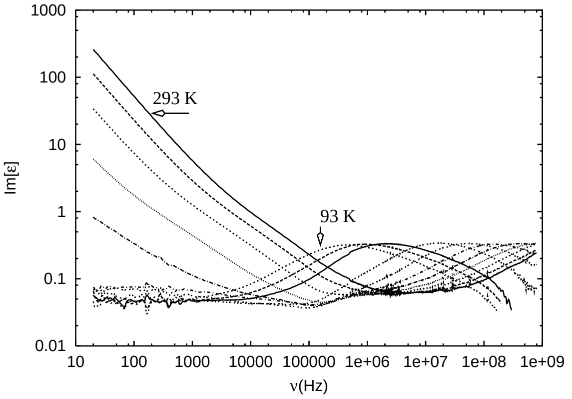

Fig. 1. Log–log plot of the imaginary part of the dielectric function for the sample with $f = 19\%$, at steps of 20 K.

process is due to additional polarisation, caused by small polaron hopping between particles belonging to clusters. Below the freezing point of the carrier, the contributions of DC-conductivity and the related polarisation vanish and the spectra can be fitted by a function of the form

$$\varepsilon(\nu) = \frac{\Delta\varepsilon_{\mathrm{h}}}{\left(1 + \left(\mathrm{i}\frac{\nu}{\nu_{\mathrm{h}}}\right)^{1-\alpha_{\mathrm{h}}}\right)^{\gamma_{\mathrm{h}}}} + \varepsilon_{\mathrm{hf}} + \varepsilon_{\mathrm{fl}}(\nu). \tag{1}$$

The first term is the Havrilia–Negami [7] fitting function for a relaxation of strength $\Delta\varepsilon_{\mathrm{h}}$ and characteristic frequency $\nu_{\mathrm{h}}$ ($\alpha_{\mathrm{h}}$, $\varepsilon_{\mathrm{fl}}(\nu)$ are shape parameters). $\varepsilon_{\mathrm{fl}}(\nu)$ is a small complex contribution due to a "flat losses" mechanism [6], causing the "offset" by 0.04 in the imaginary part of $\varepsilon(\nu)$ in Fig. 1 and a constant slope of the real part.

Due to the high conductivity of the particles, the Maxwell–Wagner interfacial polarisation (MWP) is expected at much higher frequencies $\nu_{\mathrm{MW}} \gg 100\,\mathrm{GHz}$. Our frequencies are quasi-static with respect to the MWP. There is no other mechanism of significant strength up to the MWP frequency, as proved by the excellent agreement between the permittivity data at high frequencies ($\nu_{\mathrm{h}} \ll \nu \ll \nu_{\mathrm{MW}}$) and the Bruggeman formula [8] (Figs. 2 and 3)

$$\varepsilon_{\mathrm{hf}} = \varepsilon_{\mu}/(1-f)^3, \tag{2}$$

where $\varepsilon_{\mu} = 2.28$ is the dielectric constant of Isopar. This formula holds for the MWP quasi-static values in random polydisperse systems [5,8,9]. Any change in the microstructure of the ferrofluids, e.g. due to an external magnetic field, is reflected in a deviation of $\varepsilon_{\mathrm{hf}}$ from the predictions of this model.

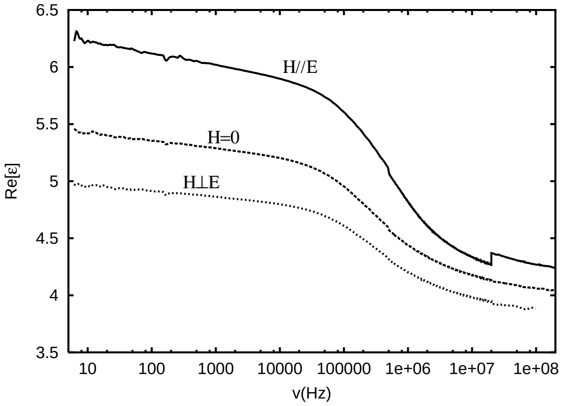

Fig. 2. The MDA for the most concentrated sample: The middle, upper and lower curves show the real part of $\varepsilon$ vs. $\nu$ for the field-free case, and with parallel and perpendicular field.

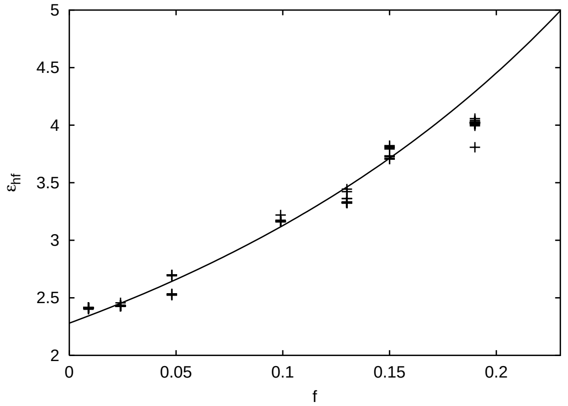

Fig. 3. $\varepsilon_{\mathrm{hf}}$ ($10^9$ Hz) vs. $f$ compared to the Bruggeman model. The data was obtained from non-linear fits on the measurements at low temperatures (<140 K). One point is plotted for every temperature to give a feeling for the errors introduced by measurement and fit.

## 4. The magnetodielectric effect

In Fig. 2 a plot of the real part of the permittivity vs. frequency is presented (for $f = 19\%$, $T = 93\,\mathrm{K}$). The middle curve corresponds to a measurement without magnetic field. The strong decrease in the MHz range is due to the relaxation at $\nu_{\mathrm{h}}$. Neglecting for simplicity the small contribution of the flat losses, the low-frequency values are the sum of $\varepsilon_{\mathrm{hf}}$ and $\Delta\varepsilon_{\mathrm{h}}$. The other two curves in Fig. 2 show the MDA: A homogeneous magnetic field induces anisotropy in the microstructure of the ferrofluids. This affects the MWP strength and consequently $\varepsilon_{\mathrm{hf}}$, which can no longer be described by Eq. (3). It is increased in the field direction and reduced in the perpendicular one.

At frequencies much lower than $\nu_h$ the anisotropy is further enhanced. It is obvious from Fig. 2 that $\Delta\varepsilon_h$ is also affected by the magnetic field. In other words, in the presence of a magnetic field hopping is enhanced in the field direction and weakened perpendicular to it. This can be understood, if we accept the formation of elongated agglomerates orientated parallel to the field direction.

## 5. Conclusions

Concluding, a quantitative comparison with theoretical models for MDA in terms of the interfacial polarisation alone, that is, using effective media analysis, should be based on the high-frequency permittivity. Only $\varepsilon_{hf}$ reflects purely the change in the microstructure, while static or low-frequency measurements can result in much higher permittivity and anisotropy values, due to the additional change of the hopping related polarisation.

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## References

[1] M.M. Radulescu, J. Magn. Magn. Mater. 85 (1990) 144.

[2] A. Siblini, L. Jorat, G. Noyel, J. Magn. Magn. Mater. 122 (1993) 182.

[3] P.C. Fannin, S.W. Charles, T. Relihan, J. Magn. Magn. Mater. 167 (1997) 274.

[4] R. Pelster, IEEE Trans. Microwave Theory. Tech. 43 (7) (1995) 1494.

[5] R. Pelster, U. Simon, Colloid Polym. Sci. 277 (1999) 2.

[6] A.K. Jonscher, Universal Relaxation Law, Chelsea Dielectric Press, London, 1996 (Chapter 4).

[7] S. Havriliak, S. Negami, J. Polym. Sci C 14 (1966) 99.

[8] D.A.G. Bruggeman, Ann. Phys. 24 (1935) 636.

[9] A. Spanoudaki, R. Pelster, Phys. Rev. B 64 (2001) 064205.