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MAGNETIC PROPERTIES OF FERROFLUID EMULSIONS: MODEL OF NON-INTERACTING DROPLETS

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Experimental study of the static magnetic properties of ferrofluid emulsions has demonstrated the nonmonotonic field dependence of the emulsion magnetic permeability. In a weak magnetic field, the emulsion permeability rapidly grows and reaches a maximum, and then it decreases slowly in stronger fields. We suggest a theoretical description of the effect based on the following idea. The weak field growth of the emulsion magnetic permeability is caused by the droplet elongation and the resulting reduction of demagnetizing field under the constant value of the ferrofluid magnetic susceptibility. Subsequent decrease of the emulsion magnetic permeability in a stronger magnetic field is explained by the decay of the ferrofluid magnetic susceptibility under an approximately constant degree of droplet elongation.

Introduction. Ferrofluid emulsion is a colloidal suspension of ferrofluid droplets suspended in an immiscible liquid [1, 2]. An applied magnetic field induces a magnetic dipole moment in each droplet, hence, the ferrofluid becomes magnetized. So the induced droplet magnetic moment is dependent on the droplet volume and the magnetization behaviour of the bulk ferrofluid. In case of a weak external field, the droplet magnetic moment is a linear function of applied field strength H_0. The droplet shape is greatly dependent on the surface tension value; all droplets are spherical in zero magnetic fields. For ferrofluid emulsions with strong surface tension, the droplets can be regarded as spherical even in a rather strong magnetic field [1, 2]. Here the emulsion magnetic permeability μ_e might be constant in a wide range of magnetic field strengths. The behaviour is much more interesting for emulsions, the interfacial tension σ on the droplet surfaces of which is rather weak ($\sigma \sim 10^{-5} - 10^{-6}\,\mathrm{N/m}$). Here the surface forces cannot stabilize the spherical shape of droplets, and the applied magnetic field tends to elongate the droplets along the field direction. In a simple way, the droplet shape might be described by the elongated ellipsoid of revolution with the eccentricity e [3–6].

The emulsion magnetic permeability can be defined as

$$\mu_\mathrm{e} = 1 + 4\pi M_\mathrm{e}/H_0, \tag{1}$$

where M_e stands for the emulsion magnetization, which is the product of the droplet concentration n_d and the induced droplet magnetic moment m_d:

$$M_\mathrm{e} = n_\mathrm{d} m_\mathrm{d}.$$

For simplicity, we consider the surrounding liquid as totally non-magnetic. Assuming a linear magnetization law, for an ellipsoidal droplet we get

$$m_\mathrm{d} = \chi_\mathrm{f} V_\mathrm{d} H_\mathrm{d} = \frac{\chi_\mathrm{f} V_\mathrm{d} H_0}{1 + 4\pi\chi_\mathrm{f} n_z(e)}, \tag{2}$$

$$n_z(e) = \frac{1-e^2}{2e^3}\left[\ln\left(\frac{1+e}{1-e}\right) - 2e\right]. \tag{3}$$

Here χ_f stands for a ferrofluid initial magnetic susceptibility, V_d is the droplet volume, $n_z(e)$ is the ellipsoid demagnetization factor, and H_d has a meaning of the internal magnetic field inside the ferrofluid droplet. By combining these expressions, we easily obtain the emulsion magnetic permeability as a linear function of the droplet volume fraction φ:

$$\mu_\mathrm{e} = 1 + 4\pi \frac{n_\mathrm{d} m_\mathrm{d}(H_0)}{H_0} = 1 + \varphi \frac{4\pi\chi_\mathrm{f}}{1 + 4\pi\chi_\mathrm{f} n_z(e)}. \tag{4}$$

This well-known expression for the permeability of a mixture is valid for low concentrated emulsions, and we may call this approach as “the model of non-interacting droplets”, because we suggest that droplets do not influence on each other.

The demagnetization factor $n_z(e)$ of stretching ellipsoid varies from $n_z = 1/3$ (for a sphere, $e = 0$) to zero (for an infinitely elongated ellipsoid, $e = 1$). For this kind of ferrofluid emulsions, the magnetic field induces both droplet magnetic dipoles and droplet elongation. And the demagnetization factor is a decreasing function of the applied field strength. It means that the effective emulsion permeability increases with the magnetic field. Therefore, a further increase of the magnetic field is accompanied by a decrease of the ferrofluid susceptibility χ_f. So from the expression 4 we have the changeover in the behaviour of the emulsion permeability: the field induced growth of the permeability changes to its decrease.

Recently, such nonmonotonic field dependence of the magnetic permeability has been experimentally reported [7] for ferrofluid emulsions (Fig. 2, experimental dots) produced by dispersing a kerosene-based ferrofluid in immiscible aviation oil. The weak field permeability demonstrates the rapid growth, and the further field strengthening leads to a long-tail decrease of the magnetic permeability. This effect could be observed only for the non-stabilized ferrofluid emulsions characterized by rather weak values of the interfacial tension σ. The maximum value of the effective emulsion permeability increases with the volume concentration φ of the droplets. During measurements, the coalescence of the droplets was not experimentally observed [7]. The correct theoretical description of this nonmonotonic dependence needs a solution of the droplet elongation problem with account for the nonlinear magnetization of the droplet.

1. Model. The main approximations of our model on non-interacting droplets are the following. All ferrofluid droplets are considered to be of equal volume V_d. The shape of the droplets, elongated under the action of an external field, is modeled by the elongated ellipsoid of revolution. We assume that the magnetic field geometry inside and outside the droplet is independent on other droplets; and the internal magnetic field inside the droplet is uniform. The magnetic permeability of the carrier liquid (oil) is considered to be equal to unity. To describe the magnetic parameters of the ferrofluid, we use the so-called 1st order modified mean-field model [8, 9], which has been proved to provide excellent agreement with the experiments and computer simulations both for ferrofluids [10] and for ferrogels [11]. In the framework of this model, the magnetization M_d of the ferrofluid is given by

$$M_\mathrm{d}(H) = M_\mathrm{L}\left[H + \frac{4\pi}{3} M_\mathrm{L}(H)\right], \tag{5}$$

$$M_\mathrm{L}(H) = M_\infty L\left(\frac{mH}{k_B T}\right), \quad L(\alpha) = \coth\alpha - \frac{1}{\alpha}.$$

Here H is the magnetic field strength, $L(\alpha)$ and $M_{\mathrm{L}}(H)$ are the Langevin function and the Langevin magnetization, M_∞ has the meaning of the ferrofluid saturation magnetization, m stands for the ferroparticle magnetic moment, and $k_{\mathrm{B}}T$ is the thermal energy.

Assuming the droplet magnetic moment m_{d} as the product of the droplet volume V_{d} and the magnetization M_{d} of a ferrofluid droplet, $m_{\mathrm{d}} = V_{\mathrm{d}}M_{\mathrm{d}}$, the definition of the emulsion magnetic permeability (1) could be easily converted to

$$\mu_{\mathrm{e}} = 1 + 4\pi\varphi M_{\mathrm{d}}(H_{\mathrm{d}})/H_0, \tag{6}$$

where the droplet magnetization M_{d} is the function of the strength of the internal magnetic field H_{d} inside the droplet. This internal field is determined by the solution of the magnetostatic problem, defining the magnetic field geometry inside and outside the magnetizing droplet exposed to a uniform static external magnetic field H_0. For the prolate ellipsoidal droplet, this solution gives the well-known relation between the magnetization M_{d}, the applied magnetic field strength H_0, the strength H_{d} of the internal field inside the droplet and the droplet elongation through the droplet demagnetizing factor n_z:

$$H_0 = H_{\mathrm{d}} + 4\pi n_z(e)M_{\mathrm{d}}(H_{\mathrm{d}}). \tag{7}$$

To close the model for the case of an external magnetic field of arbitrary strength, we use the minimization condition for the droplet free energy F consisting of two parts: the surface energy and the magnetic energy:

$$F = \sigma S_{\mathrm{d}}(e) - V_{\mathrm{d}} \int\limits_0^{H_0} M_{\mathrm{d}}(H_{\mathrm{d}})\mathrm{d}H_0, \tag{8}$$

$$S_{\mathrm{d}}(e) = 2\pi\sigma \left(\frac{3V_{\mathrm{d}}}{4\pi}\right)^{2/3} \left(1-e^2\right)^{1/3} \left(1 + \frac{\arcsin e}{e\sqrt{1-e^2}}\right).$$

Here S_{d} is the surface area of the elongated ellipsoid of revolution expressed in terms of the droplet volume V_{d} and eccentricity e. The problem is that the integral in Eq. (8) has to be calculated within the external field. Changing the integration variable from H_0 to H_{d} on the basis of the relation (7) yields

$$F = \sigma S_{\mathrm{d}}(e) - V_{\mathrm{d}} \int\limits_0^{H_{\mathrm{d}}} M_{\mathrm{d}}(H_{\mathrm{d}})\mathrm{d}H_{\mathrm{d}} - 4\pi n_z(e)V_{\mathrm{d}}\frac{M_{\mathrm{d}}(H_{\mathrm{d}})^2}{2}. \tag{9}$$

The droplet elongation is to be obtained via the minimization of the energy F with respect to the eccentricity e taking into account that the internal field H_{d} is also a function of the eccentricity:

$$\frac{2\pi V_{\mathrm{d}}M_{\mathrm{d}}(H_{\mathrm{d}})^2}{\sigma} = -\frac{\partial S_{\mathrm{d}}(e)/\partial e}{\partial n_z(e)/\partial e}. \tag{10}$$

It should be noted that the shape of a droplet exposed to an external magnetic field could be also studied within the pressure approach, since the driven force of the droplet elongation is the magnetic pressure. This method was used, for example, in [4], and the obtained relation for the case of arbitrary magnetic field strength is coincident with that of Eq. (10).

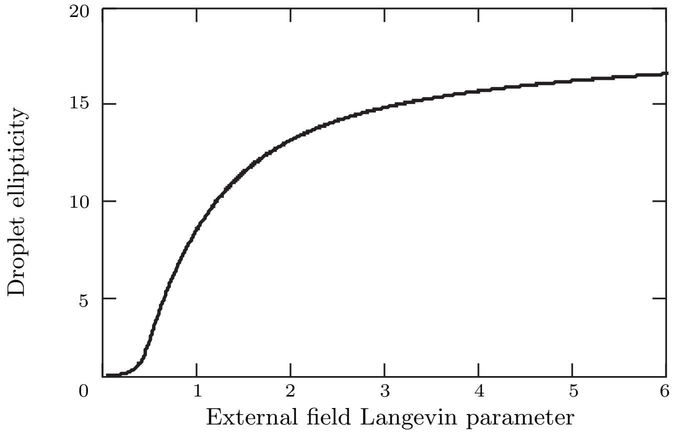

Fig. 1. The droplet ellipticity (long-to-short semi-axis ratio) as a function of the external magnetic field strength given in units of the Langevin parameter α.

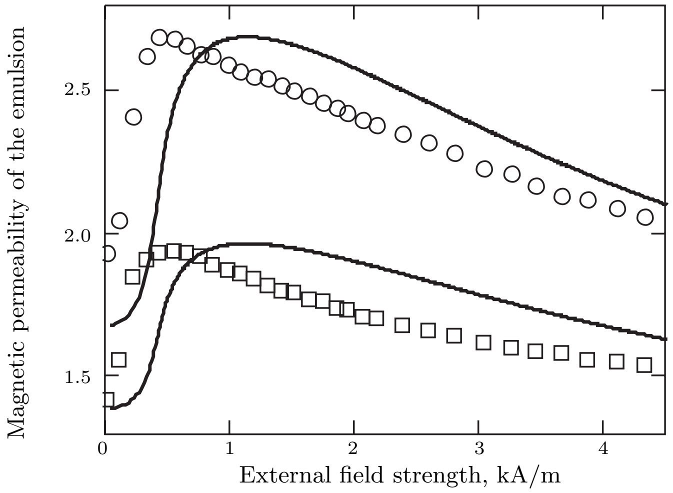

Fig. 2. Field dependence of the magnetic permeability of ferrofluid emulsion. Experimental data [7] are presented for the emulsions with the droplet volume fraction $\varphi = 0.2$ (boxes) and 0.35 (circles). Theoretical predictions are shown by lines for the same emulsions.

2. Results. The numerical solution of the set of equations (3), (5), (7), and (10) gives us, first, the degree of the droplet elongation induced by the applied magnetic field. The calculated typical ellipticity (long-to-short semi-axis ratio) is shown in Fig. 1 as the function of the Langevin parameter $\alpha = mH_0/k_{\mathrm{B}}T$ for the external field. As expected, the degree of the elongation grows rapidly in weak magnetic fields. For strong magnetic fields, it is well known that the use of the linear magnetization law results in unlimited elongation of a droplet, while the real magnetization behaviour of the ferrofluid (see Eq. (5)) gives practically the termination of the elongation process even in moderate magnetic fields for $\alpha > 3$.

The dependence of the magnetic permeability of ferrofluid emulsions on the external magnetic field strength is illustrated in Fig. 2 in comparison with the experimental data [7]. Two emulsions with different volume fractions of ferrofluid droplets were studied: $\varphi = 0.2$ and 0.35. The magnetic permeability under zero field is an increasing function of the droplet volume concentration. For both emulsions, the magnetic permeability grows rapidly in weak magnetic fields and reaches a maximum at a certain field strength, which is practically independent on the droplet concentration. Theoretical curves are calculated for the same droplet volume fractions, and the magnetic parameters of the ferrofluid were chosen as $4\pi M_\infty = 20.3\,\mathrm{kA/m}$ and $4\pi\chi_\mathrm{f} = 5.4$ according to the data in [7]. Qualitative agreement is good; some quantitative deviations might be caused by the mutual influence of droplets during their magnetization and by the polydispersity of the droplets.

3. Conclusions. Three main conclusions can be drawn.

- The presented simple model describes qualitatively just the nonmonotonic field dependence of the ferrofluid emulsion magnetic permeability.
- The growth of the magnetic permeability under weak fields is caused by the droplet elongation and the resulting reduction of demagnetizing field.
- The decrease of the magnetic permeability in strong fields is explained by the decay of the ferrofluid magnetic susceptibility at termination of further droplet elongation.

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