Journal of Magnetism and Magnetic Materials 322 (2010) 2575–2580

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

Magnetophoresis and diffusion of colloidal particles in a thin layer of magnetic fluids

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ARTICLE INFO

Article history:
Received 17 August 2009
Received in revised form
2 February 2010
Available online 2 April 2010

Keywords:
Magnetic fluid
Magnetophoresis
Diffusion
Magnetic field
Interparticle interaction
Chain
Aggregate

ABSTRACT

Experimental and theoretical studies were carried out to investigate the spatial distribution of colloidal particles in magnetic fluids formed under the influence of magnetophoresis and gradient diffusion in a strong magnetic field. Several theoretical models, describing the equilibrium concentration profiles for rigid chain-like and quasispherical aggregates, are discussed. The experiment was made for four samples of magnetic fluids, differing in the average diameter of magnetic particles and the width of the particle size distribution. The analysis of the experimental data shows that the aggregates essentially change the concentration profile, making it nonlinear even in small (2 mm) magnetic fluid samples. Good agreement between the experimental and theoretical curves is observed in the case when the aggregates contain on the average 40–50 particles. The average diameter of single particles, calculated from the concentration profile curves, coincides with the average diameter, found from the magnetogranulometric analysis.

1. Introduction

In this study we pursue two interrelated goals. First, we intend to investigate the concentration stratification in a thin layer of magnetic fluids in a gradient magnetic field and to compare the experimental results with the predictions of simple theoretical models in order to estimate the applicability of these models for description of real magnetic fluids. Second, we expect to get additional information about the aggregates in magnetic fluids and to estimate their influence on magnetophoresis.

It is known that profound changes in the magnetic [1–7] and rheological [2,8–11] properties of magnetic fluids observed in experiments are usually attributed to the existence of nanoscopic aggregates formed under the action of magnetodipole or van der Waals forces. Based on the results of experimental investigations [2,4,5,9], computational modeling [11–14] and analytical calculations [15,16], it may be concluded that the quasispherical aggregates dominate in the concentrated solutions, whereas in dilute solutions the aggregates are commonly observed in the form of short chains. The only reason why the aggregates are shaped into chains is the anisotropic magnetodipole interactions. The influence of the magnetodipole interactions is more profound in the case when the dimensionless constant of coupling (the ratio of dipole–dipole energy to thermal energy) exceeds two. The quasispherical aggregates are formed due to anisotropic magnetodipole and van der Waals interactions. According to Refs. [2,5] the main reason for the appearance of quasispherical aggregates in the magnetic fluids of the “magnetite–oleic acid–kerosene” type are the defects in the protected layers of the colloidal particles. These aggregates dramatically affect the dynamic processes in solutions: they cause a many-fold increase in the relaxation time of the magnetization and a decrease in the diffusion constant of colloidal particles. Since the nanoscopic aggregates are invisible with the light microscope, the information about their shape, dimensions and quantity is collected in the process of rheological, magnetic and diffusion measurements. Each of these methods of measurement has its own merits and demerits. In particular, determination of the aggregate sizes using experimentally measured diffusion coefficients is one of the few methods that do not disturb mechanically the testing samples. The main drawback of the diffusion methods is its low resolution due to weak dependence of the diffusion coefficient on the size of diffusing particles (aggregates) and relatively high error of measurements. In recent years, a series of investigations on the diffusion processes in magnetic fluids have been made to study the structure of aggregates [2,17,18], to evaluate the contribution of the magnetic dipolar interactions to the magnetic fluid stratification [19], and to detect thermodiffusion effects [20–22].

In this study we use the method, which is based on the analysis of the spatial distribution of particles inside the measuring cell, placed in a gradient magnetic field. The reason of concentration stratification in magnetic fluids is magnetophoresis — the motion of magnetic particles under the action of the gradient magnetic field. The only kinetic mechanism, which equalizes concentration of the magnetic phase in the samples of magnetic fluids, is the gradient diffusion of the particles.

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doi:10.1016/j.jmmm.2010.03.023

The equilibrium distribution of particles inside the samples of magnetic fluid is sustained due to competition of these two processes (magnetophoresis and gradient diffusion) and does not depend on the kinetic coefficients (including particle mobility). In this case the use of the proposed experimental method for measuring the particle concentration provides a more reliable interpretation of the experimental results. Furthermore, the equilibrium distribution of particles depends on the number of particles in the aggregate, but is quite independent of the shape of the aggregate, which allows one to count the total amount of all aggregates regardless of their structure.

2. Equilibrium distribution of single particles in dilute magnetic fluids

In dilute magnetic fluids, in which the volume fraction of particles $\phi \ll 1$, the interparticle interactions (steric, magnetodipole and hydrodynamic) are weak and the equilibrium distribution of particles in the magnetic and gravitation fields can be described analytically. The fact, that the fields are potential and the boundaries of the cavity are impermeable essentially simplifies the problem. In this case, the system is in the state of thermodynamic equilibrium (there are no fluxes of mass, momentum and energy), and stratification of the fluid is described by the Boltzmann distribution. The potential energy U of a single-domain particle is

$$U=-\mu_0 mH(x,y,z)\cos\vartheta-\Delta\rho V_s g(z\cos\alpha+x\sin\alpha), \tag{1}$$

and the distribution function is

$$f(r,\theta)=A\exp\left(-\frac{U(r,\theta)}{kT}\right). \tag{2}$$

Here θ is the angle between the magnetic moment $\mathbf{m}$ and the field intensity $\mathbf{H}$, $\Delta\rho$ is the density difference between the solid kernel of colloidal particles and the disperse medium, V_s is the volume of the solid particle kernel, α is the angle between the z axis and the gravity vector $\mathbf{g}$, lying in the x–z plane. The last term in expression (1) describes the influence of the Archimedean force. The numerical density of particles at the arbitrary point of the space can be determined by averaging (2) over the orientations of the magnetic moment.

$$n(x,y,z)=A\frac{\sinh\xi}{\xi}\exp[G(z\cos\alpha+x\sin\alpha)]. \tag{3}$$

Here the Langevin parameter $\xi=\mu_0 mH/(kT)$ is the known function of coordinates, and $G=\Delta\rho V_s g/(kT)$ is the gravitational parameter (the reciprocal height of the barometric distribution). The normalization constant A can be evaluated in terms of the average volume fraction of particles $\tilde{\phi}$ in the sample. In this case, the local concentration of particles ϕ is described by the following equation:

$$\phi=\tilde{\phi}\,\frac{\frac{\sinh\xi}{\xi}\exp[G(z\cos\alpha+x\sin\alpha)]}{\frac{1}{V}\int_V\frac{\sinh\xi}{\xi}\exp[G(z\cos\alpha+x\sin\alpha)]dv}. \tag{4}$$

In the limit of weak fields ($\xi \ll 1$), Eq. (4) coincides with the barometric formula. In the opposite case ($\xi \gg 1$, $Gz^* \ll 1$, z^* — is the typical cavity dimension) this equation also describes distribution, similar to the barometric one provided that the magnetic field gradient $\partial H/\partial z$ changes inesentially inside the cavity. In this case the typical "height of the barometric distribution" is

$$z^*=\frac{kT}{\mu_0 m}\left(\frac{\partial H}{\partial z}\right)^{-1}.$$

The main disadvantage of Eq. (4) is that it neglects the interparticle interactions (steric, magnetodipole and van der Waals interactions) and therefore cannot be used for highly concentrated fluids including the situations, in which high concentrations of particles are found only in some parts of the cavity. The equation, similar to (4), was derived recently in [23,24] However, it was derived in a different way and did not take sedimentation into account. Since Eq. (4) is valid only for a system in the equilibrium state, it does not contain any kinetic coefficients. It can be used for cavities of arbitrary shape (including 3-D problems) and for arbitrary magnetic fields.

3. Estimation of the influence of colloidal particle polydispersity

Eq. (4) can also be used in the case of polydisperse suspensions. In this case, we need to write it for each fraction, and then to summarize the left- and right-hand sides of the equations. Let us perform this operation with reference to the experimental conditions used in this study. The experimental conditions can be characterized by two small dimensionless parameters: the product of the gravitational parameter by the thickness of the measuring cell $Ga\approx 10^{-3}$, and the relative variation in the intensity of the magnetic field inside the measuring cell $\Delta H/H_0<2\times 10^{-2}$. In view of smallness of theses parameters, the influence of the gravity can be neglected, and mean value of the function *sinh*$(\xi)/\xi$ in the denominator of Eq. (4) can be replaced by its value, measured at the center of the measuring cell. After performing these manipulations, the contribution of a separate fraction to the local concentration of colloidal particles can be expressed as

$$d\phi=d\tilde{\phi}\,\frac{\xi_0}{\xi}\frac{\sinh\xi}{\sinh\xi_0},\quad d\tilde{\phi}=\frac{\pi n}{6}x^3 f(x)dx, \tag{5}$$

where ξ_0 is the Langevin parameter, expressed in terms of the field intensity H_0 in the center of the cell, $d\tilde{\phi}$ is the contribution of the fraction to the average volume concentration, x is the magnetic kernel diameter of the particles, and $f(x)$ is the function of size distribution of particles at the initial time, when the distribution of particles inside the measuring cell is homogeneous. According to [24], the $f(x)$ function can be approximated by the Γ-distribution

$$f(x)=\frac{(x/x_0)^{\alpha}\exp(-x/x_0)}{x_0\Gamma(\alpha+1)}, \tag{6}$$

where $\Gamma(\alpha+1)$ is the gamma function. The k-th moment of x can be evaluated through the distribution parameters x_0 and α, according to the known formula $\langle x^k\rangle=x_0^k(\alpha+1)(\alpha+2)\ldots(\alpha+k)$. Here, the angle brackets denote averaging over the particle ensemble. After introducing a new integration variable $y=x/x_0$, the concentration field for dilute polydisperse fluid can be described by the following equations:

$$\phi=\frac{\tilde{\phi}}{(\alpha+1)(\alpha+1)(\alpha+1)\Gamma(\alpha+1)}\frac{H_0}{H}\int_0^{\infty}\frac{\sinh\xi}{\sinh\xi_0}y^{\alpha+3}\exp(-y)dy, \tag{7}$$

$$\xi_0=\frac{\pi\mu_0 M_s}{6kT}x_0^3 H_0 y^3,\quad \xi=\xi_0 H/H_0. \tag{8}$$

Eq. (7) is considered to be approximate to an extent the difference between the particle concentration in the center of the cavity and the averaged concentration can be neglected. In the limit $\alpha \gg 1$, the approximate expression for distribution of monodisperse particles can be obtained from Eq. (7)

$$\phi=\tilde{\phi}\,\frac{H_0}{H}\frac{\sinh\xi}{\sinh\xi_0}, \tag{9}$$