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Thermodiffusion motion of electrically charged nanoparticles

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Abstract: The present work deals with experimental studies to examine the theoretical model of thermodiffusion of electrically charged nanoparticles. Three different ionic magnetic colloid samples have been synthesized and profoundly analyzed. The theoretical model is a classical one, based on the calculation of the temperature and the electric potential distribution around nanoparticles. The discrepancy between experimental data and theory turns out not to exceed 20%. We focus on applying different approximations between calculated electrical double layer in the theoretical model and experimental determination of the surface charge density of colloidal particles. We assume this is the main reason for obtained discrepancy.

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1.   Introduction

The thermodiffusion coefficient D_T is defined by the particle flux equation, written for small particle volume concentration $c \ll 1$ with respect to the gradients of particle volume concentration and temperature T:

$$j = -D(\nabla c - D_T c \nabla T),$$

where D is the translational particle mass diffusion coefficient.

At the stationary state ($j = 0$), it is convenient to exclude D from the equation, therefore D_T usually is replaced by $D_T = D \cdot S_T$, where S_T is called the Soret coefficient:

$$j = -D(\nabla c + S_T c \nabla T).$$

The Soret coefficient of molecular systems is quite negligible, whereas in disperse systems (colloids and suspensions) it turns out to be some orders of magnitude higher, and therefore significant. Regarding colloidal systems, the magnetic colloids are taken as a particular subject. In a magnetic colloid, each colloidal particle, made from a ferromagnetic material $5 \ldots 20$ nm in diameter, is a magnetic monodomain. Magnetic colloids have superparamagnetic properties, i.e., they are characterized by volume magnetization without hysteresis [1, 2]. Besides investigations

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of magnetic properties, magnetic colloids in absence of magnetic fields may be studied as usual colloidal systems. Even at non-magnetic subject studies, the magnetic properties of an examined colloid are an advantage because some important additional information of the sample can be obtained by experiments with applied external magnetic fields.

Systematic measurements of the thermodiffusion coefficient with magnetic colloids, known to us, started on 1996 [3–5]. Both methods: particle separation in the thermodiffusion column and forced Rayleigh light scattering (FRS) in thermally induced optical grating, gave as a result $S_T \approx 0.10 \dots 0.15$ K^{-1} with ferroparticles coated by surfactant. Some years later these results were, in addition, confirmed by optical measurements with incoherent exciting light [6, 7].

Experimental measuring of the Soret coefficient of electrically stabilized ferroparticles, so called ionic magnetic fluids, came out much harder. Due to weak optical signal, the first published results [4] were unfaithful, as proved years later. Thermodiffusion column experiments with ionic magnetic fluids failed due to the destruction of their colloidal stability. Faithful results of S_T with ionic magnetic fluids, synthesized by the Massart method [8], appeared in 1998, and they turned out to be of the same magnitude as with surfaced magnetic fluids. Nevertheless, all measurements with ionic magnetic fluids indicated opposite (by definition, negative) sign of the Soret coefficient, which means particle flux from a colder region to a warmer one.

Following up the first successful measurements, the thermodiffusion coefficient has been measured with a wide variety of synthesized ionic magnetic fluids. Measured values of S_T normally did not exceed 0.15 K^{-1}, but what was really surprising is that it could be either negative or positive. Issued in the meantime, the theoretical model [9] explained this phenomenon quite well. Experimental data of some ionic magnetic fluid samples were used in verification of Morozov's theoretical model, and the accordance usually turned out to be in the range 20 . . . 30%. Actually, this error range concerns the lack of particle surface potential, obtained by independent methods. The main reason for this permanent discrepancy is discussed afterwards in this paper.

On the basis of preparing ionic magnetic fluids, we turn to an experimental verification of Morozov's model. With identical maghemite γ-Fe$_2$O$_3$ particles, three substantially different samples have been synthesized and experimentally analyzed in depth, in accordance with Morozov's model.

2. Theoretical model and its fitting with experimental data

The basic theoretical model, developed by K. I. Morozov [9, 10], for ionic magnetic fluids is made within Gouy–Chapman model of the electrical double layer. Operating with Boltzmann distribution of the electrolyte ions and the Poisson equation, in the frame of linear solution, it finds the link between the velocity of thermodiffusion motion u and the Soret coefficient S_T:

$$S_T = -\frac{3}{4}\frac{R_H}{L_B T}u(\lambda, \zeta),\qquad(1)$$

where R_H is the hydrodynamic radius of a particle and $L_B = e^2/3\pi\varepsilon k_B T$ is the Bjerrum length. The thermodiffusion motion $u(\lambda, \zeta)$ is a function of ratio λ between double layer thickness and particle radius R, and $\zeta = e\varphi_R/k_B T$ – the non-dimensional particle surface potential. For the case of infinitely thin double layer ($\lambda \to 0$), by the method of matched asymptotic expansions, an analytical expression is found:

$$u(0, \zeta) = -\frac{2}{3}(1 - k)\left[\zeta^2 - 8(3 + \alpha)\ln\cosh\frac{\zeta}{4}\right],\quad(2)$$

where $\alpha = \mathrm{d}\ln\varepsilon/\mathrm{d}\ln T$, $k = (k_1 - k_2)/(k_1 + 2k_2)$, k_1 and k_2 being the thermal conductivity coefficients of the particle and the electrolyte, respectively.
For $\lambda \neq 0$, $u(\lambda, \zeta)$ was found numerically. Obtained curves with respect to different ratios λ are displayed in Fig. 1. We plot the points in Fig. 1, coordinates ζ, u of which are derived from experiments and independently acquired data. The particle surface potential φ_R is calculated from the superficial charge density σ [11]:

$$\varphi_R = \frac{2k_B T}{e}\operatorname{arcsh}\frac{2\pi\sigma L_B}{ke},\qquad(3)$$

where the double layer thickness is the Debye length k^{-1}:

$$k = \sqrt{4\pi N_A L_B \sum c_i z_i^2}.\qquad(4)$$

In Eq. (4) the sum represents the total ionic strength, where z_i is the charge number of the respective ions with concentration c_i. Note that Eq. (3) is the solution of the Poisson equation for the case of an infinite flat surface [12]. Nevertheless, in [11] the authors consider this analytical solution for the present case of a superficial charged sphere as permissible because only the surface potential is calculated. It is verified that Debye–Huckel approximation, derived for spherical particles of the surface potential
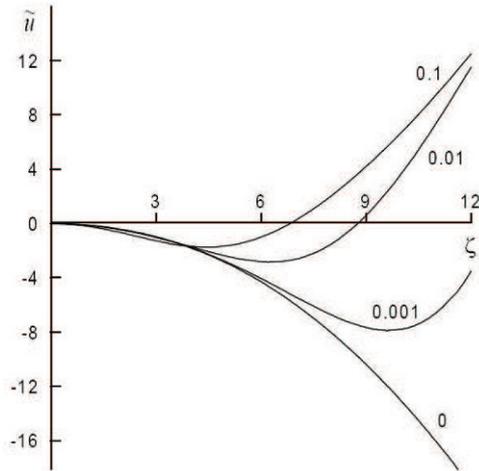
not exceeding ≈ 25 mV, gives faulty values of φ_R with actual colloidal particles. The superficial charge density of maghemite particles, finished as an ionic ferrofluid by the Massart method, is close to 0.20 C/m^2 [11]. This value is used in Eq. (3).

3. The samples, measuring technique and fitting results

The first sample S1 is synthesized with the aim to be an "ideal" sample for comparing with Morozov's model. Hard particle volume concentration is only 1.6% with the aim to minimize possible collective effects of particles. However, we evaluate assumptive aggregation by comparing the measured hydrodynamic radius and that, derived for one particle, as shown afterwards. The magnetic particles bear positive surface charges and the measured pH of the carrier liquid is 1.6. Since the pH level is gained only by excess of H^+ ions, and the dissociation constant of water at room temperature is 10^{-14}, the total ionic strength of electrically neutral bulk solution results 0.050 mol/l. The Debye length, accordingly Eq. (4), is 1.96 nm.

The radius of hard particle, R, is derived from material magnetization measurements with a commercial vibrating sample magnetometer VSM 7404 (Lake Shore). As obtained by the VSM, the magnetization curve is processed with a special software, developed by M. M. Maiorov, which returns the size distribution of the magnetic content of particle material, Fig. 2. In order to be accurate within feasible limits, we prefer to add to the magnetic
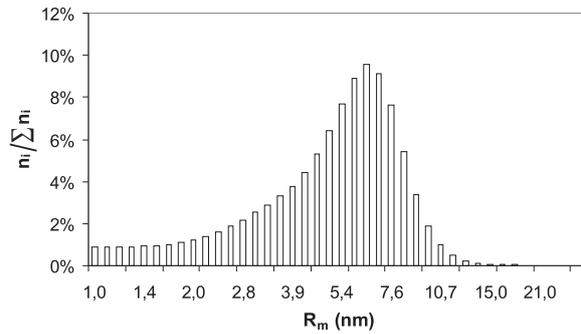
radius one lattice spacing as an outer non–magnetic layer [2]. For the particular case when the average magnetic radius is 6.6 nm, the lattice spacing of magnetite ≈ 0.8 nm, therefore R is taken to be 7.4 nm.

The Soret coefficient is measured by the method of forced Rayleigh light scattering. Unlike [4, 5], the present setup works with medium power continuous laser exciting beam, modulated at low frequency: 80 ms on, 20 ms off [13]. Such a regime is favorable from the point of view that the time-averaged power is only a small amount less than continuously emitted. Experiments prove that an exciting beam of green light of 0.5 W is enough for performing measurements. Reduced power of the laser beam is important for exciting the samples with intense aggregation (afterwards the sample S2). Measurements of S_T with the sample S1 are very steady, giving the result -0.17 ± 0.01 K^{-1} (necessary to note that due to some constant bias in input data, i.e., the derivatives of light refraction coefficients, the true absolute value of S_T may be slightly out of the error range 0.01 K^{-1}).

The FRS setup allows us to determine the average hydrodynamic radius of a particle, R_H by measuring the translational mass diffusion coefficient. Nevertheless, independent measurements of R_H with the commercial device Zetasizer Nano–S90 (Malvern) are considered as primary. Zetasizer gives as a result the size distribution of particles in motion, Fig. 3.

Now the comparison between the measured hydrodynamic radius R_H and that derived for one particle, takes place. The average magnetic radius is 6.6 nm, by adding the lattice spacing and double layer thickness one gets 9.4 nm. The difference compared to the average hydrodynamic radius $R_H = 17$ nm (Fig. 3) is less than half R_H, that means a possibility of very slight aggregation of particles. Additional testing, int.al. with magnetic field, indicates a feasible aggregation of the double layer shells, not of the
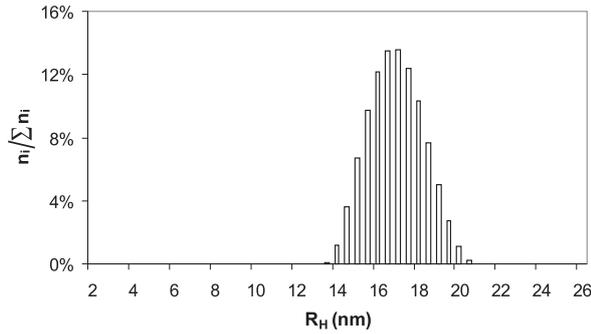
Figure 3. The size distribution of hydrodynamic radius of particles measured by Zetasizer Nano-S90, sample S1

hard particles.

With the data above, the variables λ, ζ and u, necessary for fitting with Fig. 1, can be obtained:

$$\lambda = \frac{1}{kR} = 0.27; \quad \zeta = \frac{e\varphi_R}{k_B T} = 2\mathrm{arcsh}\frac{2\pi\sigma L_B}{ke} = 6.1;$$

$$u = -\frac{4}{3}\frac{L_B S_T T}{R_H} = 2.8 . \tag{5}$$

For a perfect fit with Fig. 1 the demanded value of the surface potential is $\zeta \approx 7.5$. Equation (5) provides with a value 20% less, which is a typical error for such a comparison.

The second sample S2 is synthesized with the aim to have agglomerations of particles, aggregated by the shells. The hard particle volume concentration is 3.0%. The solvent is a mixture of 50% water and 50% glycerol by volume. Calculated dielectric permittivity of the solvent $\varepsilon = 63$ slightly changes the Bjerrum length from that in pure water [14]. The surface charge of magnetic particles is positive and the measured pH of the carrier liquid is 1.2. As glycerol does not dissociate, the calculated total ionic strength is 0.126 mol/l, and the Debye length 1.09 nm.

Measured by Zetasizer, the average $R_H = 35$ nm at $T = 20°C$ is twice as large as for S1. The agglomerations of such kind are investigated in [11], and the particle volume concentration in the agglomeration, independent of several parameters, is found to be ≈ 24%. Thus one can estimate that agglomeration consists, in average, of 20 particles, aggregated at distance $\approx 4k^{-1}$. Additional tests prove reversible aggregation that did not lead to flocculation and solid precipitate [11].

Measurements of the Soret coefficient by FRS setup fluctuate. The reason is the induced temperature grating in the sample, where high temperature partly splits the agglomerations. Measurements become more stable by decreasing the power of the exciting laser beam. The most

credible measured value of S_T is -0.11 ± 0.02 K^{-1}. Finally, the obtained parameters are: $\lambda = 0.14$; $\zeta = 5.4$ and $u = 0.86$. For a perfect fit with Fig. 1 the demanded value of ζ is approximately 6.7, proving the same lack of 20% as the sample S1.

The third sample S3 is synthesized to have zero charge on the particle coat. In accordance with Fig. 1, all curves start from point (0;0), i.e., independently of λ, the velocity of thermodiffusion motion u must be zero with $\zeta = 0$. Such sample is prepared from a usual cationic ferrofluid pH = 2, hard particle volume concentration 3.8%, by titrating trisodium citrate $Na_3C_6H_5O_7$. Trisodium citrate dissolves in water completely, and citrate ions by the one of three carboxyl groups stick to the particle. The needed amount of citrated ions is controlled during the titration by measuring pH. The titration has to be ended at pH = 7, which means that all OH$^-$ ions are released from the electrical double layer. In initially acid medium the two free carboxyl groups of adsorbed ligand are protonated, therefore the particle's coats bear no charge [15]. Due to the absence of charge no electrical double layer is created, thus the ionic strength and the Debye length are not in action. They are calculated (see Table 1) just for comparison with those of S1 and S2.

Measurements with Zetasizer give $R_H = 15$ nm, proving that flocculation does not lead to precipitation or to formation of agglomerations. We focused on measuring the Soret coefficient with the sample S3. As expected, nonzero value of S_T was not detected. It means that within the measuring accuracy, the velocity of thermodiffusion motion is $u = 0$, Eq. (1). All the exact data described above are gathered in Table 1.

4. Discussion

By comparing the samples of charged particles (S1 and S2) it is seen that their sizes differing by a factor of 2 as well as the existence of agglomerations do not affect the discrepancy with Morozov's model. Persisting discrepancy of 20% with pure water based ionic magnetic fluids is a typical error for such a comparison, known by time of issue of Ref. [10] in 2002.

In this paper we point out a different interpretation of the electrical double layer as the main reason for that 20% discrepancy. Morozov's model regards only the Boltzmann distribution of ions and counts the surface potential, therefore it neglects the potential difference over the Stern layer. The hard particle is assumed to move with the Gouy–Chapman layer of thickness k^{-1}. Considerations in Refs. [11, 16] are quite different, and an adequate explanation of them needs to refer to Green's theory (1949).

Table 1. Data collection of analyzed synthesized samples in accordance with Morozov's model.

sample	medium	pH of medium	Debye length, k^{-1} (nm)	radius of particle, R (nm)	hydrod. radius, R_H (nm)
S1	water	1.6	2.0	7.4	17
S2	water:glycerol (1:1)	1.2	1.1	7.9	35
S3	water with trisodium salt	7.0	1.1	7.7	15

sample	Soret coeff. S_T (K^{-1})	velocity of thermodif. motion, u	ratio, $\lambda = (kR)^{-1}$	particle surface potential ζ	ζ discrepancy with theoret. model
S1	–0.17	2.78	0.27	6.1	20%
S2	–0.11	0.86	0.14	5.4	20%
S3	0	0	0.14	0	0%

This theory splits the Stern layer in the inner and outer Helmholtz plane. The inner Helmholtz plane is packed by ions that are adsorbed by specific short–range acting forces. The ions, anchored by the Coulomb force, are located in the outer Helmholtz plane. This plane gradually transfers to the Gouy–Chapman plane where ions, being at larger distance than the Bjerrum length, obey the Boltzmann distribution.

Since the superficial charge density is very hard to measure directly, it may be calculated either from the electrokinetic potential, measured at electrophoresis, or from protometric and conductometric titration. Both methods count the charge of outer Helmholtz layer and give the same result $\sigma \approx 0.20$ C/m^2 with maghemite particles, charged by the Massart method [11, 16]. Neglecting here the inner Helmholtz layer may be a reason why in some other ways the estimated maximal superficial charge density is close to 0.3 C/m^2 [11, 17]. The discussed 20% of the surface charge density may be lost here. Experiments with the sample S3 validate Morozov's theory, which states that thermodiffusion motion is caused by the behavior of ions in the electrical double layer. Adjusting the particle coat potential to zero leads to zero value of the Soret coefficient by detecting with FRS setup (± 0.01 K^{-1}).

5. Summary and conclusion

Since the experimental equipment provides with all the necessary data, the thermodiffusion motion of electrically charged particles was analyzed in comparison with an existing theoretical model, developed by K.I. Morozov. Three different samples indicate 20%, 20% and 0% discrepancy with Morozov's model. The main reason of discrepancy is supposed to be the application of different theoretical approximations of the electrical double layer. The case of 0% discrepancy is the "zero signal" case in which the electrical double layer does not exist.

From another point of view, the actual discrepancy is sufficiently small to be caused by different reasons: the ion-ion correlations, the polarization, the finite size of ions and the polydispersity of the grains [18]. Gained experimental data could be compared with other independent data and analyzed in comparison to other theoretical models, published later [19–23].

The experimental equipment provides with results of polydispersity of the particle's magnetic and hydrodynamic radius that enables to study polydispersity effects within this subject. Such studies are planned in the immediate future. Considering Fig. 3, the half width of the spectrum is from 15 nm to 19 nm, which makes only $\sim 10\%$ difference from its maximum at 17 nm. Since the motion of nanoparticles obeys the Stokes approximation [9, 10], and measurements count integrated signal of a rather symmetrical spectrum, we estimate that such a slight polydispersity of the present samples is not a plausible reason for actual discrepancy of 20%. To proceed the studies of polydispercity effects, the synthesis of more polydisperse samples becomes topical.

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