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Invited paper

# Mass transfer in nonisothermal ferrocolloids under the effect of a magnetic field

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## Abstract

The paper presents a review of newest experimental results on particle thermal diffusion in hydrocarbon based ferrofluids. The measurements are performed using a vertical thermal diffusion column, the Soret coefficient is evaluated from particle separation curves employing a simple column theory which accounts for thermal convection in the vertical channel forced by a concentration buoyancy force arising during the thermophoretic transfer of heavy particles. High positive values of the Soret coefficient of lyophilized  $\text{Fe}_3\text{O}_4$  and  $\text{Mn}_x\text{Zn}_{1-x}\text{Fe}_2\text{O}_4$  particles in surfacted tetradecane based colloids are measured. Experiments confirm the theoretically predicted anisotropy of particle thermophoretic mobility in the presence of a uniform magnetic field oriented parallel or perpendicular to the temperature gradient. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Soret effect; Thermal diffusion column; Ultrafine particles; Ferrofluids

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## 1. Introduction

Transport properties of magnetic ultra-fine particles play a significant role in the problem of long-term stability of magnetic fluids. Usually, in the colloidal stability research besides the agglomeration problems mainly a magnetophoresis of ferroparticles in the presence of a nonuniform external magnetic field is taken into account. If high temperature gradients are present, a thermophoretic

transfer of particles effects the long-term stability of ferrocolloids also. Recently, a strong Soret effect in ferrofluids is established by particle separation measurements in thermal diffusion columns [1,2]. Measurements of nanoparticle grating in the forced Rayleigh scattering experiment also indicate high particle thermophoretic mobility in colloids [3]. From the analysis of a magnetic Stokes problem accounting for thermomagnetic forces it follows that the thermal diffusion of nanoparticles in ferrocolloids may be significantly effected by internal magnetic field gradients [4]. Results of our latest research aimed to investigate the above effects experimentally are reviewed in the paper.

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## 2. Magnetophoretic transfer of particles in colloids of nonuniform magnetization

The hydrodynamic theory of mass transfer in ferrocolloids is based on calculations of particle phoretic mobility. Usually, the magnetophoretic velocity induced by gradient of an external magnetic field  $\nabla H$ , is calculated from balance between the magnetic and the viscous forces. Such analysis, if it is based on classical solutions of hydrodynamic Stokes problem, is valid only for uniform magnetic fluids. If temperature and/or particle concentration gradients in the fluid are present, it is necessary to reconsider the Stokes problem by taking into account for a nonpotentiality of magnetic force. In a general case [5], the summary force acting upon a particle may be obtained by performing an integration of fore  $f_i = \sigma_{ik}n_k$  over its surface with the account in the stress tensor  $\sigma_{ik}$  for hydrodynamic and magnetostatic stresses. The distribution of magnetic field in the vicinity of a particle of magnetic permeability  $\mu_p$  different from that of a surrounding liquid  $\mu_f$  is described by the equation of scalar magnetic potential  $\psi$  which, instead of the conventional form of a Laplace equation  $\Delta\psi = 0$  includes a term proportional to  $\nabla\mu_f$  (the permeability  $\mu_f$  depends on temperature and on particle concentration,  $\mu_f = \mu_f(T, c)$ ). The temperature perturbations in the proximity of particle governed by the difference in particle and liquid thermal conductivity's  $\lambda_p$  and  $\lambda_f$  is described by a solution of the Laplace equation  $\Delta T = 0$ . The hydrodynamic part of the problem is advisable to write in a form of an equation for vorticity with the respect of a non-potential driving force  $\text{rot } \mathbf{f}_m = -\mu_0\eta\nabla\mu_f \times \nabla H^2$  ( $\eta_f$  is the fluid viscosity,  $\mu_0$  is the magnetic constant).

The magnetic Stokes problem firstly was analyzed in 1979 [4] considering the thermophoresis ( $\mu_f = \mu_f(T)$ ) of spherical particles under the effect of a uniform field  $\mathbf{B}$  oriented parallel to the temperature gradient  $\nabla T$ . It was found that in fluids of negative pyromagnetic coefficients  $\beta_m = M^{-1}\partial M/\partial T$  the particles are transferred towards increasing temperatures. If  $\mathbf{B}$  is arbitrarily oriented to the  $\nabla T$  or, more general, to the gradient of magnetic permeability  $\nabla\mu_f$ , particles are transferred along  $\nabla\mu_f$  as well as along  $\mathbf{B}$  [6,7]. In two cases,

$\nabla\mu_f \parallel \mathbf{B}$  and  $\nabla\mu_f \perp \mathbf{B}$ , particles still are moving along  $\nabla\mu_f$  only [5,8]. The magnetic permeability gradient  $\nabla\mu_f$  depends both on temperature and on particle concentration gradients  $\nabla T$  and  $\nabla c$ . Therefore, the particle mass flux may be written in the classical form

$$\mathbf{j}_c = -D\nabla c - D_0 \frac{\alpha_T}{T} \nabla T c. \quad (1)$$

The translation diffusion coefficient  $D$  and the thermal diffusion ratio  $\alpha_T$  consist of the ordinary values of  $D_0$  and of  $\alpha_T^0$  and the corresponding parts of magnetophoretic particle transfer. Both of them depend on the orientation of a magnetic field. Considering spherical particles, in [8] it is found that if  $\mathbf{B} \parallel \nabla\mu_f$ , the magnetic field causes an increase in  $D$  and a decrease in  $\alpha_T$ :

$$D^p = D_0(1 + \frac{1}{5}K_\mu A f_1), \quad \alpha_T^p = \alpha_T^0 + \frac{1}{5}K_\mu A f_1 \beta_m T. \quad (2)$$

On the other hand, if  $\mathbf{B} \perp \nabla\mu_f$ , a reduction of  $D$  and an increase in  $\alpha_T$  takes place,

$$D^t = D_0(1 - \frac{6}{5}K_\mu A f_2), \quad \alpha_T^t = \alpha_T^0 - \frac{6}{5}K_\mu A f_2 \beta_m T. \quad (3)$$

Here  $f_1$  and  $f_2$  are coefficients slightly dependent on parameters  $K_\mu = (\mu_p - \mu_f)/(\mu_p + 2\mu_f)$  and  $K_\lambda = (\lambda_p - \lambda_f)/(\lambda_p + 2\lambda_f)$  which account for a demagnetization factor and for temperature perturbations near the particle. For colloids obeying the Langevin law  $M = \varphi M_p L(\xi)$  with  $\xi = \mu_0 m H / k_B T$  ( $m = M_p V_p$  is the magnetic moment of particle of a volume  $V_p$  and a magnetization  $M_p$ ,  $\varphi = c V_p$ ), the multiplier  $A$  and the coefficient  $K_\mu$  may be written in the form of  $A = \mu_f \varphi \xi L(\xi) / (1 + \varphi(M_p/H)\xi L(\xi))$  and  $K_\mu = (1 - \varphi)M_s L(\xi) / (3H + (1 + 2\varphi)M_p L(\xi))$ .

Fig. 1 presents the theoretical curves  $D = D(\xi)$  and  $\alpha_T = \alpha_T(\xi)$  plotted in accordance with Eqs. (2) and (3) for tetradecane based ferrocolloids containing monodisperse  $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  particles. The curves  $D = D(\mathbf{B})$  calculated in a single particle approximation  $\varphi \ll 1$  [8] agree well with the theory [9] based on a Batchelor model accounting for particle hydrodynamic and magnetic interactions as well with the experimental results [10] obtained from measurements of particle grating dynamics in

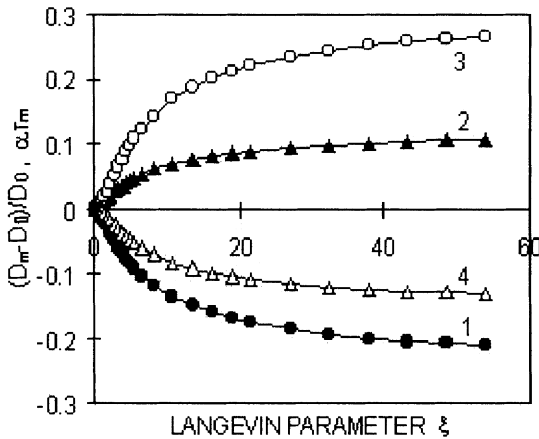


Fig. 1. Transport properties of  $Mn_{0.5}Zn_{0.5}Fe_2O_4$  particles in tetradecane,  $d = 6$  nm,  $\varphi = 0.024$ . 1 -  $\alpha_{Tm}$ ,  $B \parallel \nabla T$ , 2 -  $\alpha_{Tm}$ ,  $B \perp \nabla T$ , 3 -  $D_m$ ,  $B \parallel \nabla T$ , 4 -  $D_m$ ,  $B \perp \nabla T$ .

forced Rayleigh scattering experiment. It is interesting to note, that, contrary to the thermodynamic approach [10] assuming that the reduction of  $D$  in the presence of a transversal field  $B \perp \nabla c$  is a result of particle magnetic interactions, the theories [8,9] explain this effect by a more general action of magnetic driving force regardless of the magnetic interactions like it takes place when  $B \parallel \nabla c$ .

### 3. Unsteady separation of particles in thermal diffusion column

It is not easy to perform direct measurements of Soret effect in colloids employing the conventional optical methods. Holographic interferometry which has been successfully used to examine HGMS processes in colloids under isothermal conditions [5,11], cannot be employed to measure the mass transfer if temperature gradients are present. More preferable seem to be indirect measurements using, for example, thermal diffusion columns. The advantage of such technique is the possibility to measure the magnetic particle separation dynamics permanently during the separation process [1].

The thermal diffusion column consists of a vertical flat channel (a small gap  $\delta$  between two plates of different temperatures  $T_0$  and  $T_\delta$ ) of a length  $L \gg \delta$

and two separation chambers of equivalent volumes  $V_c$ . Thermodiffusive motion of particles is directed along temperature gradient  $\Delta T / \delta (\Delta T = T_\delta - T_0)$  across the channel. Free convection causes a particles transfer in a vertical direction and a formation of concentration difference in chambers  $\Delta c = f(t)$ . In the initial stage of separation until  $\Delta c \ll c_0$ , the particle concentration changes in chambers do not influence the vertical particle flux and the measurements may be analyzed employing a relation

$$\frac{\Delta c}{c_0} = -\frac{2S_\delta}{\delta V_c} \int_0^t \int_0^\delta u(x) \left( \frac{c(x)}{c_0} - 1 \right) dx dt, \tag{4}$$

where  $u(x)$  denotes the convection velocity distribution across the channel and  $S_\delta$  the cross sectional area of the channel. Thermal convection in column is strongly effected by a concentration buoyancy force (so-called ‘forgotten’ effect [12]). Taking into account for the unsteady horizontal concentration profile  $c = c(x)$  in a boundary layer near channel walls, for low separation parameters being equal to [5]

$$\frac{c}{c_0} = 1 + \frac{2k\sqrt{\tau}}{\sqrt{\pi}} [\exp(-\zeta^2) - \sqrt{\pi}\zeta \operatorname{erfc}(\zeta)],$$

$$\zeta = \frac{x}{2\sqrt{Dt}}, \tag{5}$$

from Eqs. (4) and (5) it follows

$$\frac{\Delta c}{c_0} = \frac{8}{45\sqrt{\pi}} kGr_T Sc \frac{\delta}{L_c} \tau^{2.5} \times \left[ 1 - \frac{15\sqrt{\pi}}{8} \tau^{0.5} + \frac{24}{7} \tau + S \left( \frac{12}{7} \tau - \frac{15\sqrt{\pi}}{8} \tau^{1.5} \right) \right]. \tag{6}$$

Here  $Gr_T = \beta_T \Delta T g \delta^3 / \nu^2$  and  $Gr_c = \beta_c c_0 g \delta^3 / \nu^2$  are the thermal and the concentration Grashoff numbers,  $Sc = \nu / D$  is the Schmidt number,  $\nu$  is the fluid kinematic viscosity,  $k = \alpha_T \Delta T / T$  is the thermal diffusion parameter,  $\tau = Dt / \delta^2$  is the diffusion Fourier number and  $L_c = V_c / S_\delta$  is the effective length of the separation chambers. From Eq. (6) we can see that

in the initial stage at  $\tau \ll 1$  even at high values of parameter  $S = kGr_c/Gr_T$  the effect of a concentration buoyancy force on particle separation is small and the separation curves follow to a simple law  $\Delta c \sim t^{5/2}$ . The results of computer simulation of the nonstationary particle separation problem [13] allow us to conclude (see Fig. 2) that for  $S = 0$  the approximation (6) is valid till  $\tau < \tau_1 \approx 0.025$  before the concentration boundary layers on both walls reach the center of channel. The ‘forgotten’ effect ( $S \neq 0$ ) may significantly affect the convection and the separation dynamics. For negative  $\alpha_T$  even a change of the direction of convection in the column is expected [1,2].

At durable separation, starting a certain transition time  $\tau_2 \approx 65(Gr_T Sc \delta / L_c)^{-1}$  [14], the concentration difference in both column chambers starts to saturate. In this regime a time interval exists in which the curve  $\Delta c = f(\tau)$  may be approximated by a square-root function [15]

$$\frac{\Delta \varphi}{\varphi_0} = \gamma \frac{L}{L_c} k \sqrt{\tau}. \tag{7}$$

The coefficient  $\gamma$  slightly depends on the ratio  $L/L_c$ . For devices of approximately equal volumes of the active column  $V$  and of the upper and lower containers  $V_c$ , a value  $\gamma \approx 0.619$  is found [1].

#### 4. Thermophoretic mobility of particles in hydrocarbon based colloids

Relationships (6) and (7) are used to evaluate Soret coefficient of particles from the unsteady separation curves. In our experiments we use a column with a vertical flat channel of width  $\delta = 0.52$  mm and of height  $L = 86.5$  mm. Particle concentration is determined from a resonance frequency of LC oscillators inductance coils of which are mounted inside the both separation chambers [1]. Experiments are performed employing tetradecane based ferrofluids of a chemically coprecipitated magnetite (the mean magnetic moment of particles determined by magnetogrulometry technique [16] is  $m = 1.4 \times 10^{-19}$  Am<sup>2</sup>) [2] and Mn-Zn ferrite ( $m = 2.22 \times 10^{-19}$  Am<sup>2</sup>) [14]. The colloids are stabilized using oleic acid as a surfactant.

Fig. 3 presents the dynamics of separation of lyophilized magnetite particles [17] in a colloid of relatively low particle concentration ( $\varphi = 0.0055$ ,  $\Delta T = 10^\circ\text{C}$ ). We can see that experimental results confirm both the dependence  $\Delta c/c_0 \sim t^{5/2}$  (initial regime,  $t < 800$  s) and the empirical relation (7) (starting approximately  $t = 2000$  s). In a nondimensional form both these transition times agree well with  $\tau_1$  and  $\tau_2$  given above.

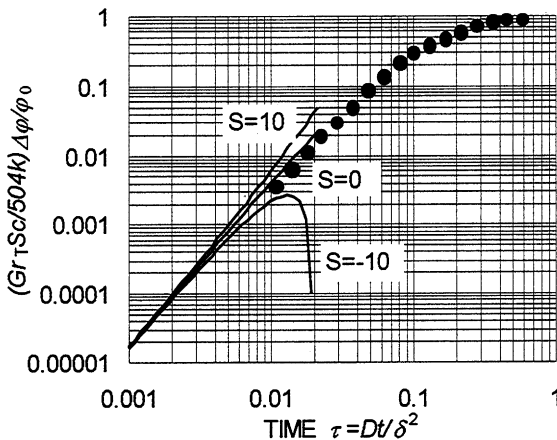


Fig. 2. Dynamics of particle separation in vertical column,  $Gr_T = 3$ ,  $Sc = 10^5$ ,  $L/\delta = 160$ ,  $L/L_c = 1.2$ . Solid curves— Eq. (6),  $S = 0$ ,  $+10$  and  $-10$ . Dots represent results of computer simulation,  $S = 0$  [13].

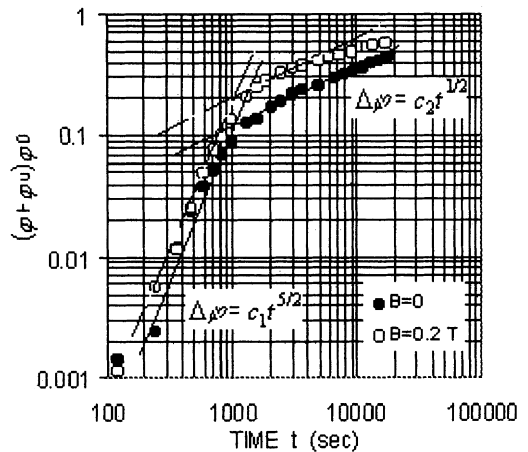


Fig. 3. Particle separation curves ( $\text{Fe}_3\text{O}_4$  in tetradecane,  $\varphi = 0.0055$ ,  $\Delta T = 10^\circ\text{C}$ ),  $B = 0$  and  $B = 0.2$  T ( $B \perp VT$ ).

Analyzing the particle separation curves of various series of experiments we have come to a conclusion that surfacted nanoparticles in hydrocarbons like the micron sized particles in suspensions [18] are moving towards decreasing temperatures. Such direction of thermophoresis agrees with the Derjugin's theory accounting for a slip velocity [19]. The values  $\alpha_T^0 \approx +25$  (magnetite) [2] and  $\alpha_T^0 \approx +20$  (Mn-Zn ferrite) [14] qualitatively well agree with the results obtained from diffraction signals of an optically induced particle grating in thin layers [3]. The coefficients of relations (6) and (7), necessary to calculate  $\alpha_T$ , are detected experimentally except the diffusion coefficient which is evaluated using the Stokes approximation  $D = kT/(3\pi\eta d)$  for monodisperse colloids employing the mean 'magnetic' diameter of particles and assuming that thickness of the surfactant layer around the particle is equal to 2 nm. The particle concentration of examined samples is relatively low, therefore, the Batchelor's correction of  $D$ , obviously, may be neglected. On the other hand, the parameter of magnetic interaction  $\gamma = \mu_0 nm^2/(3k_B T d^3)$  for all samples reaches the value  $\gamma \approx 4$  and, according to theoretical predictions [9], a remarkable reduction of  $D$  may take place. Therefore, the  $\alpha_T^0$  values calculated from separation curves should be considered being approximate only.

### 5. Magnetic Soret coefficient of $\text{Fe}_3\text{O}_4$ and $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ nanoparticles

External magnetic field oriented horizontally along the isothermal walls of the channel ( $\mathbf{B} \perp \nabla T$ ) causes an increase in the separation intensity of surfacted particles (see Fig. 3) whereas in the presence of  $\mathbf{B}$  oriented transversally to these walls ( $\mathbf{B} \parallel \nabla T$ ) a remarkable reduction of vertical particle flux is observed. Fig. 4 represents the thermophoretic mobility of  $\text{Fe}_3\text{O}_4$  and  $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  nanoparticles under the effect of a uniform field  $\mathbf{B} \perp \nabla T$  [14,17,20] and  $\mathbf{B} \parallel \nabla T$  [14]. The dots represent average values of results calculated using the expressions (6) and (7) and assuming that only the particle thermal diffusion is affected by a magnetic field. Both effects, the in-

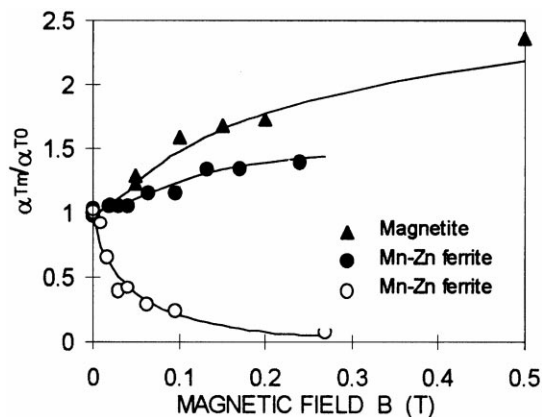


Fig. 4. Magnetic Soret effect in tetradecane based colloids stabilized by oleic acid,  $\mathbf{B} \perp \nabla T$  (black points),  $\mathbf{B} \parallel \nabla T$  (white points) plotted according to results [14,20].

crease in  $\alpha_T$  in the presence of a transversal field  $\mathbf{B} \perp \nabla T$  and the approximately two times stronger reduction of  $\alpha_T$  if  $\mathbf{B} \parallel \nabla T$ , agree well with the hydrodynamic theory [8]. Nevertheless, the magnetic effects presented in Fig. 4 are stronger than the theoretically predicted ones (compare with Fig. 1, the curves there correspond to parameters of a fluid used in the experiment [14]). Obviously, if thermodiffusive transfer of nanometer scaled particles is analyzed, the hydrodynamic theory must be specified taking into account for slip a velocity and a temperature jump on the particle solid-liquid interface.

Magnetic field may influence also the fluid viscosity and the particle diffusivity. We expect that the effect of a fluid magnetoviscosity on the particle separation dynamics in column is insignificantly small because the measurements are performed using colloids of a relatively low particle concentration. The second effect is more important. The predicted increase in  $D$  at  $\mathbf{B} \parallel \nabla T$  (about 25% in the saturation regime of strong fields, see Fig. 1) and reduction of  $D$  at  $\mathbf{B} \perp \nabla T$  (about 12%) may influence the separation dynamics. Nevertheless, if such effect in our experiments really takes place, the corresponding analysis of separation curves by using the corrected coefficients in Eqs. (6) and (7) would give the thermomagneto-thermophoretic effect even stronger than that presented in the Fig. 4.

## 6. Conclusions

Experiments on particle separation in thermal diffusion columns indicate a high thermophoretic mobility of magnetic nanoparticles in ferrofluids. The direction of particle motion in surfacted colloids (positive Soret coefficients) agrees with predictions of thermodynamic theory which accounts for the slip velocity of lyophilic solid–liquid boundaries. The Soret coefficient of ferroparticles is strongly affected by an external uniform magnetic field. Experimental results agree qualitatively well with the hydrodynamic theory considering the nonpotentiality of magnetic forces acting on particles in nonisothermal and nonhomogeneous ferrocolloids.

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