

EXPERIMENTAL INVESTIGATION OF MAGNETIC NANOPARTICLE TRANSFER WITHIN A POROUS MEDIUM AND UNDER INFLUENCE OF A MAGNETIC FIELD

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Abstract: Diffusive and thermodiffusive transfer of magnetic nanoparticles within a porous medium is investigated in series of experiments. While observed changes in mass transfer coefficient that are associated with the medium itself are evidently significant, emphasis has been put on effects of magnetic field. Dependence of transfer coefficients on magnetic field has been investigated for a range of ferrofluids and compared with theoretical predictions, to find good correspondence.

1. Introduction

Diffusion and thermodiffusion processes of ferrofluids were investigated with the aim of understanding mass transfer coefficient changes within a porous environment and under the influence of a magnetic field. Ferrofluid is a stable colloid with solid phase made of single domain magnetic nanoparticles; liquid phase of the ferrofluid is not magnetic and is referred to as carrier fluid. As is the case of colloids in general, the thermodiffusion coefficients exceed those seen in molecular liquids by several orders of magnitude, making thermodiffusion an effect of interest. Furthermore, depending on the coating method used to prevent particle agglomeration, thermodiffusive mass transfer in ferrofluids can be directed to either hotter or colder temperatures.

Performing the experiments in a porous environment gives the advantage of suppressing convective motion at temperature gradients high enough to be of interest in thermodiffusion research. An obvious drawback of such setup, however, is the effects that the porous environment itself has upon mass transfer. Experimental results described in this article include measurements of both diffusion and thermodiffusion coefficients of the two kinds of ferrofluids – surfactant and ionic, in a magnetic field of various intensity values and orientation relative to temperature and concentration gradients. Effects of the porous environment are briefly discussed, while changes in mass transfer coefficients resulting from the magnetic field are compared to theoretical predictions.

2. Influence of magnetic field on ferrofluid mass transfer

Particle mass flow resulting from diffusion and thermodiffusion can be written as

$$\vec{j} = -D\nabla\rho_i - \rho_i(1 - n_i)DS_T\nabla T \quad (1)$$

Here \vec{j} is particle mass flux, ρ_i is particle mass concentration, n_i is mass fraction of particles, D is the diffusion coefficient and $S_T = D_T/D$, where D_T is thermodiffusion coefficient, is the Soret coefficient. The flux is proportional to gradients of particle mass concentration and temperature.

Theoretical model to predict changes in the Soret coefficient in the presence of magnetic field is described in detail in [1]. By introducing a flow associated with magnetic sedimentation and assuming that a uniform magnetic field is aligned with temperature gradient, as is the case in our thermodiffusion experiments, we can write the mass flow equation as

$$\vec{j} = -D\left(1 + \frac{\gamma L^2(\xi)}{1 + \gamma L'(\xi)}\right) \nabla \rho_i - \rho_i(1 - n_i) D S_T \left(1 - \frac{\gamma L^2(\xi)}{1 + \gamma L'(\xi)} \cdot \frac{\alpha_T}{S_T}\right) \nabla T \quad (2)$$

Here $\gamma = \varphi \xi M_S / H$ is a parameter of particle magnetic interaction (φ being volume concentration of particles, $\xi = \mu_0 m H / k_B T$ and M_S is saturation magnetization of particle material, m – magnetization of a single particle), $L(\xi)$ is the Langevin function and $L'(\xi)$ is the derivative of Langevin function, α_T is pyromagnetic coefficient.

Should a stationary state be attained and the mass flux become equal to zero, particle mass distribution would be described by

$$\nabla \rho_i = \rho_i(1 - n_i) S_T \left[\left(1 - \frac{\gamma L^2(\xi)}{1 + \gamma L'(\xi)} \cdot \frac{\alpha_T}{S_T}\right) / \left(1 + \frac{\gamma L^2(\xi)}{1 + \gamma L'(\xi)}\right) \right] \nabla T. \quad (3)$$

Which allows us to introduce the effective magnetic Soret coefficient

$$S_{T,M} = S_T \left[\left(1 - \frac{\gamma L^2(\xi)}{1 + \gamma L'(\xi)} \cdot \frac{\alpha_T}{S_T}\right) / \left(1 + \frac{\gamma L^2(\xi)}{1 + \gamma L'(\xi)}\right) \right]. \quad (4)$$

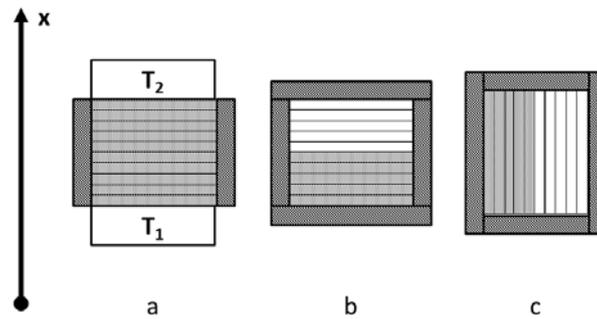
On the other hand, if temperature gradient is zero and magnetic field is aligned along the concentration gradient, the effect of magnetic field on diffusion coefficient can likewise be calculated from equation (2), as

$$D_{Mparallel} = D \left(1 + \frac{\gamma L^2(\xi)}{1 + \gamma L'(\xi)}\right). \quad (5)$$

However, (5) only accounts for particle transfer caused by inhomogeneity of the magnetic field due to particle distribution. Another cause of changes in diffusion coefficient is related to magnetic interaction between the particles[2]. If there is no gradient of magnetization along the magnetic field lines – that is, if the field is normal to the concentration gradient, interaction among particles is the sole mechanism of magnetic field affecting magnetic particle transfer. Then, mass diffusion coefficient in a magnetic field normal to the concentration gradient is

$$D_{Mnormal} = D \left(1 - \frac{\lambda \gamma L^2(\xi)}{1 + \lambda \gamma L'(\xi)}\right). \quad (6)$$

Here λ is a parameter of magnetic interaction called the effective field constant and can be calculated within the effective field model presented in[3].



2. Experimental setup

Figure 1: layouts of porous layers in various experiments

Particle transfer is investigated in a porous environment of a flat cylindrical shape, $l = 1.3$ mm in height and $d_{layer} = 67$ mm in diameter. Porous layer itself is made of ten sheets of filter paper saturated with ferrofluid and pressed together to form a continuous porous environment. Porosity of the layers is $\varepsilon = 0.8$ and pore diameters of size $d_{pore} = 9-20$ μm .

In thermodiffusion experiments, there is no mass flux and no heat exchange at side walls, no mass flux at top and bottom walls and temperatures at top and bottom walls are fixed, with

temperature at top wall being the biggest of two and temperature difference being $\Delta T = 40\text{ K}$ (Fig.1 a). Magnetic field, when applied, is parallel to the temperature gradient. Diffusion experiments are much like the thermodiffusion case, with the defining difference being that only lower five of the ten layers are saturated with ferrofluid, while the other five are saturated with pure carrier fluid. Obviously, there is also no temperature gradient present (Fig.1 b). A variation of the diffusion experiment includes the layers being positioned so that magnetic field is aligned parallel to the layers and perpendicular to the concentration gradient (Fig.1 c).

In all experiments, magnetic particle distribution is attained by splitting the layers apart at the end of each experiment and measuring the particle concentration in each layer by the method of vibrational magnetometry that allows us to learn the distribution of magnetic moments. Particle mass distribution can then be determined, as in single domain particles magnetic moment is proportional to size of the particle.

3. Experimental work

The two major types of ferrofluids are identified by the choice of method of stabilization – either applying a surfactant to form a layer of molecules that covers the particles and prevents them from coming too close together, or forming a double ionic layer around the particles to the same effect. A notion of the type of ferrofluid is added to results in Table 1. There, the default values of Soret coefficient are measured directly with the method of Forced Rayleigh scattering, while diffusion coefficients are either measured in magnetic grating experiments or calculated from the Stokes' formula.

Thermodiffusion experiments are conducted for 24 hours. By this time, the Fourier number $Fo = Dt/l^2$ has reached sufficient values to indicate that a stationary state has formed. Solving the mass flux equation (2) with the necessary boundary conditions yields

$$\frac{\varphi}{\varphi_0} = \frac{S_T \Delta T}{2 \sinh(\frac{S_T \Delta T}{2})} \exp\left[-\frac{S_T \Delta T \cdot x}{l}\right]. \quad (7)$$

Experimental values of effective separation (Soret) coefficient are attained by fitting (7) to experimental data. Examples of data with the respective approximation functions are presented in Figure 2. It should be pointed out that for the ferrofluid sample with $S_T = 0$, an inversion of particle flow direction has been observed.

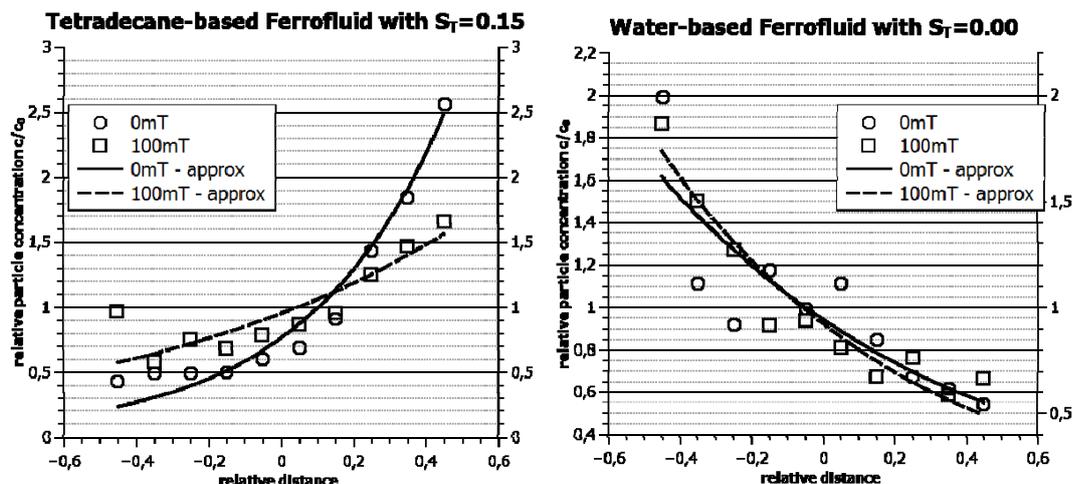


Figure 2: relative distance concentration profiles for surfactanted (df-105) and ionic (FF 13-04) ferrofluid, along with exponential approximation curves. Temperature gradient is directed toward positive distance values.

In diffusion experiments, as no meaningful stationary state exists, measurements are performed after various intervals of time have passed, observing the decay of initial step-like concentration profile. At sufficiently small values of Fourier number, concentration profile is described by[4]

$$\frac{\varphi}{\varphi_0} = \frac{1}{2} \left[\operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) + 1 \right] \frac{\Delta c(t=0)}{c_0}. \quad (8)$$

Equation (8) is relevant to both two and four hour experiments. From $Fo > 0.1$, however, particle distribution is described by

$$\frac{\varphi}{\varphi_0} = \frac{4}{\pi} \exp(-\pi^2 Fo) \sin \left(\frac{\pi x}{l} \right). \quad (9)$$

Data from 2 hour (equation (8) fitted to data points) and 24 hour (equation (9) fitted to data points) diffusion experiments of a surfactant ferrofluid are given in Figure 3.

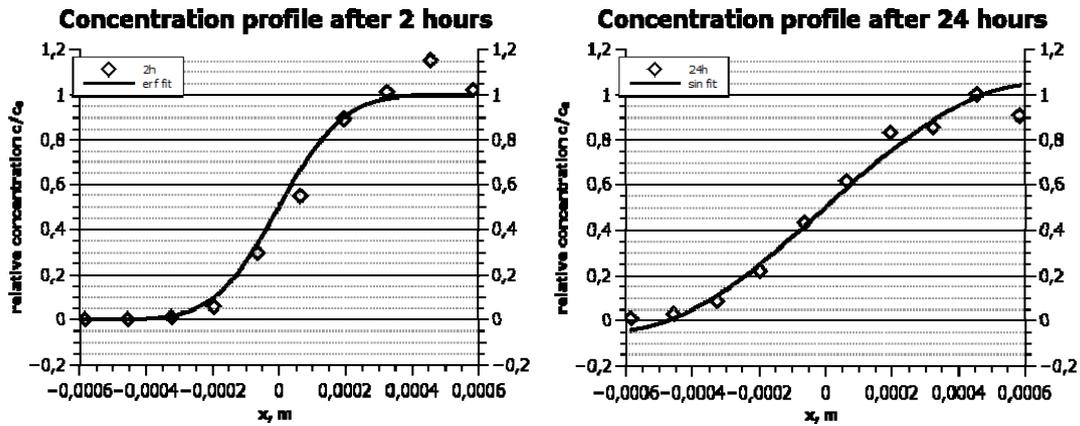


Figure 3: concentration profiles in diffusion experiments with surfactant ferrofluid df-105 after 2 and 24 hours

Results of the initial experiments, without magnetic field, have been summarized in Table 1.

Ferrofluid	$S_T, 1/K$	$S_{T,exp.} (0mT), 1/K$	R^2	$D, m^2/s$	$D_{exp.} (0mT, 2h), m^2/s$	R^2	$D_{exp.} (0mT, 4h), m^2/s$	R^2
df-105 (surfactant)	1.50E-01	4.75E-02	0.99	1.86E-11	1.61E-12	0.98	1.25E-12	0.98
S-1 (surfactant)	2.00E-02	6.21E-02	0.59	2.46E-11				
U5 (surfactant)	1.50E-01	5.64E-03	0.98	3.50E-11				
FF13-04 (ionic)	0.00E+00	-3.00E-02	0.72	1.34E-11	1.36E-11	0.98	3.71E-12	0.44

Table 1: results from experiments without magnetic field. R^2 denotes the coefficient of determination

Two conclusions can immediately be drawn from these results. The first is that both Diffusion and thermoseparation (Soret) coefficients in the porous environment are significantly lower than in free fluid. One of the possible causes is being related purely to the geometry of the porous layer, namely to tortuosity that should decrease diffusion coefficient (though a decrease by an order of magnitude seems unlikely)[5], but not effective Soret coefficient, and the other to gradients of chemical potential near pore walls that could cause slip velocity directed towards higher temperatures to arise[6]; it is assumed that neither is affected by magnetic field, therefore only relative values to coefficients in the porous environment, and not free fluid, are used in result analysis. The other conclusion is that values of diffusion

coefficient do not seem entirely reliable. This is associated with possible non-diffusive mass transfer occurring at very early stages of the experiment and diminishes quickly. Only 24 hour diffusion experiments are analyzed further.

6. Results

Values of relative Soret coefficient in magnetic field of $B = 100 \text{ mT}$ are summarized in Table 2. All values are relative to the experimental value of S_T at $B = 0 \text{ mT}$. Theoretical values are calculated from (4).

ferrofluid	$S_{T, \text{experimental}}(100\text{mT})/S_T(0\text{mT})$	$S_{T, \text{theoretical}}(100 \text{ mT})/S_T(0\text{mT})$
df105	0.480	0.482
U-5	0.560	0.618
S1	0.035	0.034
FF1304	-0.739	-0.323

Table 2: comparison of experimental and theoretical values of relative S_T

Relative values of the diffusion coefficient are given in Table 3. As before, all values are relative to experimental value at zero magnetic field. Theoretical values in parallel and normal fields are calculated by (5) and (6), respectively.

field orientation	$D_{\text{experimental}}(100\text{mT})/D(0\text{mT})$	$D_{\text{theoretical}}(100 \text{ mT})/D(0\text{mT})$
parallel	1.35	2.03
normal	0.92	0.81

Table 3: comparison of experimental and theoretical values of relative D

7. Conclusions

While it is undeniable that diffusive mass transfer of colloidal particles in a porous medium is significantly affected by the porous medium itself through mechanisms not fully understood, measurements of mass transfer coefficients undergoing changes when a ferrofluid is subjected to a magnetic field give results well comparable with theoretical values. Theoretical model presented in [1] gives reasonably accurate predictions of dependence of mass diffusion and Soret coefficients in a magnetic field.

8. References

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