Experimental, numerical, and theoretical investigation on the concentration-dependent Soret effect in magnetic fluids

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Applying a temperature gradient to a layer of a binary fluid establishes a diffusive transport mechanism called thermophoresis or Soret effect which separates the two fluid’s components and is measured by the Soret coefficient. Recent investigations carried out on concentrated magnetic fluids showed that the intensity of the Soret effect depends on the concentration of the nanoparticles transported. The present article, therefore, deals with the concentration-dependence of the Soret coefficient using five equally composed magnetic fluids only varying in the concentration of the particles from 2 vol. % to 10 vol. % of magnetic material. The current investigations point out that the determination of the Soret coefficient and especially its dependence on the particles’ concentration is based on the determination of the thermal and particle diffusion coefficient. The article, therefore, presents a theoretical approach for the determination of the thermal diffusion coefficient and adapts a commonly used Ansatz for the particle diffusion coefficient for the present case of concentrated magnetic fluids. It is thereby possible to determine a theoretical Soret coefficient in dependence on an empirical parameter $\alpha$. The coefficient is compared with the experimental approaches which have been previously used, these will be referred to as “analytical approach” throughout the text. A second comparison is achieved with a hybrid Soret coefficient which fits the experimentally detected separation curves numerically. Within the investigations, the hydrodynamic concentration of the particles is used, assuming a surfactant layer’s thickness of 2 nm per magnetic particle which leads to concentrations between approximately 11 vol. % and 47 vol. %. The diffusion coefficient ranges from $0.6 \times 10^{-11}$ m$^2$/s to $2.5 \times 10^{-11}$ m$^2$/s depending on the analytical model used. The theoretical Soret coefficient decreases with increasing particles’ concentration; the experimental values derived from the analytical approach decrease from 0.06 K$^{-1}$ to 0.01 K$^{-1}$ for increasing particles’ concentration. The numerically determined coefficient ranges from 0.11 K$^{-1}$ to 0.022 K$^{-1}$. The experimental values are smaller than former experimental results suggest (0.16 K$^{-1}$), which is due to the fact that in former works, only magnetic concentrations had been considered. All three current investigations prove what could also be partly seen in former experiments that the higher the particles’ concentration the weaker is thermophoresis. The particle diffusion coefficient has to be known for the determination of the Soret coefficient. It is carried out a proof of principle in the article showing that the horizontal thermophoresis cell can also be used to determine the rehomogenisation process which takes place after separating the fluid by applying a homogeneous temperature to the fluid. The diffusion coefficients that could be determined experimentally range from $1 \times 10^{-11}$ m$^2$/s to $6 \times 10^{-11}$ m$^2$/s. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4906841]

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I. INTRODUCTION

The Soret effect is known to evoke a separation process in binary liquids by the application of a gradient in temperature over a layer of such a fluid. It is characterised by the so-called Soret coefficient \( S_T = D_T / D \) as quotient of the thermal and molecular diffusion coefficient. The effect is significantly strong in colloidal suspensions and of two orders of magnitude larger than in binary fluid mixtures.\(^1\)\(^-\)\(^5\) Former experimental investigations resulted in coefficients in the range of 0.16 K\(^{-1}\)-0.3 K\(^{-1}\) in magnetic fluids.\(^5\)\(^,\)\(^6\) The coefficient was thereby determined indirectly, by measuring the thermal diffusion coefficient and estimating a diffusion coefficient. Throughout former investigations into thermophoresis in magnetic fluids, the Soret coefficient was established as the leading parameter for characterisation. Within this article, a closer look is taken at the two diffusion coefficients instead.

Magnetic fluids, also called ferrofluids, consist of magnetic nanoparticles with an approximate diameter of 10 nm dispersed in organic or inorganic carrier liquids.\(^7\) A stable colloidal suspension is on the one hand achieved by the size of the particles resulting in a predominant thermal mixing and on the other hand by a surfactant layer leading to a steric stabilisation of the liquid.\(^7\) The magnetic fluids under investigation in this context do not show magnetic-dipole-related particle interaction and structure formation, such as chain formation, can be excluded. Therefore, particles can be regarded as single particles. Thermophoresis in these magnetic fluids drives a particle motion leading to an enrichment of particles close to the colder (hotter) side of the considered layer if the Soret coefficient is positive (negative). The effect is best investigated experimentally if no other motions such as convection can influence the diffusive transport process. This is realised in a horizontal, convection-free, thermodiffusion cell.\(^6\) In such a setup, the layer of fluid is placed horizontally between two fluid reservoirs, and the temperature gradient is applied perpendicular to the layer.\(^5\)\(^,\)\(^6\)\(^,\)\(^8\)\(^,\)\(^9\) The particles’ motion is detected via the two fluid reservoirs forming a part of the interior of the sensor coils. Their inductance is, thereby, sensitive to the amount of magnetic material in the embedded fluid volume.\(^5\)\(^,\)\(^6\)\(^,\)\(^8\)

From the theoretic point of view, the separation process can be described in two ways. First, the phenomenological diffusive particles’ mass flux \( \mathbf{j} \) reads\(^10\)\(^-\)\(^15\)

\[
\mathbf{j} = -\left[D\nabla(c) + D_T c(1 - c)\nabla(T)\right],
\]

with \( D \) and \( D_T \) as diffusive transport coefficients, \( c \) denoting the fluid’s particles’ mass concentration, \( \rho \) the fluid’s density, and \( T \) denoting the temperature. The term \( c \cdot \rho \) equals \( \rho_1 / V \) which is the density of the particles in a unit volume of ferrofluid. The second way to describe thermal diffusion is the thermodynamic Ansatz referring to the particles’ mass density, called ferrofluid-dynamics (FFD)\(^12\)\(^,\)\(^16\) via

\[
\mathbf{j} = -\xi \frac{\partial \mu_c}{\partial \rho_1} \nabla c - \left( \frac{\xi}{\rho} + \frac{\xi}{\rho} \frac{\partial \mu_c}{\partial T} \right) \nabla T.
\]

Beside the temperature \( T \) as flux-driving term, the chemical potential \( \mu \), mass-related by the molar mass \( M \) of each component, is denoted \( \mu_c = \mu / M \) with\(^12\)\(^,\)\(^16\)

\[
\mu_c(\rho_1, \rho_2, T) = \frac{k_B T}{m_1} \ln \frac{\rho_1}{\rho} = \frac{k_B T}{m_2} \ln \left( 1 - \frac{\rho_1}{\rho} \right) + \text{const}
\]

and drives the diffusive mass flux. The general thermodynamic transport coefficients are \( \xi \) and \( \xi_1; \rho_1 = c \cdot \rho \) is the product of the mass concentration and the fluid’s density. Additionally, the mass-related chemical potential contains the Boltzmann constant \( k_B \), and \( m_1 \) is assumed being one nanoparticle’s mass and \( m_2 \) is assumed being the mass of one carrier liquid’s molecule.\(^10\) This Ansatz for the chemical potential used in this theory is based on the assumption of an ideal mixture.\(^10\) Such a mixture is characterised by no interaction between the different components. The time dependent separation process is then generally determined by the divergence of the diffusive
mass flux\textsuperscript{10}

\[ \frac{\partial c}{\partial t} = -\nabla \cdot \vec{j} / \rho. \]  

(4)

The determination of thermal and molecular diffusion coefficient, as features of the intensity of thermophoresis, is done by the comparison of experimental data on the development of the concentration with the theoretical one. Therefore, partial differential Eq. (4) has to be solved regarding the experimental setup of the horizontal thermodiffusion cell. With this setup, the concentration difference of a lower and upper fluid reservoir \((c_{\text{lo}} - c_{\text{up}})/c_0\) normalised by the homogeneous initial concentration is detected as measured signal. Recent experimental and numerical investigations have shown that former analytical approaches to the experimental separation curve via\textsuperscript{5,6}

\[ \frac{c_{\text{lo}} - c_{\text{up}}}{c_0} = 2 l D_t \frac{dT}{dz} t, \]  

(5)

with \(l\) being one fluid reservoir’s height, only hold for highly diluted fluids.\textsuperscript{5} Numerical investigations on thermodynamic diffusion Eq. (2) via an Ansatz of the finite differences method (FDM) enable a hybrid analysis of the experimental separation curve and the determination of the thermal diffusion coefficient even in concentrated magnetic fluids.\textsuperscript{5} Recent investigations pointed out that the application of Eq. (5) for concentrated fluids leads to a significant underestimation of the thermophoretic effect.\textsuperscript{5} By also considering former investigations into collective diffusion effects in colloidal suspensions with charged particles,\textsuperscript{13,17–21} the question about a dependence of the transport coefficients on the concentration in the case of uncharged particle systems, where particles do not show any structure formation, rises and is focused on in this article. Former, mainly, theoretical investigations into colloidal systems\textsuperscript{22–24} focused on the determination of the forces acting on the single particles including specifically all effects present in the vicinity of the particles. Since not all of these effects on the particles’ surfaces can be reliably determined experimentally in magnetic fluids, the present article focuses on the experimental and theoretical determination of the phenomenological diffusion coefficients summing up experimentally inaccessible effects in a general parameter \(\alpha\).

For the determination of the diffusion coefficient as a first step, the Einstein-Stokes-relation\textsuperscript{25}

\[ D_{\text{ES}} = \frac{k_B T}{3\pi \eta_{\text{CL}} (d + 2s)} \]  

(6)

is used, with \(\eta_{\text{CL}}\) being the viscosity of the suspension’s carrier liquid, \(d\) the particles’ average diameter, and \(s\) being the thickness of the stabilising surfactant layer. With this Ansatz, effects of the concentration of the particles on the diffusivity are not taken into account. A second approach is the Batchelor-corrected form\textsuperscript{26}

\[ D_B = \frac{k_B T}{3\pi \eta_{\text{CL}} (d + 2s)} (1 + 1.45 \varphi_h) \]  

(7)

with \(\varphi_h\) denoting the hydrodynamic particles’ volume concentration. The carrier liquid’s viscosity is calculated via\textsuperscript{7}

\[ \eta_{\text{CL}} = \eta \left[ 1 - 2.5 \varphi_h + \varphi_h^2 \frac{2.5 \varphi_c - 1}{\varphi_c^2} \right] \]  

(8)

which is an Ansatz accounting for effects on the viscosity generated by the volume concentration of the suspension’s particles.\textsuperscript{7} The fluid’s viscosity \(\eta\) as well as the concentration \(\varphi_h\) can be determined experimentally. \(\varphi_c\) denotes the critical concentration when the fluid behaves like a solid. Assuming spherical particles, this concentration becomes approximately 74%. The different concepts for the diffusion coefficient will be investigated in this article and compared with a modified theoretical approach as well as a proof of principle for the experimental detection of this coefficient in magnetic fluids, see Sec. IV.

The determination of the thermal diffusion coefficient from the experimental data is done in three different ways: The hybrid FDM-based analysis leads to the absolute magnitude of the coefficient (Sec. V C), which can be compared with the analytically obtained coefficient from Eq. (5)
The third way is a new theoretical description of the concentration-dependence of the two phenomenological diffusion coefficients resulting as well in a value for the Soret coefficient, presented in Sec. III. The explicit aim of the article is the evaluation and comparison of the thermal diffusion coefficient calculated via these methods presented in Sec. V.

Technical applications of magnetic fluids especially depend on the concentration of nanoparticles and are often related to temperature profiles in the fluid under use. The knowledge of the extent of thermally driven transport processes which can affect the fluid’s parameters and stability is an important issue. The present article, therefore, deals with the experimental determination of the separation process in ferrofluids in dependence on the particles’ volume concentration. Former experimental investigations on the concentration-dependence of the Soret coefficient lead to diverging results: while Völker et al.\textsuperscript{27} find a decrease of the intensity of thermophoresis with increasing volume concentration, Lenglet et al.\textsuperscript{28} determined an increase in diffusivity with the increase in number of particles dispersed. The article aims at contributing to this discourse.

II. EXPERIMENTAL SETUP

As already mentioned in the introductory part, the experimental detection of the thermal separation process in magnetic fluids is carried out with a horizontal thermodiffusion cell. The experimental setup has been illustrated in detail in former articles of the authors\textsuperscript{5,8,9} and will be explained only shortly here. The fluid cell, 14 mm high, depicted in Figure 1 contains the magnetic fluid during the separation process. The temperature gradient is applied via two water baths (1), the concentration development is determined via sensor coils (3) wrapped around the upper and lower fluid reservoir (2), each reservoir is about 6.5 mm high. The double-layer grid (4), with $h_g = 1.5$ mm is originally used in the magnetic setup only, since it hinders the onset of thermomagnetic convection.\textsuperscript{6,29} It does not have an impact on the non-magnetic measurement\textsuperscript{5} and this is why it is also used in the presented experiments to guarantee the possibility of a comparison with future magnetic experiments.

In the current context, there are two different experiments carried out: the separation process by applying a temperature gradient to the fluid kept in the experimental cell\textsuperscript{5} and a homogenising process by afterwards applying a constant temperature. The separation undergoes four different steps: (1) empty cell, tempered to a constant temperature of 298 K; (2) empty cell tempered to a constant temperature gradient of approximately 1 K/mm, by applying 291 K at the lower and 305 K at the upper boundary; (3) filling of the cell and adjusting the temperature to 298 K; (4) applying the temperature gradient by 291 K and 305 K at the boundaries. This last step, which describes the separation process itself, is carried out for about 42–72 h. Details about the applicability of this setup and measurement process for thermal diffusion can be found in a former article of the authors.\textsuperscript{5}

FIG. 1. Fluid container of the horizontal thermodiffusion cell: (1) container boundaries, tempered by water baths; (2) upper (lower) fluid reservoir; (3) sensor coils for the detection of the amount of magnetic material in the reservoir; (4) double-layer grid, hindering thermomagnetic convection in a magnetic setup.\textsuperscript{5,6,8,9}
The homogenisation of the thermally separated fluid is then initiated by adjusting the temperature of both water baths back to 298 K. Thermal diffusion, as can be seen in Eqs. (1) and (2), vanishes and the diffusive mass flux, governed by the diffusion coefficient, drives the particles in the opposite direction than the beforehand established concentration gradient. The development of the difference in concentration detected experimentally, as assumed by the authors, is then linked with the diffusion coefficient only and makes it, thereby, experimentally determinable.

The adjustment of the temperature going back to constant 298 K provokes the question if only diffusion is present in the homogenising motion. At the upper cell’s boundary, \( T_{up} = 305 \text{ K} \) is applied during the separation process. With the sudden application of \( T_m = 298 \text{ K} \) at that boundary, a thermally unstable setup appears across the upper reservoir. Figure 2 shows the upper part of the fluid’s container and the change in the upper boundary’s temperature at the start \( t = 0 \text{ s} \) of the homogenisation process. The same phenomenon appears across the lower reservoir where the boundary’s temperature of 291 K is suddenly changed to 298 K at the starting point of the homogenisation. It is necessary to check if convection in this setup can be set on and what time it takes to establish the constant temperature over the cell’s total height. The onset of thermal convection is defined by the critical Rayleigh number \( Ra_c = 1708^{30} \). If the Rayleigh number of the fluid cell is smaller than the critical one, convection does not set in. The Rayleigh number is described by

\[
Ra = \frac{g \rho \beta T \Delta T h^3}{\eta \kappa}
\]  

with \( g \) denoting the gravitational acceleration, \( \beta_T = 7.9 \times 10^{-4} \text{ K}^{-1} \) the thermal expansion coefficient, \( h \) the fluid cell’s height, \( \eta \) the dynamic fluid’s viscosity, \( \kappa = 1.8 \times 10^{-7} \text{ m}^2/\text{s} \) the heat diffusivity, and \( \Delta T \) the temperature difference at the boundaries. Since the fluid parameters as well as the cell’s geometry are the same in the upper and lower container half, the Rayleigh number of the homogenisation process is calculated only over the upper part. The temperature gradient at the start is assumed constant with 1 K/mm leading to an overall temperature difference of 7 K over the upper container half of 7 mm. When the temperature at the upper boundary is switched back to 298 K, it is supposed that the temperature difference across the first millimeter of the container length \( (h = 1 \text{ mm}) \) is approximately 6 K, and at \( h = 2 \text{ mm} \), the difference is still 5 K. This means that the Rayleigh number has to be calculated in dependence of the position in the fluid container. The corresponding values are shown in Figure 3. The viscosity and fluid’s density as well as the concentration values are taken from Sec. IV. The Rayleigh number only exceeds the critical value for the less concentrated fluid so that a convection-free diffusion process cannot be guaranteed for this fluid. Additional to regarding the system’s Rayleigh number, it should be mentioned here that due to the separation process, the concentration of the nanoparticles in the fluid at the point when the homogenisation starts is not homogeneous but with rising number of particles along the container axis from top to bottom. This concentration gradient, leading to a gradient in the fluid’s density, additionally stabilises the fluid and thereby also hinders buoyancy-driven convection.

The second question arising in this context is how long does it actually take until the constant temperature is fully developed in the fluid container. The equation of heat conduction is supposed to
be one-dimensional and is described via
\[ \frac{\partial T}{\partial t} + v_z \frac{\partial T}{\partial z} = \kappa \frac{\partial^2 T}{\partial z^2}. \]  

(10)

Since the development of the temperature in the cell is assumed to be convection-free, the fluid’s velocity \( v_z \) in axial direction of the fluid cylinder vanishes. Solving this partial differential equation assuming the constant temperature gradient \( (T_{up} - T_m)/h \) with \( h = 7 \) mm as initial condition and the constant temperature \( T_m = 298 \) K as boundary conditions, refer to Figure 2, leads to \( T(z,t) = \sum_{n=1}^{\infty} \left\{ e^{-\gamma z^2} \sin(\gamma z) \frac{2}{\gamma h} \left[ -(T_{up} - T_m)(-1)^n \right] \right\} + T_m, \)

(11)

where \( \gamma = n\pi/h \), \( h \) denotes half of the fluid container’s height, and \( T_{up} = 305 \) K. The so-called critical temperature \( T_c \) is the spatial maximum temperature of the profile and it is plotted as normalised temperature difference \( (T_c - T_m)/T_m \) in Figure 4. As the figure shows, it takes about 1 min to reach a temperature deviation of less than 0.3 K over the regarded half of the fluid’s container. Since the sample rate of the experimental setup is 1/60 Hz, it is reasonable to assume a constant temperature at least starting at the second sample data point of the homogenisation.
III. THEORETICAL DESCRIPTION

The starting point for the theoretical description of thermodiffusive characteristics is the dependency of the Soret coefficient from the thermal and molecular diffusion coefficient. These two will be regarded separately and only in the last step, they will result in $S_T = D_T/D$. According to Batchelor, a particle density flux due to molecular diffusion can be described theoretically by

$$\vec{j}_{pd1} = -D_{th} \nabla n$$

(12)

with $D_{th}$ denoting the theoretical diffusion coefficient, and $n = \varphi_h/V_p$, the number of particles, where $V_p$ is the volume of one particle. Analogue to this definition, the particle density flux due to thermal diffusion can be defined by

$$\vec{j}_{pd2} = -D_{T_{th}} \vec{\nabla} T$$

(13)

with $D_{T_{th}}$ denoting the theoretical thermal diffusion coefficient. As long as the two fluxes do not level each other out, they result in an overall diffusive particle flux

$$\vec{j}_{pd} = -D_{th} \vec{n} - D_{T_{th}} \vec{\nabla} T.$$  

(14)

In order to obtain the functional connection between the two phenomenologically used diffusion coefficients from Eq. (1) and the theoretical ones, Eqs. (1) and (14) have to be compared. The particles’ mass density flux defined in Eq. (1) describes the particles’ mass diffusing through a cross-section in time while the particle density flux defined in Eq. (14) describes the number of particles diffusing through a cross-section in time. Therefore, one can write

$$\vec{j} = V_p \rho_p \vec{j}_{pd},$$

(15)

where $V_p$ is one particle’s volume, and $\rho_p$ is an effective particle density accounting as well for the magnetic core $(l)_m$ of the particle as for the surfactant layer $(l)_a$ by

$$\rho_p = \frac{\rho_m V_m + \rho_a V_a}{V_p}.$$ 

(16)

Using Eq. (14) and Eq. (15) leads to

$$\vec{j} = V_p \rho_p \vec{j}_{pd} = -V_p \rho_p \left( D_{th} \vec{n} \frac{\varphi_h}{V_p} + D_{T_{th}} \vec{\nabla} T \right)$$

$$\quad = -\rho \left( D_{th} \vec{\nabla} c + V_p \frac{\rho_p}{\rho} D_{T_{th}} \vec{\nabla} T \right)$$

(17)

with $\varphi_h$ being $c \cdot \rho / \rho_p$. Therefore, the theoretical and phenomenological molecular diffusion coefficients are equal, but for the thermal diffusion coefficients, one can write $c_0(1 - c_0)D_T = V_p \rho_p / \rho D_{T_{th}}$, with $c_0$ denoting the homogeneous initial mass concentration of the magnetic fluid.

A. Theoretical diffusion coefficient

Classical Einstein formula (6) for the diffusion coefficient has been obtained in the approximation of non-interacting particles and can be used as long as the particle concentration $\varphi_h$ does not exceed a small percentage. Batchelor relation Eq. (7) is derived from the well-known pair approximation, taking into account the interaction of two particles and ignoring effects of any third particle. As a rule, this approximation leads to good agreement with experiments when the concentration $\varphi_h$ is lower than 10%-15%.

The particle density flux reads

$$\vec{j}_{pd1} = -D_{th} \nabla n = n \left( \langle \vec{U} \rangle - \langle \vec{u} \rangle \right),$$

(18)

where $\langle \langle \vec{U} \rangle - \langle \vec{u} \rangle \rangle$ denotes the average particle velocity relative to the velocity of a reference system, which is the average velocity of the binary fluid $\langle \vec{u} \rangle$ in one point. Batchelor claims that
the thermodynamic force acting on one particle is driven by the gradient in the particles’ chemical potential \( \mu_p \). It can be described by Ref. 26
\[
\vec{F} = -\frac{1}{1 - \varphi_h} \nabla \mu_p(n, p, T) = -\frac{1}{1 - \varphi_h} \left( \frac{\partial \mu_p}{\partial n} \right)_{p, T = \text{const.}} \vec{n},
\]  
(19)
where \((1 - \varphi_h)^{-1}\) takes into account that the fluid molecules are force-free in the diffusive flux which also leads to constant pressure \( p \) and temperature \( T \) when regarding the chemical potential of the particles. The particles’ average velocity can then be obtained by the equilibrium of the thermodynamic force \( \vec{F} \) and the friction force \( \vec{F}_f = \left\{ \langle \vec{U} \rangle - \langle \vec{u} \rangle \right\} 3\pi \eta_{\text{CL}}(d + 2s) \). An additional mobility factor \( K(\varphi_h) \) is introduced to this equation. It accounts for hydrodynamic effects coming from the motion of a large number of particles suspended in a carrier liquid; the binary fluid in the present case is assumed isotropic. The average particle velocity then reads
\[
\{ \langle \vec{U} \rangle - \langle \vec{u} \rangle \} = \frac{K(\varphi_h)}{3\pi \eta_{\text{CL}}(d + 2s)} \vec{F} = \beta \vec{F},
\]  
(20)
where \( \beta = K(\varphi_h)/(3\pi \eta_{\text{CL}}(d + 2s)) \) denotes the overall particle mobility. In the Batchelor approach,\(^{26}\) the numerator of the fraction usually reads \( K(\varphi) = 1 - 6.55 \varphi_h \). The generalization of this approach to more concentrated systems has been suggested by Buyevich and Ivanov\(^{32}\) by \( K(\varphi) = (1 - \varphi_h)^4 \). The latter relation leads to reasonable agreement with experiments in a wide region of concentration \( \varphi_h \) (see discussion in Buyevich and Ivanov\(^{32}\)) which we will, therefore, use as estimate in the following.

Entering Eq. (20) and Eq. (19) into Eq. (18) leads to the diffusion coefficient
\[
D_{th} = \beta \frac{\varphi_h}{1 - \varphi_h} \frac{\partial \mu_p}{\partial \varphi_h}_{T = \text{const.}} = \beta k_B T \left[ 1 + 2 \varphi_h \frac{4 - \varphi_h}{(1 - \varphi_h)^4} \right]
\]  
(21)
considering the particle’s chemical potential of Buyevich and Ivanov\(^{32}\) as
\[
\mu_p = \text{const} + k_B T \left[ \ln(\varphi_h) - \varphi_h + \varphi_h \frac{8 - 5 \varphi_h}{(1 - \varphi_h)^2} \right].
\]  
(22)

B. Thermal diffusion coefficient

In order to determine the thermal diffusion coefficient \( D_{th} \), we will use the main idea suggested by Einstein\(^{25}\) for the calculation of the coefficient of diffusion of Brownian particles. Let us consider a suspension of particles. We suppose that a uniform temperature gradient \( \nabla T \) is created and kept in the system, and the concentration \( n = \varphi_h/V_p \) of the particles does not depend on the coordinate. Following the Einstein idea, we suppose that an external effective force \( \vec{F} \), which provides the mechanical equilibrium in the system of the particles, acts on each of the particles. The mechanical equilibrium of the force density can be presented as
\[
0 = -n \vec{F} - \nabla p - \alpha k_B n \nabla T,
\]  
(23)
where \( p \) is the osmotic pressure on the particles, \( \alpha k_B T \) is a force density, which acts on a particle due to specific effects near the particle’s surface.\(^{22,24}\) A similar idea is suggested by Piazza\(^{24}\) based on an approach of Derjaguin\(^{25}\) relating collective effects in the thermophoretic transport of the particles to an effective external field derived from the single particle’s thermophoretic slip velocity. The latter, in contrast to the here presented Ansatz, is given explicitly considering the vicinity of a single particle. Unfortunately, the specific microcomposition of particles in magnetic fluids is unknown and experimentally inaccessible so that these effects are summed up in the parameter \( \alpha \).

From the equilibrium state, one can derive the overall diffusive particle flux as
\[
\dot{j}_{pd} = -n \beta \vec{F} - \beta \nabla p - \alpha k_B n \nabla T = -n \beta \vec{F} - \beta \left( \frac{\partial p}{\partial T} + \alpha k_B n \right) \nabla T.
\]  
(24)
Comparing Eq. (24) with Eq. (14), we get

$$D_{T_{th}} = \beta \left( \frac{\partial p}{\partial T} + \alpha k_B n \right).$$  \tag{25}$$

In order to get an explicit relation for $D_{T_{th}}$, one needs to use an appropriate approximation for the osmotic pressure $p$. Here, we will use the well known Carnahan-Starling formula\textsuperscript{33}

$$p = k_B T \frac{\varphi_h}{V_p} \left[ \frac{1 + \varphi_h + \varphi_h^2 - \varphi_h^3}{(1 - \varphi_h)^3} \right],$$  \tag{26}$$

which leads to a good agreement with computer simulations in a wide region of the concentration $\varphi_h$. Substituting Eq. (26) into Eq. (25), we get

$$D_{T_{th}} = \beta k_B \frac{\varphi_h}{V_p} \left[ \frac{1 + \varphi_h + \varphi_h^2 - \varphi_h^3}{(1 - \varphi_h)^3} + \alpha \right].$$  \tag{27}$$

Theoretical determination of the parameter $\alpha$ requires the detailed study of the effects near the particle surface and inside the stabilizing layers, induced by the temperature gradient $\nabla T$. This presents a separate problem, which is beyond our consideration. That is why, here, we will consider $\alpha$ as an empirical parameter, which can be easily estimated by comparing the theoretical and experimental results for very small concentrations $\varphi_h$.

The Soret coefficient is finally determined either from the experimental separation curves analysed by the numerical solution ($S_T = D_T/D$) or based on the theoretical description according to Eq. (17) resulting in

$$S_T = \frac{\rho p}{\rho \ c_0 (1 - c_0)} \frac{D_{T_{th}}}{D_{th}}.$$  \tag{28}$$

For a vanishing concentration of particles in the fluid, the Soret coefficient becomes

$$S_T = \frac{1 + \alpha}{T}.$$  \tag{29}$$

Equation (29) is used to estimate the parameter $\alpha$ from the experimental investigations.

IV. FLUID CHARACTERISATION

For a proper determination of the concentration-dependence of transport coefficients, a set of magnetic fluids had been provided by the Ferrotec Corporation assuring an identical composition of five different fluids varying only in the particles’ volume concentration. The fluids are kerosene-based with magnetite nanoparticles dispersed. The chosen concentrations are 10 vol. % (NF4000A), 8 vol. % (NF4000B), 6 vol. % (NF4000C), 4 vol. % (NF3890D), and 2 vol. % (NF3890E) of magnetic material. In addition to these fluids, a sample of the carrier liquid (NF3890F) was also provided. The fluids named NF4000 have been provided in a later series than the NF3890-fluids. The first paragraph of this section deals with the determination of magnetic and rheological properties also leading to the volume concentration and particle size distribution. The second paragraph presents investigations on the diffusivity of the magnetic fluids.

A. Magnetic and rheological properties

The magnetic properties of a ferrofluid are determined by the magnetisation curve, which describes the change in the strength $M$ of the magnetisation $\vec{M}$ of the fluid by the change in the strength $H$ of the magnetic field $\vec{H}$, where $M$ and $H$ are the absolute values of the corresponding vectorial quantities. The curve is usually approximated by a Langevin function\textsuperscript{7}

$$L(\xi_L) = \coth(\xi_L) - 1/\xi_L$$

via

$$M = M_s L \left( \frac{\mu_0 M_s V_m H}{k_B T} \right).$$  \tag{30}$$
Magnetisation curves of the magnetic fluids presenting magnetisation in dependence on the inner magnetic field and in descending order regarding the magnetic volume concentration $\phi$: NF4000A (■), $\phi = 9.9$ vol. %, $d = 9.1$ nm; NF4000B (●), $\phi = 7.79$ vol. %, $d = 8.9$ nm; NF4000C (×), $\phi = 6.07$ vol. %, $d = 8.8$ nm; NF3890D (▲), $\phi = 4.43$ vol. %, $d = 9.2$ nm; NF3890E (♦), $\phi = 2.24$ vol. %, $d = 9.0$ nm.

with $M_s = \phi M_d$ denoting the saturation magnetisation as product of the magnetic volume concentration $\phi$ and the bulk magnetisation $M_d$ (magnetite: 450 kA/m), $\mu_0$ the magnetic permeability of vacuum, $V_m$ being one particle’s magnetic volume, $k_B$ the Boltzmann constant, and $T$ the temperature. For small magnetic fields, the change in magnetisation is linear with the change in the magnetic field and the slope is described by the initial susceptibility

$$\chi_i = \frac{\pi \phi \mu_0 M_d^2 d^3}{18 k_B T}.$$ (31)

The particles’ average magnetic diameter $d$ can be determined by this, while the particles’ volume concentration is obtained by the saturation magnetisation at high field strengths. Figure 5 shows the magnetisation curves for all five ferrofluids. Since the Langevin-approximated magnetisation curve only gives the opportunity to determine an overall average particle size, the Chantrell-method$^{35}$ is used to calculate a particle size distribution by fitting a lognormal size distribution of $d$ to the measured data. The result is equal for all investigated fluids and an example is shown in Figure 6.

The particles’ volume concentration $\phi_i$ per particle diameter $d_i$ is related to the overall concentration $\phi$. The average magnetic diameter is then determined via $d_m = \sum d_i \phi_i / \phi$ and leads to 5.9 nm.

The rheological property of interest is the dynamic viscosity $\eta$ of the fluids. It is determined by the so-called flow curve $\tau = \eta \dot{\gamma}$ which links the shear stress $\tau$ generated by a cone-plate-rheometer.
FIG. 7. Dynamic viscosity of the magnetic fluids and the carrier liquid measured at 291 K, 298 K, and 305 K: NF4000A (■); NF4000B (●); NF4000C (×); NF3890D (△); NF3890E (○); NF3890F (▼).

with the shear rate $\dot{\gamma}$. The rheometer used is an Anton Paar Physica MCR301. The flow curves are determined at three different temperatures, namely, 291 K, 298 K, and 305 K. As can be seen in Figure 7, the viscosity decreases with rising temperature and decreasing particle concentration. What can also be learned from this figure is that there is a slight difference in the composition of the earlier (NF3890) and the later (NF4000) fluid series when regarding the fluid’s viscosity and most likely also its diffusivity. Since the magnetic part of the ferrofluids is equal, the difference is expected to be evoked by the surfactant used to stabilise the fluid.

As already mentioned in the introductory part, it is necessary to determine the carrier liquid’s viscosity for each magnetic fluid by Eq. (8), taking into account that the volume concentration here must be substituted by the hydrodynamically relevant concentration. Since the magnetic particles are stabilised in the fluid by a layer of surfactant with a thickness $s$ of approximately 2 nm, the hydrodynamic particle volume $(d_m + s)^3\pi/6$ is 4.7 times larger than the magnetic volume $d_m^3\pi/6$. This leads to hydrodynamic concentrations of 46.8 vol. % (NF4000A), 36.8 vol. % (NF4000B), 28.7 vol. % (NF4000C), 20.9 vol. % (NF3890D), and 10.6 vol. % (NF3890E). The carrier liquid’s viscosity calculated by this is 6.0 mPa s (NF4000A), 4.1 mPa s (NF4000B), 3.7 mPa s (NF4000C), 4.8 mPa s (NF3890D), and 3.9 mPa s (NF3890E) at 298 K. These values are larger than the measured one for the NF3890F-carrier liquid which can be drawn back to the excess amount of surfactant possibly dispersed in the ferrofluids. Here, again it becomes clear that the NF3890-series may differ in its amount or type of surfactant.

B. Diffusivity

On the basis of magnetic and rheological fluid properties, three different diffusion coefficients can be calculated and compared. The first one is determined via Eq. (6), not taking into account any concentration-related effects on the diffusivity. The second one is obtained by Eq. (7) considering hydrodynamic effects coming from the fluid’s concentration. The third one is then taken from this article’s theoretical investigations in Eq. (21). The diffusion coefficients are plotted in Figure 8. Comparing the three Ansätze, the absolute diffusion coefficient shows the smallest values for the Einstein-Ansatz (●) and the highest value for the model based on investigations of Buyevich and Ivanov\(^{32}\) (■). The hydrodynamic particle-particle-interaction considered in the last Ansatz results in an enhancement of diffusivity for a fixed concentration.

The change in diffusivity by the particles’ concentration depends on the carrier liquid’s viscosity, which in magnetic fluids is dependent on an unknown amount of excess surfactant. In the present case, applying experimental data, the two series of magnetic fluids have to be regarded independently and as a result diffusivity decreases with increasing concentration. Since the effect of the viscosity on diffusivity enters the definition of the thermal diffusion coefficient according to
Eq. (25) equally, it will not have an influence on the Soret coefficient in Fig. 10 but rises the need for a direct measurement method for the determination of the molecular diffusion coefficient.

In Figure 9, the theoretical thermal diffusion coefficient $D_{Th}$ is plotted according to Eq. (25). The theoretical value for this coefficient can be compared with the phenomenological one derived from Eq. (1) when comparing Eqs. (1) and (17) and assuming that the mass concentration is the homogeneous initial one ($c_0$). The phenomenological coefficient then results in

$$D_T = \frac{\rho_p}{\rho} \frac{V_p}{c_0(1-c_0)} D_{Th}. \tag{32}$$

When regarding Figure 9, the order of magnitude of the differently defined thermal diffusion coefficients strikes first but can be derived from the description in the theoretical definition denoting thermal diffusivity by a thermal diffusion coefficient’s density $\left[ m^2/s K^{-1} m^{-3} \right]$. Else, the diffusivity increases for small hydrodynamic concentrations and decreases for high concentrations.

From the two theoretically determined diffusion coefficients, the Soret coefficient in dependence on the concentration can be estimated which is plotted in Figure 10. The Soret coefficient decreases for increasing hydrodynamic particle concentration and saturates for high concentrations. The coefficient is thereby only dependent on the particle’s, and the fluid’s density and the hydrodynamic particle concentration. The particle density is determined by $\rho_p = \frac{d^3_m}{(d_m + 2s)^3} (\rho_m - \rho_{sl}) + \rho_{sl}$ to approximately 1947 $kg/m^3$ and the fluid’s density by $\rho = \varphi_h \rho_p + (1 - \varphi_h) \rho_{CL}$ ($1496$ $kg/m^3$; $1412$ $kg/m^3$; $1343$ $kg/m^3$; $1277$ $kg/m^3$; $1190$ $kg/m^3$). The carrier liquid’s

![Figure 8](image1)

**FIG. 8.** Diffusion coefficients at 298 K at different hydrodynamic particles’ volume concentrations: $D_{ES}$: Eq. (6) ($\bullet$); $D_B$: Eq. (7) ($\times$); $D_{Th}$: Eq. (21) ($\blacksquare$).

![Figure 9](image2)

**FIG. 9.** Thermal diffusion coefficient at 298 K at different hydrodynamic particles’ volume concentrations: the theoretical coefficient $D_{Th}$ is plotted on the left axis ($\bullet$) and the phenomenological coefficient $D_T$ is plotted on the right axis ($\times$).
FIG. 10. Theoretical Soret coefficient based on the new model for the diffusion and the thermal diffusion coefficient for various $\alpha$. Experimentally determined fluid parameters enter the determination.

($\rho_{CL}$) as well as the surfactant layer’s density ($\rho_{sl}$) is assumed to be 1100 kg/m$^3$; the density of magnetite $\rho_m$ is assumed to be 5100 kg/m$^3$. These values were chosen to match the ferrofluid’s density which can be approximately determined experimentally. The theoretical decrease of the Soret coefficient has already been seen in former experiments on a magnetic fluid with the same range of particle concentration.$^{27}$ Section V will provide the experimental results of the separation experiments and the determination of the thermal diffusion and the Soret coefficient.

V. RESULTS

A. Experimental separation curves

Presenting the results of the separation experiments starts with the experimental separation data in Figure 11. The separation curves shown here are calculated as mean average over three independent separation experiments for each fluid. The fluid with the lowest particle concentration (NF3890E) shows the most intense separation due to thermophoresis. The highest concentrated fluid (NF4000A) shows the weakest separation intensity. Since the experimental determination of the separation is very sensitive to environmental influences, the experiments, as mentioned, have been carried out three times for each fluid. This provides the opportunity to estimate the quality

FIG. 11. Experimental separation curves plotting the relative change in mass concentration ($c = \varphi_h \rho P/\rho$) during the separation experiment in dependence on the process time for five magnetic fluids: NF4000A ($\bullet$); NF4000B ($\blacklozenge$); NF4000C ($\times$); NF3890D ($\triangle$); NF3890E ($\triangledown$).
of reproduction of the measuring process as well as the error of the separation curves plotted in Figure 11 by the experimental span of the curves.

Figure 12 indicates that the measurement with the two older fluids NF3890D and NF3890E with approximately 20 vol. % and 10 vol. % of particles is far less exact than the measurement for the higher concentrated fluids. Figure 13 makes this a bit clearer by only showing the separation curves for the three NF4000-fluids. It cannot be said here if the problem is linked with the different series of the fluids or if it is more a problem of the resolution of the measurement process which is not able of detecting highly diluted fluids with respect to the magnetic volume concentration which is the one providing the measurement signal. This should be taken into account when interpreting the results for the thermophoretic transport.

B. Analytical approach to thermophoretic coefficient

In the first step, the experimentally obtained separation curves are used to determine the thermal diffusion coefficient $D_{Ta}$ via Eq. (5). The length $l$ of one fluid reservoir is approximated with 0.0065 m; the temperature gradient is determined to approximately 900 K/m. Even though a temperature difference of 14 K is applied to the overall cell of a height of 14 mm, and due to the environmental temperature, only about 13 K actually reaches the cell’s boundaries. The time of separation is set to 2500 min for all experiments. Figure 14 depicts the experimentally determined
thermal diffusion coefficient in comparison with the theoretically derived one, $D_{Th}$, from the new model, Eq. (27), as described in Chapter III, and first presented in Figure 9. The empirical parameter $\alpha = 22.8$ is chosen according to the estimate of Eq. (29) and the Soret coefficient depicted in Fig. 15. The change in the thermal diffusion coefficient with the change in concentration is thereby represented very well by the theoretical method. The smaller the number of particles suspended, the higher is thermal diffusivity of the fluid. The error bars of the experimental values are derived from the span of the separation curves as shown in Figures 12 and 13. They point out that the measurement process is especially imprecise for a small number of particles in the magnetic fluid.

The measured thermal diffusion coefficient is then used to calculate the Soret coefficient as $S_{Th} = D_{Th}/D$, which is plotted in Figure 15, also in comparison with the theoretically determined value which had been introduced in Figure 10. The experimental Soret coefficient is determined via the theoretical diffusion coefficient of Eq. (21). The coefficient, as also measured in a former work of Völker et al., decreases for increasing particle concentration which means that the separation process is hindered by the number of particles dispersed in the magnetic fluid. The constant factor $\alpha = 22.8$ in the theoretical Soret coefficient leads to a very good representation of the coefficient especially for high concentrations. The deviation for small concentration might be drawn back to the precision of the measurements of dilute magnetic fluids. The error bars depicted in the figure are taken from the error of the experimentally determined thermal diffusion coefficient and go back to the span of three independent measurements.

![Graph showing comparison of thermal diffusion coefficients and Soret coefficients](image-url)

**FIG. 14.** Comparison of the experimentally determined thermal diffusion coefficient $D_{Ta} = DS_{Ta} (\blacktriangle)$ and the new theoretical model ($\blacksquare$, $D_{Th}$), considering $\alpha = 22.8$.

![Graph showing comparison of Soret coefficients](image-url)

**FIG. 15.** Comparison of the experimentally determined Soret coefficient ($\blacktriangle$, $S_{Ta}$), the one determined by the new theoretical model ($\blacksquare$, $S_{Th}$, $\alpha = 22.8$), and the one determined from the numerical fit of the experimental data ($\bullet$, $S_{Th}$).
When comparing the order of magnitude of the experimental Soret coefficient shown in Figure 15 with the Soret coefficient being said to be about 0.16 K\(^{-1}\) in the introductory part, the one determined within this work is a factor of 3 smaller than the measured one in former works.\(^{3,27}\) The difference in the determination of the two mentioned Soret coefficients can be found in the definition of the concentration, while earlier works relied on the magnetic volume concentration since the surfactant layer thickness as well as the surfactant’s composition is unknown, the new investigations here include the full perspective of hydrodynamic influence on the process as far as assumptions can be made reasonably.

C. Hybrid approach to thermophoretic coefficient

The hybrid approach starts with the numerical determination of the concentration profile of the fluid during the separation process in space and time based on Eq. (2). Due to the profile’s dependence on the thermal diffusion coefficient, the numerical profile is fitted to the experimental one with \(D_{Th}\) being the fit parameter. In contrast to the analytical approach presented in the previous paragraph, the numerical investigations minimise the assumptions made, which in the analytical case lead to governing Eq. (5). These assumptions are mainly based on considering a dilute fluid in the experiments leading to \((1 - c) \approx 1\). The numerical investigation is based on the description of the diffusive mass flux in Eq. (2) assuming the chemical potential being of the form of Eq. (3). The overall partial differential equation (4) describing as well the spatial development of the concentration as the development in time

\[
\frac{\partial c}{\partial t} = -\nabla \cdot \vec{j} = \frac{1}{\rho} \vec{\nabla} \cdot \left[ \rho \nabla c + \left( \xi + \xi_1 \frac{\partial \mu_c}{\partial T} \right) \nabla T \right]
\]

is then solved numerically on the basis of the finite differences method as described in a former work of the authors.\(^5\) The initial condition states that at \(t = 0\), the concentration of the particles equals the homogeneous concentration by \(c(x, y, z) = c_0\). The boundary conditions state that no mass flux \(\vec{j}\) exists normal to the cylindrical cell boundaries. Additionally, the temperature gradient is assumed constant.

Analogue to the experiments, the numerically determined concentration results in a spatial and time-dependent profile over a total cell’s height of 14 mm. To fit these data to the experiments, a numerical separation curve to the experimental one by adjusting this coefficient. The result of this fit is presented in Figure 16, where lines represent the numerical results while symbols depict measured data. For the better comparison of the new with previous experimental results, the Soret coefficient is calculated from the thermal diffusion coefficient using the diffusion coefficient according to Eq. (21). The Soret coefficients derived from the three different methods presented in this article are compared in Table I and depicted in Figure 15. \(S_{Th}\) stands for the analytical approach, \(S_{Th}\) for the
FIG. 16. Plot of the experimental separation curves (symbols, refer also to Figure 12) in comparison with the numerically fitted separation profiles (lines): \( \varphi_h = 47 \text{ vol.\% (■); } \varphi_h = 37 \text{ vol.\% (●); } \varphi_h = 29 \text{ vol.\% (×); } \varphi_h = 21 \text{ vol.\% (△); } \varphi_h = 11 \text{ vol.\% (○).}

theoretical one, and \( S_{Th} \) comes from the hybrid approach. The corresponding Onsager coefficients are also listed in Table I. The hybrid Soret coefficient almost monotonously decreases with the increase in particles’ concentration in conformance with the experimental and the theoretical Soret coefficients. The values’ magnitudes in the hybrid case point out that the linear approximation of the separation curve via Eq. (5) leads to an underestimation of the intensity of the thermal transport process which can be overcome by the hybrid method. The factor of 2 separating analytical and hybrid Soret coefficients can be traced back to the assumption of a dilute fluid made for the analytical case.

D. Remarks on the diffusion coefficient

In the experimental determination of the fluid’s separation, it is actually the thermal diffusion coefficient which is detected. To determine the Soret coefficient, the molecular diffusion coefficient is always a value which is estimated by the experimental detection of various fluid parameters. The difficulty about this is that the absolute value of the Soret coefficient solely depends on how the molecular diffusion coefficient is defined in the first place. Nonetheless, it is not the thermal diffusion coefficient, which would be the recommendable coefficient in this context, but the Soret coefficient which is used to compare thermal diffusivity of different fluids. This is why the authors carry out the proof of principle here whether the diffusion coefficient could be detected as a follow-up experiment to the separation. As mentioned in Sec. II, the experimental setup should be able of processing the convection-free diffusion to homogenise the magnetic fluid under investigation. The resulting homogenisation curves are depicted in Figure 17. Unfortunately, there is only one such curve for each magnetic fluid investigated, therefore there is no possibility to estimate the error of the experiment.

<table>
<thead>
<tr>
<th>( \varphi_h ) (vol.%)</th>
<th>( D ) ((\times 10^{-11} \text{ m}^2/\text{s}))</th>
<th>( S_{Ta} ) ((1/\text{K}))</th>
<th>( S_{Th} ) ((1/\text{K}))</th>
<th>( S_{Th} ) ((1/\text{K}))</th>
<th>( \xi ) ((\text{kg s/m}^2))</th>
<th>( \xi_1 ) ((\text{kg/(ms K)}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>1.559</td>
<td>0.05634</td>
<td>0.04324</td>
<td>0.11</td>
<td>( 1.356 \times 10^{-12} )</td>
<td>( 2.824 \times 10^{-10} )</td>
</tr>
<tr>
<td>21</td>
<td>1.618</td>
<td>0.02294</td>
<td>0.02469</td>
<td>0.033</td>
<td>( 1.248 \times 10^{-12} )</td>
<td>( 1.301 \times 10^{-10} )</td>
</tr>
<tr>
<td>29</td>
<td>2.43</td>
<td>0.01068</td>
<td>0.01651</td>
<td>0.023</td>
<td>( 1.692 \times 10^{-12} )</td>
<td>( 1.479 \times 10^{-10} )</td>
</tr>
<tr>
<td>37</td>
<td>2.41</td>
<td>0.01271</td>
<td>0.01097</td>
<td>0.026</td>
<td>( 1.487 \times 10^{-12} )</td>
<td>( 1.813 \times 10^{-10} )</td>
</tr>
<tr>
<td>47</td>
<td>1.816</td>
<td>0.00824</td>
<td>0.00678</td>
<td>0.022</td>
<td>( 0.944 \times 10^{-12} )</td>
<td>( 1.089 \times 10^{-10} )</td>
</tr>
</tbody>
</table>
FIG. 17. Change in the normalised concentration difference for the five differently concentrated magnetic fluids: 47 vol. % (■); 37 vol. % (●); 29 vol. % (×); 21 vol. % (△); 11 vol. % (★). The change is set to zero at the starting point.

When determining the diffusion coefficient from the experimental slopes of the homogenisation curves, it is first of all assumed that diffusion is driven by Eq. (4). It is supposed that

\[ \vec{n} \cdot \vec{j} = \frac{\vec{n} \cdot \vec{j}}{l} = \frac{\vec{n} \cdot \vec{j}}{l} \left( -pD \nabla c \right) \]  

is valid, where \( \vec{n} \) is the direction of the mass flux, as similarly used to calculate Eq. (5), and as presented in a former work of the authors.\(^5\)

The concentration gradient is assumed to be \( 2(c_{\text{up}} - c_{\text{lo}})/h_z \), as depicted in Fig. 18. Additionally, assuming that the separation process led to a symmetric concentration profile with reference to the middle cross-section of the cell leads to \( c_{\text{lo}} + c_{\text{up}} = 2c_0 \) with \( c_0 \) being the initial homogeneous mass concentration, refer to Fig. 18.

Entering these assumptions and Eq. (36) into Eq. (4) results in one differential equation for each fluid reservoir

\[ \frac{dc_{\text{up}}}{dt} = \frac{2D}{lh_z/2} (c_0 - c_{\text{up}}), \]  \( 37 \)

\[ \frac{dc_{\text{lo}}}{dt} = \frac{2D}{lh_z/2} (c_{\text{lo}} - c_0). \]  \( 38 \)

FIG. 18. Fluid container at constant temperature after separating the fluid, \( c_{\text{lo}} (c_{\text{up}}) \) is the average concentration in lower (upper) half of the container, positioned at a distance of half the container height \( h_z \).
Solving these equation with the initial conditions $c_{\text{up}}(t = 0) = \tilde{C}_{\text{up}}(t = 0)$, calculating the difference of the two concentration profiles, and again taking a symmetric separation into account ($-\tilde{C}_{\text{up}} = \tilde{C}_{\text{lo}}$) result in

$$\frac{c_{\text{lo}} - c_{\text{up}}}{c_0} = \frac{-2C_{\text{up}}}{c_0} \exp \left( \frac{-4D_{\text{lh}}z}{l} t \right).$$

(39)

For the experimental determination of the diffusion coefficient, a linear approximation of this equation will be used, which is reasonable when considering the experimental curves in Figure 17,

$$\frac{c_{\text{lo}} - c_{\text{up}}}{c_0} = \frac{-2C_{\text{up}}}{c_0} \left( 1 - \frac{4D_{\text{lh}}z}{l} t \right).$$

(40)

The parameter $\tilde{C}_{\text{up}}$ is determined by the final concentration difference of the separation experiment after 2500 min of time, refer to Figure 12, which is also the starting concentration difference $(c_{\text{lo}} - c_{\text{up}})/c_0$ in the homogenisation process, please see Table II for details. To determine now the diffusion coefficient from Eq. (40), the normalised concentration difference after 2500 min of homogenisation is calculated as

$$\left. \frac{c_{\text{lo}} - c_{\text{up}}}{c_0} \right|_{t=2500 \text{ min}} = \left( 1 + \frac{m_{\text{re}}}{m_{\text{sep}}} \right) \left. \frac{c_{\text{lo}} - c_{\text{up}}}{c_0} \right|_{t=0 \text{ min}},$$

(41)

with $m_{\text{re}(sep)}$ denoting the slope of the experimental homogenisation (separation) curve, see Table II and Fig. 17, which in the present case works since separation and homogenisation time are equally 2500 min. Entering the result of Eq. (41), including the time and geometric parameters, in Eq. (40) and solving it for $D$ the diffusion coefficient, finally leads to Figure 19. Comparing the experimentally determined diffusion coefficients with the theoretical ones, it can be concluded that the experimental coefficients, although being quite scattered, meet the order of magnitude of the

![FIG. 19. Diffusion coefficient in dependence of the hydrodynamic particle concentration according to the theoretical investigations resulting in Eq. (21) (■), and the experimentally determined one (×) obtained by the homogenisation process.](image-url)
theoretical ones fairly well. A reliable dependence of the coefficient on the fluid’s concentration cannot be obtained by the experiments so far since the experimental precision cannot be displayed here due to the lack in number of experimental runs but is expected being rather large. Nonetheless, the diffusion coefficient, as proven here, can be detected experimentally.

VI. DISCUSSION

The present article aims at investigating the dependence of the Soret coefficient on the particles’ concentration of magnetic fluids in three different ways. A new theoretical approach based on thermodynamic principles for the thermal diffusion coefficient complementing an adapted commonly known theoretical approach for the diffusion coefficient leads to a theoretical Soret coefficient. An empirical parameter \( \alpha \), introduced accounting for forces on the particles’ surfaces, was determined by comparison with experimental data. The decrease of the Soret coefficient by the increase in particles’ concentration could already be found in an earlier work.\(^{27}\) By determining the thermal diffusion coefficient experimentally, the analytical Ansatz of former investigations\(^{9}\) represented by Eq. (5) had been used and led to a Soret coefficient spanning from 0.06 K\(^{-1}\) to 0.01 K\(^{-1}\) with a monotonous decrease of the coefficient with rising particles’ concentration. The hybrid approach fitting the numerically obtained concentration profile in space and time to the experimental separation curves resulted in Soret coefficients between 0.11 K\(^{-1}\) and 0.022 K\(^{-1}\) in dependence on rising particles’ concentration. As already known from a former work of the authors,\(^{5}\) the analytical approach according to Eq. (5) underestimates the intensity of thermophoresis especially for high particles’ concentrations in comparison with the hybrid approach. The ferrofluidynamics, as base of the hybrid approach, is by now the state of knowledge for a full macroscopic description of magnetic fluids, although leaving some crucial questions still open. The theory might be improved by editing the Ansatz for the molar-mass-normalised chemical potential. In a future step, the suggestion of Buyevich\(^{32}\) for the particles’ chemical potential should be considered and separately compared with the current results to evaluate the influence of this change. This possible weakness of the approach is not focused on in this work, the ferrofluidynamics is rather used for comparison as best approach for the evaluation of experimental data.

Since the determination of the Soret coefficient, even the theoretical one, depends on the experimental determination of several fluid’s parameters, the gap in the magnitude between the theoretical and experimental values can be drawn back to effects of the fluid that cannot be properly represented by the separately detected fluid’s parameters. This aspect is best emphasised, by regarding Fig. 8 where the Einstein diffusion coefficient shows a dependence on the particles’ concentration, which is due to the measured viscosity of the fluids leading to a concentration-dependent viscosity of the carrier liquid. Nonetheless, the advantage that the experimental Soret coefficient gains over the theoretical one is the actual detection of the separation curve which already includes effects on the thermal diffusion probably coming from surface effects of the particles in the concentrated fluids that are not properly considered in the theoretical approach. To reduce the uncertainty of these effects, it is reasonable to determine both diffusion coefficients by experimental means. Therefore after separation, and detection of the thermal diffusion coefficient, the fluid in the horizontal thermal diffusion cell is exposed to a homogeneous temperature leading to a rehomogenisation of the magnetic fluid from which the diffusion coefficient can be calculated. So far the preliminary results of this diffusion coefficient lead to values from \( 1 \times 10^{-11} \) m\(^2\)/s to \( 6 \times 10^{-11} \) m\(^2\)/s which is in the range of the analytical values but the experimental procedure as well as the analysing of the measured data has to be investigated in more detail to also evaluate the experimental accuracy of the process. A better knowledge of the dependence of the diffusion coefficient on the fluid’s concentration can probably lead to a better understanding of thermophoresis as well. By now, it is important to compare and critically evaluate different concepts on the determination of thermophoretic motion in magnetic fluids to actively contribute to the open questions in this context.
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