Nonequilibrium dynamics and magnetoviscosity of moderately concentrated magnetic liquids: A dynamic mean–field study

Patrick Ilg and Siegfried Hess

Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstr. 36, D-10623 Berlin, Germany

(Dated: January 17, 2022)

A mean–field Fokker–Planck equation approach to the dynamics of ferrofluids in the presence of a magnetic field and velocity gradients is proposed that incorporates magnetic dipole–dipole interactions of the colloidal particles. The model allows to study the combined effect of a magnetic field and dipolar interactions on the viscosity of the ferrofluid. It is found that dipolar interactions lead to additional non–Newtonian contributions to the stress tensor, which modify the behavior of the non–interacting system. The predictions of the present model are in qualitative agreement with experimental results, such as presence of normal stress differences, enhancement and different anisotropy of magnetoviscous effect and the dependence of the viscosity on the hydrodynamic volume fraction. A quantitative comparison of the concentration dependence of the magnetoviscosity shows good agreement with experimental results for low concentrations.

PACS numbers: 47.65.+a Magnetohydrodynamics and electrohydrodynamics; 75.50.Mm Magnetic liquids; 47.32.-y Rotational flow and vorticity; 83.80.Hj Suspensions, dispersions, pastes, slurries, colloids; 05.20.Dd Kinetic theory

I. INTRODUCTION

The so–called magnetoviscous effect in ferrofluids – the dependence of the rheological behavior of colloidal suspensions of nano–sized ferromagnetic particles in a carrier liquid on external magnetic fields – has attracted quite some attention in the recent literature, both from a scientific and an application point of view. In dilute ferrofluids, the magnetoviscous effect is successfully explained by the hindrance of rotation of individual, non–interacting magnetic dipoles. Experiments on commercial ferrofluids have revealed quantitative and qualitative different behavior compared to the dilute regime, such as an order of magnitude increase of the magnetoviscous effect, a dependence not only on the local vorticity but also on the local strain rate of the flow, shear thinning behavior and the occurrence of normal stresses. The failure of the kinetic model to describe these phenomena is generally attributed to the neglect of magnetic dipolar interactions of the colloidal particles. Since dipolar interactions are long–ranged, they become important at concentrations as low as a few percent which are easily attained in commercial ferrofluids. The present contribution provides an extension of the non–interacting model to moderately concentrated ferrofluids with weak dipolar interactions.

A general statistical theory of magnetic fluids that covers dilute as well as concentrated suspensions with arbitrary strength of dipolar interactions is not available at present. For strong dipolar interactions, the formation of chain–like aggregates is expected. A corresponding kinetic model has been proposed in Ref. In many ferrofluids, the interaction parameter is of order unity at room temperature, implying that thermal energy is sufficiently strong to prevent permanent aggregation. For example, rheological measurements on magnetite based ferrofluids reported in Ref. estimated to be 0.2. We here propose an extension of the kinetic model to describe these phenomena in a mean–field approximation. The model is expected to apply in the dilute and semi–dilute, weakly interacting regime. Several results are obtained: A correction to the Langevin function describing the equilibrium magnetization of non–interacting magnetic dipoles is obtained in agreement with results of Ref. The additional contributions of dipolar interactions to the hydrodynamic stress tensor are worked out. Contrary to the case of non–interacting magnetic dipoles, the stress tensor now depends also on the symmetric part of the velocity gradient. In case of uniaxial symmetry, the hydrodynamic stress tensor is of the same form as in the Ericksen–Leslie theory of nematic liquid crystals. The predictions of the present model are in qualitative agreement with experimental results and address the shortcomings of the non–interacting model, such as the modified concentration dependence and anisotropy of the magnetoviscosity and the presence of normal stresses. Some quantitative comparison to the experimental results of Ref. are offered also. It should be mentioned, that a similar approach has been proposed already in Ref. However, no dependence on the rate–of–strain tensor is considered, while such a dependence has been found experimentally in Ref. In addition, we keep higher order contributions in compared to Ref.

This paper is organized as follows: In Sec. the kinetic model of semi–dilute ferrofluids is developed for equilibrium conditions. It is shown that the equilibrium behavior of this model is agrees with the results of Ref. In Sec. the
kinetic model is extended to describe the dynamics of ferrofluids in the presence of an external flow field. The kinetic model is supplemented by the definition of the hydrodynamic stress tensor. The rheological behavior of the present model is studied in Sec. [V]. In case of uniaxial symmetry, the hydrodynamic stress tensor is found to be of the general form proposed in the Ericksen–Leslie theory of nematic liquid crystals. Explicitly expressions for the viscosity coefficients are obtained in case of weak flow and compared to experimental results. Finally, some conclusions are drawn in Sec. [VI].

II. MODEL DEFINITION AND EQUILIBRIUM PROPERTIES

Consider a system of \( N \) interacting, spherical colloidal particles in a volume \( V \). All particles are assumed to be identical, ferromagnetic monodomain particles of diameter \( d \). Let \( x^i = x^i(t); u^i \) denote the five-dimensional vector describing the position \( x^i(t) \) and orientation \( u^i \) of particle \( i \). The particles are assumed to carry a permanent magnetic moment \( m_i \). The total interaction potential may be written as

\[
U = \sum_{i=1}^{N} \frac{X}{r_{ij}} + \frac{X}{r_{ij}} + \frac{X}{r_{ij}}
\]

The first term denotes the potential energy of an ideal paramagnetic gas in the local magnetic field \( H_{loc} \). The second term is the potential energy of the non-magnetic system, where \( w_{ij}^m = w^m(r_{ij}) \), with \( r_{ij} = r^i - r^j \), \( r_{ij}^2 = r_{ij}^2 \), is a spherical symmetric, short range, repulsive potential. In particular, we consider the case of hard spheres, \( w^m(r) = 1 \) if \( \rho < d \) and zero otherwise, and soft spheres, \( w^m(r) = (r/c)^{12} \). The energy of two magnetic dipoles is described by

\[
w_{ij}^{dd}(i; j) = \frac{2}{4} \gamma k_B T d^3 (a + a^T) = 2 \text{ (r.a)} l=3 \text{ denotes the symmetric traceless part of the matrix a. The dimensionless interaction parameter}
\]

\[
\frac{2}{4} \gamma k_B T d^3
\]

is given by the ratio of the magnetic dipole–dipole energy of two colloidal particles of diameter \( d \) in contact over the thermal energy. It is well–known that due to the long range nature of the dipolar interactions, the magnetic properties of the system depend on the geometry of the container. In order to deal with this situation, we follow Ref. [3] and introduce a virtual cut–off radius \( R_c \) of the dipolar interactions. The effect of dipole \( j \) on dipole \( i \) with \( r_{ij} > R_c \) is treated in a continuum approximation. Within the Weiss model, the resulting far–field contribution leads to a local magnetic field \( H_{loc} \) which is given by

\[
H_{loc} = H + \frac{1}{2} M ; \quad (4)
\]

where \( M \) denotes the magnetization of the sample. Finally, the virtual cut–off is removed, \( R_c = R_c \). For further details see Ref. [3].

Exact results for the thermodynamic properties of the model system [11] are not available. Since the typical volume fraction of magnetic material in ferrofluids is low, the free energy of the system is conveniently expressed by the virial expansion. Let \( f(\mu) \) denote the one–particle distribution function of finding the orientation \( \mu \) of an individual colloidal particle. The normalization is chosen such that \( \int d^2 \mu f(\mu) = 1 \), where integration over the three–dimensional unit sphere is denoted by \( d^2 \mu \). The free energy functional per particle of the system, \( F[f] \), may be split into an ideal, \( F_0[f] \), and an excess part, \( F_{ex}[f] \). The ideal system consists of an ideal gas with number density \( n = N/V \) and an ideal paramagnetic gas,

\[
F_0[f] = k_B T \ln n \quad \frac{Z}{Z} \quad \frac{1}{d^2 \mu f(\mu) \mu} + \frac{1}{d^2 \mu f(\mu) \ln f(\mu)} ; \quad (5)
\]

where \( h_{loc} = H_{loc} = k_B T \) denotes the dimensionless local magnetic field. Boltzmann’s constant and temperature are denoted by \( k_B \) and \( T \), respectively. For low concentrations, the excess part may be written in terms of the virial expansion as [11]

\[
F_{ex}[f] = \frac{1}{2} n k_B T d^2 \mu d^2 \mu f(\mu) f(\mu) b_2(\mu; \mu) + O(n^2) ; \quad (6)
\]

The function \( b_2 \) is defined by

\[
b_2(\mu; \mu) = \frac{Z}{Z} \quad \frac{1}{d^2 \mu f(\mu) f(\mu) \mu} ; \quad (7)
\]
where \( g_{\text{sp}} \) denotes the pair correlation function of the reference system \( (\omega_{\text{dd}} = 0) \) and \( 1 = k_B T \). The function \( b_2 \) can be interpreted as the change of the second virial coefficient due to the dipolar interactions. The integration over the three-dimensional spherical volume is denoted by \( \int d^3 x \).

The function \( b_2 \), Eq. (4), can be expressed as a power series in the interaction parameter \( \omega \). Using the fact that the pair correlation function \( g_{\text{sp}} (x) \) is spherical symmetric, we arrive at

\[
b_2 (u; u^0) = 24v \sum_{k=2}^{\infty} \frac{k^3}{(k-1)!} \left( \frac{3}{2} \right)^k \frac{Z}{4} \left( u - u^0 \right)^k \]

where \( v = \int d^3 x \) denotes the hydrodynamic volume of the colloidal particles. The numerical coefficients depend on the particular choice of the short range potential \( \omega \) and corresponding pair correlation function. Due to the spherical integration volume the term \( k = 1 \) is missing in the sum of Eq. (5). In the low density limit, \( g_{\text{sp}} (x) \) can be approximated by \( g_{\text{sp}} (x) \approx \exp (\omega x) \).

We have found explicit expressions of functionals \( G_k \) for \( k < 5 \),

\[
G_2 [f] = \frac{2}{5} \int h u u i : h u u i + \frac{10}{3} \]

\[
G_3 [f] = \frac{2}{105} \int h u u u u u u u i + \frac{42}{5} h u i h u i \]

\[
G_4 [f] = \frac{1}{210} \int (h u u u u u u u u u u i + \frac{48}{7} h u u i : h u u i + \frac{56}{5}) \]

Angular averages of arbitrary functions \( a (u) \) with respect to the distribution function \( f \) are denoted by

\[
\int a (u) f (u) \]

Note, that functionals \( G_k [f] \) depend on the distribution function only via moments of \( f \) up to order \( k \).

The equilibrium distribution \( f_{\text{eq}} \) is found by minimizing the functional \( \mathcal{F} [f] \) subject to the constraint of fixed normalization, \( \int d^3 u f_{\text{eq}} (u) = 1 \). The result reads

\[
f_{\text{eq}} (u) = \exp [\mathcal{F} (u; f_{\text{eq}})] \]

Note that due to the occurrence of moments in Eq. (15) the equilibrium distribution \( f_{\text{eq}} \) has to be determined self-consistently signaling the mean-field character of the present model. Linearization in the volume fraction \( c \) leads to

\[
f_{\text{eq}} (u) = f (u) + \frac{8}{15} c_{2;2} L_2 (u) P_2 (u H^2) L_2 (u) + \cdots
\]

\[
+ \frac{8}{525} c_{2;3} L_3 (u) P_3 (u H^3) L_2 (u) + \cdots
\]

\[
+ \frac{8}{3675} c_{2;4} L_4 (u) P_4 (u H^4) L_2 (u) + \cdots
\]
where dots denote higher order terms in . In Eq. (16), we have used functions \(L_j\) which are defined recursively by \(L_{j+1}(\kappa) = (2j+1)L_j(\kappa) = \kappa L_0(\kappa) = 1\).

The functions

\[
\ell(u) = \frac{u}{4} \sinh(\frac{u}{2})
\]

are the equilibrium distribution functions in the absence of dipolar interactions. In Eq. (17) we have introduced the Langevin parameter \(h = H/k_0T = \tilde{h}^L\) with \(\tilde{h}^L\) the unit vector in the direction of the magnetic field. The macroscopic magnetization is expressed as \(M = M_{eq}L^L\). Thus, the local field \(h_{loc}\) can be expressed as \(h_{loc} = \frac{1}{2} \tilde{h}^L\), with the effective Langevin parameter \(s = + \frac{1}{2}L_1(\kappa)\). The Langevin function is defined by \(L_1(\kappa) = \coth(\kappa) x^1\) and the Langevin susceptibility is \(s = 8\).

Evaluating the free energy functional \(\mathcal{F}\) with the equilibrium distribution \(f_{eq}\) one obtains the equilibrium free energy \(\mathcal{F}(u) = \mathcal{F}(f_{eq})\) up to linear order in .

\[
\mathcal{F}(x) = k_0T \ln \frac{x}{\sinh(x)} \sum_{i=2}^{\infty} \frac{\ell_i}{x^i} G_k(x) + \frac{\ell_i}{x^i} G_k(x),
\]

Functions \(G_k(z)\) are defined by \(G_k(z) = G_k[f_{eq}]\). Explicit expressions for the first functions \(G_k\), obtained from Eqs. \(11-13\) combined with \(16\), are given in the appendix. We have confirmed that Eqs. \(18-21\) agree with the results of Ref. \[8\] in the case of hard spheres where \(\varphi_{jk} = 1\). The advantage of the present formulation compared to the results of Ref. \[8\] is, that Eqs. \(18-21\) simplify the discussion of the properties and asymptotic behavior of the functions \(G_k(z)\).

Define equilibrium order parameters by \(S_{eq}^{(j)} = \mathcal{P}_j(\tilde{h}^L)\), where \(\mathcal{P}_j\) are Legendre polynomials of degree \(j\). The function \(S_{eq}^{(j)}\) can be obtained by multiplying Eq. \(16\) by \(u \tilde{h}^L\) and subsequent integration over \(u\), or from Eq. \(18\) by \(S_{eq}^{(j)}(x) = \exp(x) - x\). Linearization in the small quantity \(x\) leads to the final result

\[
S_{eq}^{(j)} = L_1(x) + \varphi_{jk} x^j L_{k+1}^{(0)}(x) + \varphi_{jk} x^j L_{k+1}^{(0)}(x) + \varphi_{jk} x^j L_{k+1}^{(0)}(x),
\]

where \(s\) denotes the total derivative. Eq. (19) is identical with Eq. (4.24a) of Ref. \[8\] for \(\varphi_{jk} = 1\). Fig. 1 shows a comparison of Eq. (19) with \(\varphi_{jk} = 1\) for \(k = 4\) and \(\varphi_{jk} = 0\) for \(k > 4\) to the results of molecular dynamics simulations of Ref. \[12\]. The volume fraction was chosen as \(\varphi = 0.2\) and the dipolar interaction was \(\varphi = 1\), which is rather large for the present study. From Fig. 1, one notices that appreciable corrections to the Langevin magnetization occur for intermediate values of \(\varphi\). For the parameters considered, the simulation results are in remarkable agreement with Eq. (19) if truncated at \(k = 4\). In the regime of strong dipolar couplings, \(\varphi > 2\), where corrections to the Langevin magnetization are stronger \(\varphi\), the truncation of the expansion (19) is not admissible. This regime is left for future research. The truncation of the expansion at \(k = 2\) gives similar results to the truncation at \(k = 4\) for \(\varphi = 1\). In Fig. 1, we include also the function \(L_1(\kappa)\), which is obtained by neglecting all higher order corrections in in Eq. (19) if the linearization in is not performed. As has been noted in Ref. \[12\], this approximation describes their numerical data very well for the present choice of parameters. For later use, we give the expression for \(S_{eq}^{(2)}\) in linear order in .

\[
S_{eq}^{(2)} = L_2(x) + \varphi_{jk} x^j L_{k+1}^{(0)}(x) + \varphi_{jk} x^j L_{k+1}^{(0)}(x),
\]

where

\[
\varphi_{jk} x^j L_{k+1}^{(0)}(x) = \frac{8}{525}L_2(x) \varphi L_4(x) + 10L_2(x) + 735L_4(x)^2.
\]

### III. MEAN–FIELD KINETIC MODEL

The model introduced in Sec. II is now extended to describe the nonequilibrium dynamics of ferrofluids in the presence of an external flow field \(\mathbf{v}(\tau)\). The one–particle distribution function \(\ell(u)\) now becomes time–dependent, \(\ell(u;\tau)\), and denotes the probability density of finding the orientation \(u\) of an individual colloidal particle at time \(\tau\). For convenience, the explicit dependence of \(\ell\) on \(\tau\) is frequently suppressed in the sequel. The orientational dynamics of a ferromagnetic colloidal particle under the combined action of the local vorticity of the flow \(\mathbf{v} = \frac{1}{2} \omega \times \mathbf{v}\), Brownian motion, and the action of the potential \(\mathbf{V}^o\) is given by the kinetic equation (22)

\[
\theta_\tau \ell = \ell | \ell + \ell \varphi \frac{\partial}{\partial \ell} L \ell + \ell L \left( V^o \right),
\]
The rotational diffusion coefficient is $D_{rot} = 1/(\Omega_{rot})$, \( \Omega_{rot} = 3 \ \zeta V = k_B T \) denotes the rotational relaxation time. The rotational operator is $L = u \ \theta = \theta u$ with $\theta = \theta u$ the gradient on the unit sphere. In the absence of flow, we assume that the effective potential $V^e$ can be identified with the static mean-field potential $V^{MF}$, Eq. (15). A similar approach was proposed by one of the authors in Ref. [13] in order to describe the dynamics of nematic liquid crystals. For simple fluids such an approach has been proposed and tested recently in Ref. [14].

In the presence of a symmetric velocity gradient $D = \nabla \mathbf{v}$, an additional contribution to the effective potential $V^e$ of the kinetic equation (22) arises. In the case of nonspherical particles, this contribution leads to the so-called flow alignment phenomenon [13, 15]. In the present case, the additional contribution is due to flow–induced structures that can be formed even in a hard sphere system. The distortion of the pair correlation function due to shear flow has been studied experimentally [16] and theoretically [17]. For small distortions, the pair correlation function $g(r,t)$ satisfies the time evolution equation [17]

$$\Theta_{\mu} g + \Theta_{\nu}(\mathbf{r} \mathbf{v}) \mathbf{r} g + \frac{1}{2} \Theta_{\nu} g_{sp} = 0;$$

(23)

where $\Theta_{\mu}$ denotes a translational relaxation time. The stationary solution to Eq. (23) is given by

$$g(r) = g_{sp}(r) \quad \mathbf{D} : \mathbf{ff} = g_{sp}(r):$$

(24)

Results of recent nonequilibrium molecular dynamics simulations of a simple dipolar fluid confirm that Eq. (24) provides a reasonable description of the shear–induced distortion of the pair correlation function [18]. The distortion of the pair correlation function leads to an additional contribution to the effective potential which to lowest order in reads

$$V^D(u;\mathbf{f}) = n \ \mathbf{d}^2 u^0 \mathbf{f}(u^0) \ \mathbf{d}^3 \mathbf{r} \omega_{12}^d(\mathbf{r};u,u^0)(g(r) - g_{sp}(r));$$

(25)

Eq. (25) has an immediate interpretation as the flow–induced modification of the (self–consistently averaged) mean dipolar interaction potential. The effective potential $V^e$ entering the kinetic equation (22) is obtained as $V^e = V^{MF} + V^D$. Inserting Eq. (24) into (25), the kinetic equation (22) takes form

$$0_{\mu} f = L [f]_0 = D \mathbf{hui} \mathbf{D} \omega_{12}^d(\mathbf{V}^{MF})gf] + D \mathbf{L}^2 f;$$

(26)

where $0 = 3 = (\delta_{rot})$. In Eq. (26), we have assumed $g_{sp}(r) \neq 1$ for $r \neq 1$ and $g_{sp}(0) = 0$ due to excluded volume interactions. The kinetic equation for non–interacting dipoles, Ref. [4], is recovered from Eqs. (26) in the limit $r = 0$. The use of Eq. (24) for the flow–induced contribution of the pair correlation function limits the validity of Eq. (26) to weak flows. More precisely, we expect Eq. (24) to apply for $D \mathbf{j} = 1$. Since in Eq. (26) we have kept only the lowest order term in $\mathbf{j}$, further considerations are restricted to the regime of weak dipolar interactions $1$. In this regime, the mean–field potential (15) simplifies to

$$V^{MF}(u;\mathbf{f}) = u \ hui \quad \mathbf{D} = \frac{4}{5} q_{12} u u i : \mathbf{hui} i:$$

(27)

As has been noted in Sec. [11] the truncation (27) of the mean–field potential provides a good approximation for the equilibrium magnetization even for $1$. 1.

It is interesting to compute the hydrodynamic drag appearing in Eq. (22) to the corresponding terms in case of ellipsoidal–shaped particles with axis ratio $r$. For the latter, the contribution of $D$ to the hydrodynamic drag is quadratic in $u$ and proportional to the so-called shape factor $B = \xi^2 \ + 1 = (\xi^2 + 1)$ as well as to the rotational relaxation time $\tau_{rot}$ [15]. Spherical particles correspond to $r = 1$ and $B = 0$. If it would be allowed to replace $\mathbf{hui}$ in Eq. (26) by $u \mathbf{u}$, the flow contribution of the present model would be identical to a dilute solution of ferromagnetic ellipsoidal particles with shape factor $B = 0$. A negative value of $B$ is characteristic of an oblate ellipsoid. This finding has an intuitive interpretation since dipolar interactions favor a head–to–tail arrangement in contrast to side–side configurations. Thus, the particles effectively appear extended in the direction perpendicular to the magnetic moment. In Sec. [14] the validity and limitations of the analogy are discussed for special quantities.

For irrotational flows $\mathbf{f} = 0$, the stationary solution to the kinetic equation (22) reads $f_{sp} = \exp(-V^e) = Z_{st}$, where $Z_{st}$ denotes the normalization constant. Note, that $f_{sp}$ is formally identical to the equilibrium distribution $f_{eq}$, if the magnetic field $h_{eq}$ is replaced by the effective field $h_{eq} = h_{bc} (6=5) \ \mathbf{D} \ \mathbf{hui}$.

From the kinetic equation (22) a hierarchy of moment equations can be derived. Multiplying Eq. (22) by $u$ and integration over $u$ leads to

$$0_{\mu} hui = \mathbf{hui} + \delta_{\mu i} (\mathbf{hui} \ \mathbf{D} \ \mathbf{hui}) + \frac{1}{5} q_{12} D_{rot} (\mathbf{hui} \ \mathbf{hui} \mathbf{hui})$$

(28)
Analogously, higher order moment equations are derived. In order to study the magnetoviscous effect, the kinetic equation has to be supplemented by the expression for the hydrodynamic stress tensor \( T \). Considering only rotational degrees of freedom, the stress tensor is antisymmetric and has the form \( T^{\text{rot}} = 3_s \), where \( s \) is the conventional total antisymmetric (Levi–Civita) tensor of rank three. The average angular velocity \( \Omega \) of the colloidal particles can be inferred from the kinetic equation which can be cast into the form

\[
T^{\text{rot}} = \frac{n k_B T}{2} \left[ \hat{\Omega} \cdot \hat{\Omega} \right] \sum_{ij} \left[ \frac{6}{5} \mathcal{D} \hat{n}_{ij} \hat{n}_{ij} \right] D;
\]

(29)

One has \( \dot{\omega} = 0 \) in the non-interacting model, so that the hydrodynamic stress arises from hindered rotations of individual magnetic moments in the magnetic field. The configurational contribution to the hydrodynamic stress is given by

\[
T^{\text{conf}} = \frac{n^2 Z}{2} \sum_{ij} \left[ \frac{Z}{d^3 r} \frac{Z}{d\Omega} \frac{Z}{d\Omega} \right] \left[ f(u)f(u)g^{(2)}(\tau;u;u) \hat{r} \hat{r} \hat{r} \hat{r} + 12 (\tau;u;u) \right];
\]

(30)

where \( g^{(2)}(\tau;u;u) \) is the full two-particle interaction potential and \( g^{(2)} \) denotes the full pair correlation function. The distortion of \( g^{(2)} \) from its equilibrium \( g^{(2)}_{\text{eq}} \) is assumed to be described also by Eq. (23) where \( g \) is now replaced by \( g^{(2)} \). In this case, the stationary solution reads to leading order

\[
g^{(2)}(\tau;u;u) = g^{(2)}_{\text{eq}}(\tau;u;u) + (\tau;v): \hat{r} \hat{r} g^{(2)}_0(\tau;u;u);
\]

(31)

Note, that Eq. (31) reduces to Eq. (24) only if the (anisotropic) contribution of the dipolar potential to the pair correlation function is neglected.

Inserting Eq. (31) into (30), the deviation of \( T^{\text{conf}} \) from the equilibrium stress becomes

\[
T^{\text{conf}} = \sum_{ij} \left[ \frac{2}{3} (c_3 \hat{n}_{ij}) D \right]
\]

(32)

with the viscosity tensor

\[
T^{\text{conf}} = \frac{n^2 Z}{2 k_B T} \sum_{ij} \left[ \frac{Z}{d^3 r} \frac{Z}{d\Omega} \frac{Z}{d\Omega} \right] \left[ f(u)f(u)g^{(2)}(\tau;u;u) \hat{r} \hat{r} \hat{r} \hat{r} + 12 (\tau;u;u) \right];
\]

(33)

From Eq. (33) we notice that the viscosity tensor \( \sum_{ij} \left[ \frac{2}{3} (c_3 \hat{n}_{ij}) D \right] \) is is positive semi-definite, i.e. \( \sum_{ij} \left[ \frac{2}{3} (c_3 \hat{n}_{ij}) D \right] \) for arbitrary second-rank tensors \( a \).

Inserting the spherical and the dipole–dipole interaction potential into Eq. (33) yields symmetric and antisymmetric contributions to the stress tensor, such that the total hydrodynamic stress tensor becomes

\[
T = T^{\text{rot}} + T^{\text{conf}} = T^s + T^a;
\]

(34)

with the symmetric part,

\[
T^s = \sum_{ij} \left[ \frac{2}{3} (c_3 \hat{n}_{ij}) D \right]
\]

and the antisymmetric part

\[
T^a = \sum_{ij} \left[ \frac{n k_B T}{2} \left[ \hat{\Omega} \cdot \hat{\Omega} \right] \hat{n}_{ij} \hat{n}_{ij} \right];
\]

(36)

In Eq. (35) we have introduced \( \sum_{ij} \left[ \frac{2}{3} (c_3 \hat{n}_{ij}) D \right] + a(b(2) \sum_{ij} \left[ \frac{Z}{d^3 r} \hat{n}_{ij} \hat{n}_{ij} \right] ) \) and the quantity \( a = 2 \sum_{ij} \left[ \frac{Z}{d^3 r} \hat{n}_{ij} \hat{n}_{ij} \right] \)

(35)

where \( \sum_{ij} \left[ \frac{2}{3} (c_3 \hat{n}_{ij}) D \right] \) is the shear viscosity of the isotropic suspension is

\[
\eta_s = \eta (1 + \frac{5}{2} \alpha + \beta^2);
\]

(37)

where \( \alpha \) is the shear viscosity of the pure solvent, \( b = \frac{1}{2} \xi e \). Note, that the isotropic interactions alter the value of the Newtonian viscosity while dipolar interactions lead to additional, non-Newtonian contributions to the stress tensor. Diagonal contributions to \( T^s \) have been suppressed in Eq. (35) since they can be compensated by the scalar pressure. Note also, that the stress tensor \( T \) is symmetric in the absence of an applied magnetic field. Quantities \( c_3 \) and \( c_4 \) result from the short range interaction contribution to the stress tensor and depend on the detailed form of the interaction potential,

\[
c_3 = \int dx x^k \left[ \frac{Z}{d^3 r} \hat{n}_{ij} \hat{n}_{ij} \right] g_{\text{sp}}(x);
\]

(38)
where prime denotes the total derivative and \( x = r = d \). The coefficients \( c_2 \) are non-negative, \( c_2 \geq 0 \). Evaluation of the coefficients \( c_2 \) and \( c_4 \) for the case of hard spheres suffers from the discontinuity of the potential. For power law repulsion, \( w_s(x) = x^k \), the integration in Eq. (38) can be done analytically in the low density regime, giving \( c_2 = (\frac{k + 1}{k - 1}) \). For soft spheres, \( x = 12 \), we find \( c_2 = 12 \) and \( c_4 = 11/2 \). We mention that the \( c_2 \) contribution to \( \rho_0 \) in Eq. (37) stems from the non-magnetic interactions of the colloidal particles. This contribution is of the form \( G_x \), where \( G_x \) is the Born-Green expression of the equilibrium shear modulus of a system of spherical particles interacting with the potential \( \phi \) [19].

Eqs. (26), (27), (34), (35) and (36) constitute the mean-field kinetic model of the nonequilibrium dynamics of dilute, weakly interacting ferrofluids proposed here. The present model extends the work of Ref. [4] to the regime \( c_2 > 0 \). If the dimensionless dipolar interaction parameter \( \epsilon \) goes to zero, the model of non-interacting magnetic dipoles proposed in Ref. [4] is recovered with a renormalized zero-field viscosity \( \nu_0 \).

The present model contains the additional parameter \( \epsilon_0 \), which is a measure for the ratio of translational and rotational relaxation times. Simple estimates of the translational and rotational relaxation times lead to \( 6 (r = d)^2 \), where \( r_0 \) is a typical length scale associated with the formation of flow-induced structures. If \( r_0 \) is identified with the typical distance between colloidal particles, the parameter \( \epsilon_0 \) can be estimated as \( 2^{2 r^2} \). On the other hand, if \( r_0 \) is identified with the diameter \( d \) of the colloidal particles one obtains \( \epsilon_0 = 6 \). These estimates agree with each other for \( \epsilon \geq 2 \), which is slightly above the expected range of validity of the present model. Alternatively, if one requires the expression (37) for the zero-field viscosity to correspond to Batchelor’s result, Eq. (37) with \( b = 6 \epsilon_0 \) (see Ref. [3] and discussion therein), the parameter \( \epsilon_0 \) is given by \( \epsilon_0 = 186 \epsilon_0 (35 \epsilon_0 \) and thus related to the interaction potential \( w_s \). In case of soft spheres, agreement with Batchelor’s result leads to \( \epsilon_0 = 0 \). In the sequel, we consider as parameter with \( \epsilon_0 = 0 \) (1). Fig. 2 shows zero-field zero-shear viscosity \( \nu_0 \) of a kerosene based ferrofluid as a function of the volume fraction \( \phi \). The data are taken from Ref. [3]. From Fig. 2 we notice that Batchelor’s result describes the experimental data well for volume fractions \( \phi < 0.25 \).

IV. RESULTS FOR UNIAXIAL SYMMETRY

The stress tensor \( \mathbf{T} \), Eq. (35), depends explicitly on the first moment of the distribution function only. However, all the moments are coupled dynamically as can be seen already from the first moment equation (28), such that the values of second and third moments are needed in order to determine the first moment and the stress tensor. Therefore, closed form equations for the dynamics of the stress tensor (34) in terms of low order moments necessarily introduce approximations to the underlying kinetic model. In a previous work [21], we have studied the assumption of uniaxial symmetry of the distribution function applied to the non-interacting kinetic model of Ref. [4]. Motivated by the good accuracy of the assumption of uniaxial symmetry for that model found in Ref. [21], we employ this assumption also for the present case.

In the uniaxial phase, the distribution function \( f(\mathbf{u};t) \) is symmetric with respect to rotations around the director \( n \), \( f(\mathbf{u};t) = f_{\text{un1}}(\mathbf{u} ; n ; t) \), such that \( f \) can be represented as

\[
f_{\text{un1}}(\mathbf{u} n ; t) = \frac{1}{4} \frac{1}{4j + 1} \sum_{j=0}^{\infty} S_j(t) P_j(\mathbf{u} n) ;
\]

(39)

The scalar orientational order parameters \( S_1 \) are defined as \( S_j = \frac{1}{2} \sum_{ij} \text{Re} \left[ \mathbf{u}_i \mathbf{u}_j \right] \), where, as before, \( \mathbf{P}_j \) are Legendre polynomials. In case of uniaxial symmetry, the first moments take the form

\[
\mathbf{h} \mathbf{u} = S_1 \mathbf{n} ; \quad \mathbf{h} \mathbf{u} \mathbf{u} = S_2 \mathbf{n} \mathbf{n} ;
\]

\[
\mathbf{h} \mathbf{u} \mathbf{u} \mathbf{i} = S_3 \mathbf{n} \mathbf{n} \mathbf{n} + \frac{S_1}{5} ( \mathbf{n} \mathbf{n} \mathbf{n} + \mathbf{n} \mathbf{n} ) ;
\]

(40)

E.g. the distribution functions (10) and (17) are uniaxial symmetric with respect to the direction of the magnetic field, \( n = \mathbf{n} \). Expressions for the equilibrium order parameters \( S_i^{eq} \) are given in Eqs. (15) and (20) for \( i = 1, 2 \).

Inserting Eqs. (10) into (35) and (36) and using Eq. (28) the hydrodynamic stress tensor is of the form assumed in the Ericksen-Leslie theory of nematic liquid crystals [3].

\[
\mathbf{T} = \frac{1}{2} \left( \mathbf{D} \cdot \mathbf{n} \right) \mathbf{n} + 2 \mathbf{n} \mathbf{n} + 3 \mathbf{n} \mathbf{n} + 4 \mathbf{D} + 5 \mathbf{n} \mathbf{n} \mathbf{D} + 6 \mathbf{n} \mathbf{n} \mathbf{D} \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} (41)
\]

where \( \mathbf{N} = \mathbf{n} \mathbf{n} \mathbf{n} \mathbf{n} \) is the corotational derivative of the director \( n \) and the Leslie coefficients \( \lambda_i \) are given by

\[
\lambda_1 = 0 ; \quad \lambda_2 = 3 s \left( \frac{3 S_1^2}{2 + S_2} + 7 s \right) S_1^2 ; \quad \lambda_3 = 3 s \left( \frac{3 S_1^2}{2 + S_2} + 7 s \right) S_1^2 ;
\]

\[
\lambda_4 = 2 \left( 4 (1 + q = 3) S_1^2 + S_2^2 \right) \quad \lambda_5 = (c_3 + (q = 1) 2) S_1^2 \quad \lambda_6 = (c_3 + q = 1) 2 S_1^2 ;
\]

(42)

(43)
A relation between the Leslie coefficients can be derived from Onsager’s reciprocity relation, \( 2 + 3 = 6 \), which is
known as Parodi’s relation \([2, 15]\). Parodi’s relation is readily verified from Eqs. \([42\) and \([43\). Note, that in the
limit \( f = 0 \), the result of Ref. \([20\) is recovered from Eqs. \([41\), \([42\) and \([43\).

The balance equation for the director \( n \) can be derived from the moment equation \([28\) with the help of Eqs. \([40\),
\[
(1 \; n \; n) \; H = \gamma_1 \; n \; 1 \; n = 0; \tag{44}
\]
with the molecular field \( H = n \kappa_b T S_1 h \) and \( 1 = 3 \) and \( 2 = 6 \).

### A. Effective Field Approximation

In the so-called Effective Field Approximation (EFA) \([4\), a special family \( f_v \) of uniaxial distribution functions is considered
that is obtained by replacing the magnetic field \( h \) in Eq. \([17\) with an effective field \( e \). Motivated by the good accuracy of the
EFA for the non–interacting model \([4\), we consider the EFA also for the present model.

In more general terms, the EFA can be interpreted as the Quasi–Equilibrium Approximation where only the magnetization
is kept as macroscopic variable (see e.g. \([15\)). Extremizing the free energy functional \([10\) subject to the constraint of fixed
normalization and fixed value of the first moment yields the quasi–equilibrium distribution \( f_v \). Also in the present case, \( f_v \) is
obtained from the equilibrium distribution \( f_{eq} \) if the magnetic field \( h \) in Eq. \([16\) is replaced by an effective field \( e \). Since
the equilibrium distribution \( f_{eq} \) is uniaxially symmetric around the magnetic field direction \( f \), the distribution function \( f_v \) is
uniaxially symmetric with respect to the direction of the effective field \( n = \omega \), where \( \omega = e_\omega \) and \( \omega \) denotes the norm of \( e \). Consequently, the result of the previous section apply to the EFA. In particular, the moments \( h n \) and \( h u \) within the EFA are given by Eq. \([40\), where the scalar orientational order parameters are obtained from their equilibrium values by \( S_j = S_{ij}^{eq} (e) \).

#### 1. Magnetization Equation

From the moment equation \([28\) a closed equation for the magnetization \( M = M_{sat} h n \) can be derived within the EFA which reads
\[
M_{eq} = M = \frac{1}{1} - \frac{1}{2} M M + 2 D M + 3 D : M M M ; \tag{45}
\]
where \( h = \kappa_b T (e) h \) is the (dimensional) deviation of the effective field from the magnetic field. The coefficients \( \gamma \) and \( \beta \) are defined as
\[
\frac{1}{1} = 3 D f_0 \lambda (e); \quad \frac{1}{2} = \frac{0}{6} b (e); \tag{46}
\]
\[
2 = \frac{0}{6} f_0 (e); \quad 3 = \frac{0}{6} f_0 b (e); \tag{47}
\]
The functions \( A (e) \) and \( B (e) \) are given by
\[
A (e) = \frac{2 + S_2 (e)}{3} = 1 + \frac{L_1 (e)}{e} + \frac{L_1 (e)}{e} (L_1 (e))^2 + L_2 (e)) + \frac{1}{3} \alpha_22 \quad J_2^2 (e); \tag{48}
\]
and
\[
B (e) = \frac{S_2 (e)}{S_1 (e)^2} = \frac{L_2 (e)}{L_1 (e)^2} + \frac{5 + 2 L_2 (e)}{3 L_1 (e)^2} + \alpha_22 \quad L_1 (e) J_2^2 (e) + \frac{2 L_2 (e) G_2 (e)}{L_1 (e)^2 } \tag{49};
\]
The magnetization equation \([45\) is a special case of Eq. \((15) \) of Ref. \([21\) which has been derived within a thermodynamic
framework. The coefficients appearing in the magnetization equation, however, cannot be determined within the thermodynamic
approach. For the special case \( i = 0 \), Eq. \([45\) has been derived in Ref. \([9\) in linear order in \( \chi \) and \( \xi \), within the EFA, starting
from an \( N \)–particle Fokker–Planck equation. The expression for \( A (e) \) given by Eq. \([45\) is identical to the result of Ref. \([9\) to
first order in \( \chi \), while the result of Ref. \([9\) for the coefficient \( B (e) \), coincides with Eq. \([49\) only for \( i = 0 \). However, correcting
Eq. \((15) \) of Ref. \([9\) for the missing factor \( L_1 (e) = e \) \([22\), also the results for the coefficient \( B (e) \) agree with Eq. \([49\). In
Ref. \([15\), the magnetization equation \([45\) has been derived within a kinetic model of non–interacting, ferromagnetic colloidal
particles with an ellipsoidal shape. Comparing Eq. \([47\) to Eq. \((77) \) of Ref. \([15\), we notice that the transport coefficients \( \gamma \) are of
a similar form in both cases. For weak fields, the coefficient \( \gamma \) approaches a constant value \( \gamma (0) = \frac{2}{3} \) \( 0 \); \( \gamma \) which is identical
to the result of a non–interacting system of particles with shape factor \( B = \chi \) \( 0 \), \( B = (\chi^2 + 1) \) \( 0 \) where \( \chi \) is the
axis ratio. Note, that \( B < 0 \) corresponds to oblate, \( B > 0 \) to prolate ellipsoidal particles.
2. Relaxation Times

Analytical results for the magnetization dynamics \(^5\) can be obtained for small deviations from the equilibrium values. To linear order in \(\beta\) and in the absence of velocity gradients, Eq. \(^5\) becomes

\[
M_\beta = \frac{1}{\text{eq}} \frac{1}{2} M \text{eq} i,
\]

where \(\text{eq}\) denote the equilibrium values of the coefficients \(i\). Decomposing the off–equilibrium magnetization into components parallel and perpendicular to the magnetic field direction, \(M_\beta = M \perp \beta + M \parallel \beta\), one finds from Eq. \(^5\)

\[
M_\beta = \frac{1}{\gamma} M \gamma + \frac{1}{\kappa} M \kappa + M \text{eq} i;
\]

where the field–dependent relaxation times are defined by

\[
\gamma = \frac{3S_1^\text{eq}(\ )}{D \gamma (2 + S_2^\text{eq}(\ ))}; \quad \kappa = \frac{3S_1^\text{eq}(\ )}{2D \kappa (1 + S_2^\text{eq}(\ ))}.
\]

Linearization in the volume fraction leads to

\[
\gamma = \gamma(0)(1 + t_0^\gamma + 2 t_0^\gamma), \quad \kappa = \kappa(0)(1 + t_0^\kappa + 2 t_0^\kappa)
\]

where

\[
\gamma(0) = \frac{L_1^\gamma(\ )}{D \gamma (L_1^\gamma(\ ))}; \quad \kappa(0) = \frac{L_1^\kappa(\ )}{2D \kappa (L_1^\kappa(\ ))}.
\]

are the corresponding relaxation times in the non–interacting system and the functions \(t_0^\gamma\) and \(t_0^\kappa\) are defined in appendix B. For the case of vanishing magnetic field, \(\beta = 0\), the above expressions coincide, \(\gamma(0) = \kappa(0) = \gamma(\text{rot})(1 + t_0^\gamma = 3)\). Note, that no contribution from \(O(\beta^2)\) remains in this limit. Thus, dipolar interactions lead to an increase of the zero–field relaxation time compared to the dilute suspension. In Fig. 3 we plot the relaxation times \(\gamma\) and \(\kappa\) as a function of the magnetic field for \(\beta = 0\). From Fig. 3 we notice that the transverse relaxation time is enhanced due to dipolar interactions for arbitrary values of the magnetic field. As the magnetic field increases, however, differences between \(\gamma\) and \(\kappa\) decrease. The relaxation time parallel to the magnetic field is increased compared to \(\kappa_0\) only for small magnetic fields, while it is decreased in case of strong magnetic fields. For comparison, we included in Fig. 3 also the corresponding results of Ref. [9]. Note, however, that due to the dependence of \(\gamma\) and \(\kappa\) on the coefficient \(B\), the results of Ref. [9] for the relaxation times are incorrect [22].

V. RESULTS FOR PLANE COUETTE FLOW

To further illustrate the result, we consider in the sequel the special case of plane Couette flow, \(v(r) = (\gamma y; 0; 0)\), where \(\gamma\) denotes the constant shear rate. If the magnetization is oriented in the flow, gradient and vorticity direction, the Miesowicz shear viscosity \(\gamma = (\gamma + \gamma + \gamma) = 2\), \(\delta = (\gamma + \gamma + \gamma) = 2\) and \(\delta = 4\) is measured, respectively. From Eqs. (2) and (3) we find

\[
\gamma(0) = \frac{1}{\gamma} \frac{3S_1^2 (\ )}{2 + S_2^\gamma (\ )} (1 + \gamma_3) + c_1 \gamma S_1^\gamma,
\]

where \(\gamma = \frac{3}{2} \gamma \), \(\gamma_3\) is the Kronecker symbol, \(c_1 = (\gamma_3 + \gamma_3 + \gamma_3) = 6\), \(c_2 = (\gamma_3 + \gamma_3 + \gamma_3) = 6\), and \(c_3 = (\gamma_3 + \gamma_3 + \gamma_3) = 6\). From Eq. (56) we find \(\gamma > \gamma\). The same inequality is found for a dilute suspension of ferromagnetic oblate ellipsoidal particles [15], while \(\gamma < \gamma\) is valid for oblate, chain–like particles.

If the magnetic field is sufficiently strong to fully orient the magnetic moments, \(\gamma \parallel 1\), the Miesowicz shear viscosities approach their asymptotic values \(\gamma \gamma = \frac{1}{1}\). From Eq. (56) one finds

\[
\gamma = \frac{1}{\gamma} (1 + \gamma_3 + c_1 \gamma_3)\gamma
\]
Since $\frac{1}{r}$ is the maximum viscosity increase for $r = 0$, we find from Eq. (57) that dipolar interactions increase the value of $\frac{1}{r}$ while $\frac{1}{r}$ is decreased (for $c_2 < 24$) compared to $\frac{1}{r}$. Eq. (57) further predicts the inequality $\frac{1}{r} > \frac{1}{r} > \frac{1}{r}$, which is in qualitative agreement with the results of nonequilibrium molecular dynamics simulations on a magnetically saturated model–ferrofluid in the weakly interaction regime.

For small shear rates, the order parameters $S_i$ in Eq. (56) may be replaced by their equilibrium values. As has been pointed out in Ref. [15], the assumption of uniaxial symmetry reduces to the EFA in this limit. Inserting Eqs. (19) and (20) into Eq. (56) and expanding in the small quantities $c$ and $d$ gives

$$i 12 ( ) = 0 + 1 \frac{L_1 ( )}{L_0 ( )} 1 + \frac{1}{r} t_2 ( ) + L_1 ( ) + c_{i 12} ( 1 + \frac{L_0 ( )}{L_1 ( )} ) g + 2 t_2 ( ) + \frac{G_0 ( )}{L_1 ( )} g ;$$

(58)

and $3 ( ) = 0 + \frac{1}{r} c_3 L_1 ( )$. The functions $t_2$ are defined in the appendix B. For $L = 1$, the result (57) is recovered from Eq. (58). In the opposite limit of weak magnetic fields, $L = 0$, the viscosities increase quadratically with $L$,

$$i ( ) = 0 + \frac{1}{4} s 1 i 1 + \frac{2}{3} ( 1 + 12 ( ) ) 2 + O ( L^3) ;$$

(59)

We now consider the special case where the magnetic field and the magnetization are oriented in the plane of shear. In this case, we introduce the angles of the flow direction with the magnetic field and expanding in the small quantities and gives

$$i 12 ( ) = 0 + \frac{1}{r} L_1 ( ) L_0 ( ) 1 + \frac{1}{r} t_2 ( ) + L_1 ( ) + d_{i 12} ( 1 + \frac{L_0 ( )}{L_1 ( )} ) g + 2 t_2 ( ) + \frac{G_0 ( )}{L_1 ( )} g ;$$

(58)

and $3 ( ) = 0 + \frac{1}{r} d_3 L_1 ( )$. The functions $t_2$ are defined in the appendix B. For $L = 1$, the result (57) is recovered from Eq. (58). In the opposite limit of weak magnetic fields, $L = 0$, the viscosities increase quadratically with $L$,

$$i ( ) = 0 + \frac{1}{4} s 1 i 1 + \frac{2}{3} ( 1 + 12 ( ) ) 2 + O ( L^3) ;$$

(59)

In Eq. (60), we have introduced the Mason number $M n = \frac{n}{\cos \# \sin \#}$, which measures the relative strength of the flow compared to the magnetic field. From Eq. (60) we notice that a perfect alignment of the magnetization with the magnetic field, $L = \#, occurs for $M n = 0$. For $M n > 0$, the direction of the magnetization does not coincide with the magnetic field direction due to the effect of the flow field. With the ansatz $L = k M n^2 k$, where $0 = \#$ denotes the value of $L$ for $M n = 0$, Eq. (60) can be solved recursively for $L$. The first order result reads

$$i = \frac{3 S_{i 1}^{eq}}{2 + S_2^{eq}} + 0 \cdot S_{1} \cos (\#) ;$$

(61)

Due to dipolar interactions, the present model also predicts normal stress differences. The first normal stress coefficient $N_1$ for the plane shear flow $v = (-y; 0; 0)$ is defined as $N_1 = \frac{t_{xx} - t_{yy}}{2}$, while the second normal stress coefficient is defined as $N_2 = \frac{t_{xx} + t_{yy}}{2}$. From Eqs. (41)–(43), we find that $N_1 = 14 s_{i 1} = 2 S_{1}^{eq} n_x n_y$ if the magnetic field is oriented in the plane of shear, where $s_{i 1} = 1$, $s_{i 2} = (q + 12 = 2)$ and $n_x$, $n_y$ denote Cartesian components of the vector $n$. Note, that $s_2$ is the ratio $N_2 = N_1$. For weak velocity gradients, the normal stress coefficients take the form

$$N_1 = 14 s_{i 1} = 2 S_{1}^{eq} \sin \# \cos \# + M n \cdot S_{1} \cos (\#) ;$$

(62)

From Eq. (62) we observe that $N_1 / \frac{2}{2}$ for weak velocity gradients if the magnetic field is oriented either in flow or in gradient direction, otherwise we find $N_1 / \frac{2}{2}$. In any case, the normal stress differences vary as $N_1 / \frac{2}{2}$ for $1$ if the flow field is weak.

In a pipe flow, the so–called McTague viscosity coefficients $k = 1$ and $r = (r + 2) = 2$ are measured, if the magnetization is oriented in flow and perpendicular to the flow direction, respectively. From Eq. (56) we find to lowest order in

$$k \frac{0}{r} = 2 \left(1 + 2d_{i 1} \frac{2 + S_2}{3}\right) ;$$

(63)

From Eq. (63) we observe that dipolar interactions lead to a ratio of the McTague viscosities greater than two, the ratio being an increasing function of the magnetic field. It has been emphasized several times that McTague’s experimental results (11) can be fitted quite nicely by the predictions of kinetic model introduced in Ref. (4). However, the ferrofluid used in these experiments cannot be considered dilute and the parameters of the fit (the volume fraction and the magnetic moment of the colloidal particles) do not agree with independent estimates (5). In addition, the ratio (63) found in the experiments (11) is not constant and becomes approximately 2.3 for strong magnetic fields. This result cannot be explained within the model (4) which predicts a value of 2 independent of the magnetic field. In view of the present results, a value greater than two for the ratio Eq. (63)
is expected due to magnetic dipole–dipole interactions. It would be very interesting, to compare the prediction of Eq. 63 to experimental results on a semi–dilute ferrofluid with . 1 where the present model applies.

The maximum relative viscosity increase if the magnetization is oriented in flow direction, \( \frac{1}{k} ( \frac{1}{3} \sigma ) = 0 \), is given by

\[
\frac{1}{k} ( \sigma ) = \frac{3}{2} \left( 1 + 8d_1 \frac{5}{2} \right) + O ( \sigma ) ;
\]

(64)

where \( \frac{1}{k} = 3 \rightarrow 2 \) corresponds to the classical result of Ref. [4]. Note, that the factor 5/2 in Eq. (64) arises from the expansion of \( \sigma \) in terms of \( \sigma \). Experimental measurements of \( k \) have been performed in Ref. [7] with a capillary viscometer for a magnetite based ferrofluid with volume fractions 0.2. The interaction parameter \( k \), Eq. (3), was estimated in Ref. [7] to be \( k = 0.2 \), justifying the application of the present model to their system. Fig. 4 shows \( \frac{1}{k} ( \sigma ) \) according to the experimental results of Ref. [7]. From Fig. 4 it is seen that Eq. (3) describes the experimental data accurately up to volume fractions \( 0 \pm 5 \). A value of \( d_1 = 2.75 \) was used in Fig. 4. For a soft sphere potential we obtained \( c_1 = 12 \) in Sec. III, so that \( d_1 = 2.75 \) corresponds to \( c_3 = 2.3 \) which is within the expected range of values. For higher concentrations, the present approach needs to be extended by including higher order terms in the expansion (6). Figure 5 shows the dimensionless viscosity increase \( \frac{1}{k} ( \sigma ) = 0 \) as a function of \( \sigma \) for various values of \( \sigma \). The experimental results for \( k \) of Ref. [7] are shown together with Eq. (63) for \( i = 1 \). As in Fig. 4 a value \( d_1 = 2.75 \) has been chosen. From Fig. 5 we notice that Eq. (63) is able to describe the experimental data well for volume fractions \( 0 \pm 1 \) while strong deviations appear for \( 0 \pm 1/0 \). It has been mentioned in Ref. [7] that their experimental results can be fitted to the non–interacting model, \( \frac{1}{k} = 0 \), with the help of an effective volume fraction \( \frac{1}{k} > 0 \). Within the present model, the increase of the effective volume fraction is explained by the magnetic dipole–dipole interaction.

VI. CONCLUSION

In the present work, we have proposed a kinetic model of dilute, weakly interacting ferrofluids that extends the classical kinetic model of dilute ferrofluids [4] by the incorporation of dipolar interactions. Our model predicts several extensions compared to the classical kinetic model which are in qualitative agreement with experimental results, such as the presence of normal stress differences, enhanced magnetoviscous effect, modified anisotropy of viscosity and the dependence of viscosity on the hydrodynamic volume fraction and the symmetric velocity gradient. For a quantitative comparison with experimental results, two additional parameters have to be specified which are absent in the non–interacting model [4]: the dipolar interaction parameter and the ratio of the rotational over the translational relaxation time of the colloidal particles. While \( k \) is defined by Eq. (3) and also tabulated for several ferrofluids, determining \( c_3 \) is not straightforward. As has been discussed above, estimations of can give information only about the order of magnitude of \( k \), rather than a certain value. On the other hand, the value of \( c_3 \) can be inferred from measurements, e.g. of the maximum viscosity increase from Eq. (57). Following this route, the experimental results of Ref. [7] are described quantitatively by the present model with a reasonable value of \( k \).

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG) via the priority program 1104 'Colloidal magnetic fluids' under grant No. HE 1100/6–3. Valuable discussions with M. Kröger are gratefully acknowledged.

APPENDIX A

The functions \( G_1 ( x ) \) are defined by \( G_1 ( x ) = G_1 ( \sigma ) \), where the functionals \( G_1 ( \sigma ) \) for \( i = 2; 3; 4 \) are given by Eqs. (11)–(14) and \( f_{eq} \) is defined in Eq. (16). Evaluating the functionals \( G_1 ( \sigma ) \) with the equilibrium distribution function \( f_{eq} \) one obtains

\[
G_2 ( x ) = \frac{4}{15} L_2 ( x )^2 + 5
\]

(A1)

\[
G_3 ( x ) = \frac{4}{525} L_3 ( x )^2 - 21 L_4 ( x )^2
\]

(A2)
The functions $G_{1}(x)$, defined in Eqs. (A1)-(A3), are monotonously increasing functions of $x$. These functions depend only weakly on $x$ and have the following expansion for $x \rightarrow 0$ and $x \rightarrow 1$:

$$G_{2}(x) = 4 \frac{3}{3675} x^{2} + \frac{4}{3 \times 4} x^{4} + O(x^{5}) \quad \text{for} \quad x \rightarrow 0$$  \hspace{1cm} \text{(A4)}

$$G_{3}(x) = \frac{16}{165} x^{2} + \frac{4}{3} x^{4} + O(x^{5}) \quad \text{for} \quad x \rightarrow 0$$  \hspace{1cm} \text{(A5)}

$$G_{4}(x) = \frac{4}{15} + \frac{16}{165} x^{2} + O(x^{5}) \quad \text{for} \quad x \rightarrow 1$$  \hspace{1cm} \text{(A6)}

APPENDIX B

The contribution of dipolar interactions to the transverse and parallel relaxation times are described by the functions

$$t_{2}^{I}(x) = \frac{L_{1}(x)}{L_{0}(x)} \frac{L_{1}(x)}{L_{0}(x)} \frac{(L_{1}(x)^{2} - L_{0}(x))}{L_{0}(x)}$$  \hspace{1cm} \text{(B1)}

$$t_{2}^{P}(x) = \frac{G^{0}(x)}{3} \frac{L_{1}(x)}{L_{0}(x)} \frac{(L_{1}(x)^{2} - L_{0}(x))}{L_{0}(x)}$$  \hspace{1cm} \text{(B2)}

$$t_{2}^{I}(x) = \frac{L_{1}(x)}{x} + \frac{2L_{1}(x)}{L_{1}(x)} \frac{L_{1}(x)}{L_{0}(x)} \left( L_{1}(x)^{2} - L_{0}(x) \right) \frac{L_{2}(x)}{x}$$  \hspace{1cm} \text{(B3)}

$$t_{2}^{P}(x) = \frac{G^{0}(x)}{3} \frac{L_{1}(x)}{L_{0}(x)} + \frac{xJ^{0}(x)}{3L_{1}(x)}$$  \hspace{1cm} \text{(B4)}

The functions $t_{2}^{I}$ are positive, while functions $t_{2}^{P}$ are not sign-definite. In the limit $x \rightarrow 1$ we find $t_{2}^{I} \rightarrow 0$ and $t_{2}^{P} \rightarrow 0$, while for $x \rightarrow 0$, the following asymptotic behavior is obtained: $t_{2}^{I}(x) = 1=3 \quad 4x^{2}=45$, $t_{2}^{P}(x) = 4x^{2}=375$, $t_{2}^{I}(x) = 1=3 \quad 7x^{2}=45$, and $t_{2}^{P}(x) = 56x^{2}=1125$.

[1] J. P. McTague, J. Chem. Phys. 51, 133 (1969).
[2] E. Blums, A. Cebers, and M. M. Maiorov, Magnetic Fluids (de Gruyter, Berlin, 1997).
[3] S. Odenbach, Magnetoviscous Effects in Ferrofluids, Lecture Notes in Phys. (Springer, Berlin, 2002).
[4] M. A. Martsenyuk, Y. L. Raikher, and M. I. Shliomis, Sov. Phys. JETP 38, 413 (1974).
[5] S. Odenbach, Int. J. Mod. Phys. B 14, 1625 (2000).
[6] A. Y. Zubarev and L. Y. Iskakova, Phys. Rev. E 61, 5415 (2000).
[7] G. P. Bogatyrev and V. G. Gilev, Magnetohydrodynamics 20, 249 (1984).
[8] B. Huke and M. Lücke, Phys. Rev. E 62, 6875 (2000).
[9] A. Y. Zubarev and A. V. Yushkov, JETP 87, 484 (1998).
[10] S. Odenbach and H. W. Müller, Phys. Rev. Lett. 89, 037202 (2002).
[11] L. Onsager, Ann. (N. Y.) Acad. Sci. 51, 627 (1949).
[12] Z. Wang, C. Holm, and H. W. Müller, Phys. Rev. E 66, 021405 (2002).
[13] S. Hess, Z. Naturforsch. 31a, 1034 (1976).
[14] U. M. B. Marconi and P. Tarazona, J. Chem. Phys. 110, 80328044 (1999).
[15] P. Ilg and M. Kröger, Phys. Rev. E 66, 021501 (2002).
[16] N. A. Clark and B. J. Ackerson, Phys. Rev. Lett. 44, 1005 (1980).
[17] S. Hess, Phys. Rev. A 22, 2844 (1980).
[18] J. L. McWhirter and G. N. Patey, J. Chem. Phys. 117, 2747 (2002).
[19] S. Hess, in Rheological Modelling: Thermodynamic and Statistical Approaches, edited by D. J. J. Casas-Vázquez (Springer, Berlin, 1990), vol. 381 of Lecture Notes in Phys., pp. 51–73.
[20] P. Ilg, M. Kröger, and S. Hess, J. Chem. Phys. 116, 9078 (2002).
[21] H. W. Müller and M. Liu, Phys. Rev. E 64, 061405 (2001).
[22] A. Y. Zubarev, private communication (2003).
[23] S. Hess, T. Weider, and M. Kröger, Magnetohydrodynamics 37, 297 (2001).
FIG. 1: Equilibrium magnetization as a function of the Langevin parameter for volume fraction $\phi = 0.57$ and $\phi = 1$. Symbols are the result of molecular dynamics simulations presented in Ref. [12]. Dashed line is the Langevin function $L_1(\cdot)$, while the solid line corresponds to Eq. (19), where the infinite sum has been truncated at $k = 4$. The dotted line is the result of the approximation $L_1(\cdot) + L_1(\cdot)$.

FIG. 2: Shear viscosity $\nu = \eta$ of the isotropic suspension ($H = 0$) as a function of the volume fraction $\phi$. Dashed and full lines are the theoretical predictions $\nu = \eta = 1 + 2\phi + \phi^2$ with $b = 0$ (Einstein) and $b = 6\phi$ (Batchelor), respectively.
FIG. 3: a) Reduced transverse, $\gamma = \omega t$, and b) parallel, $\lambda = \omega t$, relaxation times as a function of the applied magnetic field. The volume fraction was chosen as $\theta = 0.15$. Curve 1 corresponds to $\theta = 0$, curve 2 to $\theta = 1$, and curve 3 to $\theta = 1.5$. Solid lines are the result of Eqs. (53) and (54), dashed lines are the result of Ref. [9].

FIG. 4: The maximum relative viscosity increase $\frac{1}{\eta}$ as a function of the hydrodynamic volume fraction. Circles represent the experimental results from Ref. [7], solid line the prediction of the present model, Eq. (64), for $\bar{d}_1 = 2.75$, and dashed line is the result of Ref. [4].
FIG. 5: Relative viscosity increase $\chi$ as a function of the Langevin parameter. Circles, squares and diamonds represent the experimental results of Ref. [7] for volume fractions $\phi = 0.07, 0.11$ and $0.06$, respectively. Solid lines are the corresponding predictions of the present model, Eq. [58] with $d_1 = 2.75$. 