

Ferrofluid Dynamics

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Abstract. It is demonstrated how the complete structure of Newtonian ferrofluid dynamics, including magneto-dissipative effects, is derived from general principles. Ferrofluids are taken as homogeneous magnetizable fluids with a magnetic relaxation time sufficiently large to compare with other hydrodynamic time scales. The derivation makes no reference to the angular momentum of the ferromagnetic grains. The results are independent of most microscopic details, such as the form or shape of the particles or whether magneto-relaxation takes place via the intrinsic Néel process or by Brownian rotational diffusion. Both the Debye theory of Shliomis and his effective-field approach are shown to be special cases of the new set of equations.

1 Introduction and Motivation

Ferrofluids, or magnetic fluids, are colloidal suspensions of nano-sized ferromagnetic particles stably dispersed in a carrier liquid. When exposed to an external magnetic field, they behave paramagnetically, with susceptibilities χ unusually large for liquids. This property opens up a wide range for interesting and promising future applications [1,2]. Equally important, ferrofluid systems are also attractive under a theoretical point of view. Combining general fluid mechanics with electromagnetism causes ferrofluids to display many unexpected behavior, severely testing and with time perfecting our understanding of the hydrodynamics of polarizable media [1,3,4,5].

The fundamental theory for ferrofluid hydrodynamics has been worked out by Rosensweig and is well described in the first seven chapters of his text book [1]. Thereby he follows the so called *quasi-equilibrium* approach, which is based on the assumption that the local magnetization $\mathbf{M}(\mathbf{r}, t)$ is in steadfast equilibrium with the local magnetic field, i.e. $\mathbf{M}(\mathbf{r}, t) = \mathbf{M}^{\text{eq}}[\mathbf{H}(\mathbf{r}, t)]$. This theory covers a wide range of interesting and relevant effects, such as the deformation of a ferrofluid drop in a homogeneous magnetic field or the instability of a ferrofluid-air interface, when it is exposed to a magnetic field perpendicular to the surface (Rosenweig instability).

However, very soon it became evident that the *quasi-equilibrium* approximation does not suffice to account for all ferrohydrodynamic behavior, even in stationary flow configurations at static applied fields. Among the more remarkable flow phenomena which go beyond the *quasi-equilibrium* approach is the magneto-viscous effect: A ferrofluid tube flow in the presence of a static magnetic field experiences an extra dissipation, which manifests macroscopically as

an enhanced effective shear viscosity [6,3]. Even more spectacular is the acceleration of the flow in response to a high-frequency AC-field [7,8,9] (also denoted as "negative viscosity", though only a negative viscosity increment was observed). That way, the oscillating magnetic field pumps energy into the rotating motion of the ferromagnetic grains resulting in an acceleration of the flow.

The occurrence of the magneto-viscous effects is intimately related to the fact that the local magnetization $\mathbf{M}(\mathbf{r}, t)$ deviates from its equilibrium value $\mathbf{M}^{\text{eq}}[\mathbf{H}(\mathbf{r}, t)]$, where $\mathbf{H}(\mathbf{r}, t)$ is the local magnetic field. Significant increments $\delta\mathbf{M} = (\mathbf{M} - \mathbf{M}^{\text{eq}})$ are expected to appear whenever the magnetic relaxation time τ compares to the other relevant hydrodynamic time scales. Phenomena related to the finiteness of τ are commonly denoted as magneto-dissipative effects.

As outlined in Rosensweig's textbook, the microscopic mechanism responsible for the magneto-relaxation is either due to particle rotation against the viscosity of the liquid carrier (Brownian rotational diffusion) or by re-orientation of the magnetic moments relative to the crystallographic orientation of the ferromagnetic grains (Néel relaxation). Which of these mechanisms predominates depends on the specific anisotropy energy of the employed ferromagnetic material, the size of the suspended grains, and the viscosity of the carrier liquid. Since real ferrofluid suspensions usually exhibit a broader particle size distribution, it is in general a combination of both processes which determines the effective magnetic relaxation time for a given ferrofluid species.

Assuming that the Brownian mechanism is the principal source of dissipation, the intuitive picture of particles rotating against the viscous carrier lead Shliomis [3] to his theory for magneto-dissipative ferrohydrodynamics. To that end he included both the magnetization \mathbf{M} and the mechanical angular momentum density \mathbf{S} of the grains as additional thermodynamic variables. After eliminating the latter, an extra momentum flux remains, which enters the stress tensor in the form

$$\Delta\Pi_{ij} = \frac{1}{2}\varepsilon_{ijk}(\mathbf{H} \times \mathbf{M})_k, \quad (1)$$

This term exactly compensates the antisymmetric part of Maxwell's stress $H_i B_j$, if \mathbf{H} and \mathbf{M} are non-parallel. Clearly, being treated as a separate independent variable, the magnetization requires an extra evolution equation. According to Shliomis there are two versions of this equations, of which the first is a phenomenological relaxation equation with a Debye-like relaxation term in the form $\delta\mathbf{M}/\tau$. In the ferrofluid literature this approach is frequently referred to as the *Debye theory*. In combination with Eq (1), many magneto-dissipative phenomena, especially the elevated shear viscosity, were successfully explained. The second variant of his relaxation equation for \mathbf{M} is more elaborate as it is derived from a microscopic, statistical investigation of the rotary diffusion of magnetic particles. Since the problem was solved with the assistance of the effective field method, this second variant is commonly denoted as the *effective-field theory*, or *EFT*. The latter is rather more complicated and unwieldy than Debye as it provides an evolution equation for a quantity called the "effective magnetic field" from which the magnetization is to be determined in a subsequent step.

The *EFT* was found to explain the “negative viscosity” experiment much more convincingly than the Debye-like approach [8].

Comparing both theories, and emphasizing that the *EFT* is the more rigorous and accurate one, Shliomis concluded that it is valid for all experimentally relevant situations [8]. The *Debye theory*, on the other hand, he considers to be adequate only in the limit of small deviations from the magnetization equilibrium [8], $\delta M \ll M^{\text{eq}}$, implying the hydrodynamic low frequency limit $\omega\tau \ll 1$, where $1/\omega$ is the characteristic time scale of the experiment.

We do think that these assessments, referring to both (i) the general validity of the *EFT* and (ii) the limited validity of the phenomenological *Debye approach* are in need of a clarification:

First, owing to their microscopic input, *EFT* is in its essence a *microscopic theory*, with necessarily rather specific inputs. In the present case, ferrofluids are considered as suspensions of noninteracting, spherical, equal sized Brownian rigid dipoles. In the framework of these restricting simplifications, *EFT* is rigorously valid. But one always has to be aware of the limitations and deficiencies purchased with the above idealizing assumptions. Regarding the fact that real ferrofluids are suspension of interacting, non-spherical, poly-dispersed particles, whose magnetic relaxation usually involves both Brownian and Néel processes, *EFT* cannot be expected to be a sufficient approach under all circumstances.

Second, the potential of a proper *macroscopic* theory is much larger than for any *microscopic* approach, because it is constructed on the sole base of general principles, without any specific microscopic information. For ferrofluids such a macroscopic theory is very similar to Shliomis’ *Debye theory* but it will not suffer from the above constraint to the low frequency regime. In the following we shall denote such a modified approach as the *rectified Debye theory*. Demonstrating how such a macroscopic theory – we shall call it *ferrofluid dynamics (FFD)* – can be derived from the concepts of non-equilibrium thermodynamics is the purpose of this article.

Generally speaking, any macroscopic theory consists of two separate ingredients. First the structure of the equations, which is solely based on conservation laws and symmetries, and second the material-specific parameters such as susceptibilities and transport coefficients. The aim of the present lecture is to show how the general structure of a hydrodynamics for ferrofluids is derived. No attempt will be undertaken to provide values for the material-dependent coefficients. Following the standard approach in macroscopic physics, those quantities (such as viscosities or susceptibilities) are usually measured. So we leave them to be determined by a series of suitable experiments. An alternative way is to calculate the coefficients from an appropriate microscopic model. Such a model is for example *EFT* but one must not forget that it is valid in its specified range of validity. In particular it does not necessarily yield – and indeed it does not, as we shall see – the most general structure of equations, which are compatible with symmetries and conservation laws.

2 Outline of the Strategy

In this section we give a layout of our strategy for deriving the structure of the ferrofluid dynamics. We are guided by the general observation that hydrodynamic theories are a very successful tool to account for low frequency large wave number phenomena in condensed matter physics. For isotropic non-magnetic fluids the relevant variables are the conserved quantities: densities of energy, mass and momentum. For magnetizable fluids it is obvious to supplement the set of variables by the magnetic field \mathbf{H} (or the magnetic induction \mathbf{B}). That way we recover the thermodynamic variables of the *quasi-equilibrium theory*. Rosensweig assumes that the magnetization relaxation is instantaneous on the time scale of the other hydrodynamic processes of interest. In other words, \mathbf{M} is in steadfast equilibrium with the magnetic field, $\mathbf{M}(\mathbf{r}, t) = \mathbf{M}^{\text{eq}}(\mathbf{H}(\mathbf{r}, t))$. Thus magneto-dissipative effects, which necessarily imply $\delta\mathbf{M} \neq 0$, are disregarded.

It is usually believed that the interpretation of magneto-dissipative effects requires to incorporate the magnetization as an extra thermodynamic degree of freedom with its own separate evolution equation. But this is incorrect: Recall that linear electrodynamics is well able to account for dissipative effects by introducing an imaginary part of the electrical susceptibility. Focusing to the more general case of simultaneous electro- and magneto-dynamic processes, the appropriate description has been worked out in Liu's *hydrodynamic Maxwell theory (HMT)* [10]. Meanwhile this theory has been demonstrated to be well able to explain magneto-dissipative phenomena such as the field enhanced shear viscosity or the fluids spin up in a rotating field [11]. But like any hydrodynamic theory, the *HMT* is valid for small deviations from equilibrium. i.e. it is restricted to the case $\delta M \ll M^{\text{eq}}$ and the low frequency limit $\omega\tau \ll 1$. In ferrofluids τ is typically of order $10^{-4} - 10^{-3}$ s and thus the above low frequency constraint is rather severe and easily violated (for instance by the “negative viscosity” experiment). When this happens, it is justified to include the magnetization as an independent variable to render the theory applicable also to the case $\omega\tau \simeq 1$ and $\delta M/M^{\text{eq}} \simeq 1$.

In the following section we shall derive the equation of motion for the magnetization. This includes also the necessary modifications in all the other equations, which are related to the fact that \mathbf{M} is turning independent. We shall denote this approach as *ferrofluid dynamics (FFD)*. The method is standard non-equilibrium thermodynamics, with the sole input of conservation laws and symmetries. Besides the assumption that the magneto-relaxation can be covered by a single relaxation time τ there is no further material specific input. Consequently our approach is fairly general, it remains valid even if the magnetic particles interact appreciably with each other, if the particles are of non-spherical shape, or if they are of different size. Moreover, the theory holds irrespective of the microscopic relaxation mechanism, whether it is governed by the Brownian or the Néel mechanism. Furthermore, since no reference is made to the angular momentum \mathbf{S} of the grains, the result is valid both for suspensions and for homogeneous magnetizable continua. Note however, that the present approach does not cover non-Newtonian rheological effects.

3 Derivation of the Equations

In the present section we derive the structure of ferrofluid dynamics. As outlined above, the granularity of the suspension is coarse-grained, and the ferrofluid is treated as a magnetizable continuum build up of two homogeneous constituents. The variables are the conserved quantities, the electromagnetic field, and the magnetization as the only one being non-hydrodynamic. The concentration field is taken into account by the mass density of the ferromagnetic material ρ_c . This is appropriate since the magnetophoresis and Soret effect, which are fairly pronounced in ferrofluids, may build up perceptible concentration gradients.

The above arguments imply that the thermodynamic energy density u is a function of the entropy density s , total density ρ , concentration ρ_c , magnetic field \mathbf{B} , magnetization \mathbf{M} , and the momentum density $\mathbf{g} = \rho\mathbf{v}$,

$$du = Tds + \mu d\rho + \mu_c d\rho_c + \mathbf{v} \cdot d\mathbf{g} + \mathbf{H} \cdot d\mathbf{B} + \mathbf{h} \cdot d\mathbf{M}. \quad (2)$$

Eq. (2) is to be understood as the definition for the conjugate variables such as temperature T , chemical and relative chemical potentials μ and μ_c , velocity field \mathbf{v} *etc.* . In particular, the quantity \mathbf{h} is associated to the magnetization. With $\mathbf{M} \equiv \mathbf{B} - \mathbf{H}$, or $\partial H_i / \partial M_j = -\delta_{ij}$ for given B , together with the thermodynamic Maxwell relation, $\partial H_i / \partial M_j = \partial h_j / \partial B_i$, we obtain

$$\mathbf{h} = \mathbf{B}^{\text{eq}}(\mathbf{M}, s, \rho_c, \rho) - \mathbf{B} = \mathbf{H}^{\text{eq}} - \mathbf{H}. \quad (3)$$

Eq.(3) results from the requirement that u has to be minimal with respect to \mathbf{M} at $\mathbf{M} = \mathbf{M}^{\text{eq}}(\mathbf{B})$, or equivalently $\mathbf{h} \equiv \partial u / \partial \mathbf{M} = 0$. So $\mathbf{B}^{\text{eq}}(\mathbf{M})$ is the inverse function of the equilibrium magnetization curve $\mathbf{M}^{\text{eq}}(\mathbf{B})$. Subtracting \mathbf{M} from both \mathbf{B}^{eq} and \mathbf{B} , we may also write $\mathbf{h} = \mathbf{H}^{\text{eq}} - \mathbf{H}$, where again $\mathbf{H}^{\text{eq}}(\mathbf{M})$ is the inverse function of $\mathbf{M}^{\text{eq}}(\mathbf{H})$. Note that the function $\mathbf{H}^{\text{eq}}(\mathbf{M})$ is frequently referred to in the ferrofluid literature as the "effective field".

The conserved variables satisfy continuity equations,

$$\dot{\rho} + \nabla \cdot (\rho\mathbf{v}) = 0, \quad \dot{\rho}_c + \nabla \cdot (\rho_c\mathbf{v} - \mathbf{j}^D) = 0, \quad (4)$$

$$\dot{u} + \nabla \cdot \mathbf{Q} = 0, \quad \dot{g}_i + \nabla_j (\Pi_{ij} - \Pi_{ij}^D) = 0; \quad (5)$$

the equations of motion for s and \mathbf{M} are

$$\dot{s} + \nabla \cdot (s\mathbf{v} - \mathbf{f}^D) = R/T, \quad (6)$$

$$\dot{\mathbf{M}} + (\mathbf{v} \cdot \nabla)\mathbf{M} + \mathbf{M} \times \boldsymbol{\Omega} = \mathbf{X}^D, \quad (7)$$

where R is the entropy production and $\boldsymbol{\Omega} = \nabla \times \mathbf{v}/2$ the vorticity.

Assuming that no external electric field is applied, the appearance of an electric field is due solely to electromagnetic induction. Taking the ferrofluid to be dielectrically neutral (i.e. $\mathbf{D} = \mathbf{E}$) the electric contributions to the equations of motion are smaller by a factor $(v/c)^2$ than their magnetic counterparts (c is the speed of light and v a typical velocity). Accordingly, we shall set it to zero.

(See [10,12] for the cases where an external electric field is applied.) As a result, we may use the Maxwell equations in the static approximation

$$\nabla \cdot \mathbf{B} = 0, \quad \nabla \times \mathbf{H} = 0. \quad (8)$$

The fluxes in Eqs (4-7) still need to be derived – although for some of them their convective contributions such as $\rho_c \mathbf{v}$ or $(\mathbf{v} \cdot \nabla) \mathbf{M} + \mathbf{M} \times \boldsymbol{\Omega}$ have already been made explicit. To derive the unknown flux contributions we employ the so-called standard procedure of hydrodynamics: Take the temporal derivative of Eq (2), substitute \dot{u} , $T\dot{s}$, $\mu\dot{c}$... using the above equations of motion, and most importantly, require that the resultant equation to hold identically (cf [10,13] and references therein). This yields the energy flux \mathbf{Q} , the momentum flux Π_{ij} , and the entropy production R as

$$\Pi_{ij} = \Pi_{ji} = [A + H_k B_k - u] \delta_{ij} + g_i v_j - H_i B_j + \frac{1}{2} (h_j M_i - h_i M_j), \quad (9)$$

$$\mathbf{Q}_i = A v_i - T f_i^D - \mu_c j_i^D - v_j \Pi_{ji}^D + \frac{1}{2} [\mathbf{v} \times (\mathbf{h} \times \mathbf{M})]_i \quad (10)$$

$$R = \mathbf{f}^D \cdot \nabla T + \mathbf{j}^D \cdot \nabla \mu_c - \mathbf{X}^D \cdot \mathbf{h} + \Pi_{ij}^D v_{ij}, \quad (11)$$

where $A \equiv Ts + \mu\rho + \mu_c \rho_c + \mathbf{v} \cdot \mathbf{g}$, $v_{ij} \equiv \frac{1}{2}(\nabla_i v_j + \nabla_j v_i)$. To make the set of equations closed and complete one still has to determine the dissipative fluxes \mathbf{f}^D , \mathbf{j}^D , \mathbf{X}^D , Π_{ij}^D . The form of the entropy production R as given in Eq. (11) implies that they are linear combinations of the forces ∇T , $\nabla \mu_c$, $-\mathbf{h}$, v_{ij}^0 , v_{kk} , such that R is always positive. (We take $v_{ij}^0 \equiv v_{ij} - \frac{1}{3} v_{kk} \delta_{ij}$.) What now follows is the construction of the fluxes on the basis of symmetry considerations and specific assumptions, the second of which are subject to experimental verifications or microscopic scrutiny.

3.1 Weak Field Limit

If the applied magnetic field is weak, the system can be considered to be approximately isotropic. In this case we have the usual diagonal relations for the diffusive entropy and concentration currents, viscous stresses and especially the magnetic relaxation [14,2],

$$\mathbf{f}^D = \kappa \nabla T + \xi_1 \nabla \mu_c, \quad \mathbf{j}^D = \xi \nabla \mu_c + \xi_1 \nabla T, \quad (12)$$

$$\Pi_{ij}^D = 2\eta_1 v_{ij}^0 + \eta_2 v_{kk} \delta_{ij}, \quad \mathbf{X}^D = -\zeta \mathbf{h}, \quad (13)$$

The transport coefficients κ , ξ , $\kappa\xi - \xi_1^2$, η_1 , η_2 and ζ are positive functions of thermodynamic variables. In particular they also depend on the magnitude of the magnetization M . As discussed in the introductory section, their actual values need to be determined either experimentally or on the basis of an appropriate microscopic model. This is beyond the scope of the present investigation.

In compliance with results given by Blums et al. [2] and a work by Felderhof and Groh [4], we observe that the magneto-relaxation term \mathbf{X}^D is proportional to $\mathbf{h} = \mathbf{H}^{\text{eq}} - \mathbf{H}$. This is in contrast to the Debye-like increment $\delta \mathbf{M} = \mathbf{M} - \mathbf{M}^{\text{eq}}$ suggested by Shliomis [3]. We therefore denote \mathbf{X}^D according to Eq. (13) as the

rectified relaxation term. Although $\delta\mathbf{M}$ and \mathbf{h} are in general not linearly related they do in two special cases: (i) For small deviations from local equilibrium, where $\delta\mathbf{M}$ and $\mathbf{H}^{\text{eq}} - \mathbf{H}$ are proportional to each other and (ii) if the applied field is sufficiently weak for the linear constitutive relation $\mathbf{M}^{\text{eq}} = \chi\mathbf{H}$ to apply.

We now turn to compare our stress tensor Π_{ij} with the traditional formulation. We start with the observation that the last term in (9) is equivalent to the magneto-dissipative element as given in Eq.(1). This term accounts for magneto-dissipation when the vectors \mathbf{H} and \mathbf{M} are twisted relative to each other. This happens for instance in the McTague experiment [6], where the vorticity of the flow deflects the magnetization vector out of the equilibrium direction.

We emphasize that the condition for the appearance of magneto-dissipative effects, $\mathbf{M} \neq \mathbf{M}^{\text{eq}}$, does not necessarily require the two vectors \mathbf{H} and \mathbf{M} to point in different directions. For instance, magneto-dissipation is also expected to occur if \mathbf{M} and \mathbf{H} oscillate *parallel* to each other but with a *temporal* phase lag. Note that in this situation Eq.(1) is inoperative, so the Shliomis theory does not yield a magneto-dissipative stress here. However, as will become clear in a moment, *FFD* does. To facilitate further comparison with the conventional notation of the stress tensor we rewrite the diagonal contribution to [Eq. (9)] in terms of the zero-field pressure $p_0(\rho, T)$. To that end we perform a Legendre transformation to the independent variables T , ρ , \mathbf{v} , H , and M (for simplicity we neglect the concentration dynamics by assuming $\rho_c = \text{const}$). The associated thermodynamic free energy $f = u - sT - \mathbf{v} \cdot \mathbf{g} - \mathbf{H} \cdot \mathbf{B}$ has the total differential

$$df = -sdT + \mu d\rho - \mathbf{g} \cdot d\mathbf{v} - \mathbf{B} \cdot d\mathbf{H} + \mathbf{h} \cdot d\mathbf{M}. \quad (14)$$

Integrating out velocity and magnetic dependencies leads to

$$f(T, \rho, \mathbf{v}, \mathbf{H}, \mathbf{M}) = f_0(\rho, T) - \frac{1}{2}\rho v^2 - \frac{1}{2}H^2 - \mathbf{M} \cdot \mathbf{H} + \int_0^M H^{\text{eq}}(T, \rho, M') dM', \quad (15)$$

where $f_0(T, \rho) = f(T, \rho, \mathbf{v} = \mathbf{H} = \mathbf{M} = 0)$. Using the thermodynamic relation for the zero-field pressure $p_0(T, \rho) = -f_0 + \rho \partial f_0 / \partial \rho$ and the integral identity

$$\mathbf{H}^{\text{eq}} \cdot \mathbf{M} - \int_0^M (1 - \rho \partial_\rho) H^{\text{eq}}(T, \rho, M') dM' = \int_0^{H^{\text{eq}}} (1 - \rho \partial_\rho) M^{\text{eq}}(T, \rho, H') dH' \quad (16)$$

the diagonal contribution to the stress [square bracket of Eq (9)] transforms into

$$\delta_{ij} \left[p_0 + \frac{1}{2}H^2 + \int_0^{H^{\text{eq}}} (1 - \rho \partial_\rho) M^{\text{eq}}(H') dH' - \mathbf{h} \cdot \mathbf{M} \right]. \quad (17)$$

The last term $\mathbf{h} \cdot \mathbf{M}$ is missing from previous works. As outlined above it accounts for magneto-dissipation in a situation where the off-equilibrium increment \mathbf{h} is *parallel* to the magnetization. For an illustration of what are the physical significances of the two different magneto-dissipative stresses, $(1/2)\varepsilon_{ijk}(\mathbf{H} \times \mathbf{M})_k \equiv (1/2)\varepsilon_{ijk}(\mathbf{M} \times \mathbf{h})_k$ and $\delta_{ij}(\mathbf{h} \cdot \mathbf{M})$ let us consider the force exerted by a ferrofluid on a rigid container wall. Multiplying the antisymmetric element with the surface normal vector leads to a *tangential* traction proportional to $\mathbf{H} \times \mathbf{M}$. On the

other hand, the diagonal tensor element implies a magneto-dissipative *normal* force linear in $(\mathbf{h} \cdot \mathbf{M})$. This term may be probed by a measurement of the pressure drop across an interface between a ferrofluid and a non-magnetic medium. Since it is a dynamical effect, the interface must be exposed to a time-dependent magnetic field. The expected effect is maximized when the oscillation frequency ω approaches the inverse magnetic relaxation time $1/\tau$.

The reason magneto-dissipative normal stresses have not been discussed until now, may be due to the present focus on incompressible flow configurations. For that kind of flow problems any extra normal stress simply re-normalizes the pressure while leaving the velocity profile unchanged. If, however, normal forces are directly recorded, the associated magneto-dissipative contribution is likely to be measurable. An alternative way to probe the implications of the extra normal stress is the study of compressible flow configurations such as sound. We expect that the coupling between density oscillations and the magnetization will contribute appreciably to the attenuation.

3.2 Strong Magnetic Fields

In the weak field limit discussed in the previous subsection we have seen that the evolution equation for \mathbf{M} as well as the stress tensor Π_{ij} deviate from the expressions given by the previous approach. In the presence of a strong magnetic field, the system can no longer be considered to be isotropic. So, further modifications arise since the resulting uniaxial symmetry of the system leads to a proliferation of the transport coefficients. This is where experimental input becomes imperative. For instance, each of the coefficients of Eq (12) turns into three, as in $\kappa \rightarrow \kappa\delta_{ij} + \kappa_{\parallel}M_iM_j + \kappa_{\times}\epsilon_{ijk}M_k$. Similarly, the two viscosities turn into 7. It is not very useful to present all these complications here because the set of isotropic coefficients needs yet to be measured. Strictly speaking, if the directions of \mathbf{M} and \mathbf{H} do not coincide (as is usually the if magneto-dissipative effects come into effect), the system becomes biaxial. This leads to an extra complication, which however will be ignored here.

In the following we focus on the complete uniaxial form of \mathbf{X}^D , since the magnetization dynamics belongs to the best studied aspects of ferrofluid physics. Following the linear construction scheme for deriving the contributions to the dissipative flux \mathbf{X}^D leads us to

$$\begin{aligned} X_i^D = & -(\zeta\delta_{ij} + \zeta_{\parallel}M_iM_j + \zeta_{\times}\epsilon_{ijk}M_k)h_j \\ & + \lambda_1M_iv_{kk} + \lambda_2M_jv_{ij}^0 + \lambda_3M_iM_jM_kv_{jk}^0 \\ & + \lambda_4\epsilon_{ikj}M_kM_{\ell}v_{j\ell}^0. \end{aligned} \quad (18)$$

Then the Onsager symmetry relations enforce the following counter terms in the stress tensor

$$\begin{aligned} \Pi_{ij}^D = & \{\eta_2v_{kk} + [\lambda_1 - \frac{1}{3}(\lambda_2 + M^2\lambda_3)]M_kh_k\}\delta_{ij} \\ & + 2\eta_1v_{ij}^0 + \frac{1}{2}\lambda_2(M_ih_j + M_jh_i) + \lambda_3M_iM_jM_kh_k \\ & + \frac{1}{2}\lambda_4[M_j(\mathbf{M} \times \mathbf{h})_i + (i \leftrightarrow j)]. \end{aligned} \quad (19)$$

Although these expressions appear complicated, one must realize that the uniaxial, and not the isotropic, case is the generic one: If we take M as small to arrive at the isotropic case, we must for consistency also neglect all term $\sim M^2$ in the Maxwell stress, which is considered too crude an approximation to be employed frequently.

The appearance of the parameters ζ , ζ_{\parallel} and ζ_{\times} in X_i^D implies different relaxation times for the respective magnetization components parallel to \mathbf{h} , parallel to \mathbf{M} and perpendicular to both of these directions. The latter one is analogous to the Righi-Leduc effect in heat conduction or the Hall effect of an electrical conductor.

In the *Debye theory*, the *EFT*, or the isotropic case considered in the previous subsection, the only velocity gradient entering $\dot{\mathbf{M}}$ is the flow vorticity $\boldsymbol{\Omega}$. This is in contrast to Eq. (18), which suggests that a compressional flow v_{kk} , and even more importantly, an elongational flow v_{ij}^0 will do this too. The coefficients λ_i are material dependent and need to be measured for each ferrofluid. They are *reactive* transport coefficients (as opposed to dissipative ones), because they do not enter the expression for the entropy production (11). Nevertheless, as these coefficients appear as a product either with velocity gradients [Eq. (18)] or with the magneto-dissipative increment \mathbf{h} [Eq. (19)], they can only be evaluated by an appropriate off-equilibrium experiment. It is noteworthy that a term similar to $v_{ij}^0 M_j$ is known to appear in the dynamics of nematic liquid crystals [15], where it gives rise to the “flow alignment” of the nematic director in response to a shear flow.

For a quantitative experimental test of whether λ_2 for a given ferrofluid material is of significant size one has to study the magnetization dynamics in flow geometries which allow to control the relative strength between elongational and rotational flow contributions. This requirement is easy to fulfill by the flow between two rotating cylinders (Couette-Taylor setup). Allowing the two cylinders to rotate independently with distinct angular frequencies Ω_1 and Ω_2 , enables to pass over from a rigid rotation ($v_{ij} = 0$), where $\Omega_1 = \Omega_2$, to a flow with a finite shear rate, where $v_{ij} \propto (\Omega_1 - \Omega_2) \neq 0$. Recording the magnetization vector within the sample (or equivalently the magnetic field outside of the sample) as a function of $\Omega_1 - \Omega_2$ allows to evaluate the transport coefficient λ_2 .

4 Comparison with Existing Theories

In the introductory section we outlined that the macroscopic ferrofluid dynamics set up here provides the general macroscopic framework, any more specific (microscopic) approach has to fit in. In the present section the focus is on the relaxation equation for the magnetization. The modifications/extensions of the stress tensor as compared to previous theories have already been discussed in the last paragraph.

It will be shown here that both the *Debye theory* and *EFT* can be embedded into the formulae given by *FFD*, each with a specific choice of parameters.

4.1 The Debye Theory

In the first variant of his description, Shliomis [3] introduces a phenomenological equation for \mathbf{M} , with a linear Debye-like relaxation term proportional to $\delta\mathbf{M} = \mathbf{M} - \mathbf{M}^{\text{eq}}$. This equation results from what we consider to be a “mesoscopic” approach, because the derivation makes use of some specific microscopic input. The ferromagnetic grains are considered to be Brownian rigid dipoles. To account for their rotation the angular momentum density \mathbf{S} is introduced as an extra dynamical variable. But not really, since in a later stage of the derivation, \mathbf{S} is re-eliminated owing to the smallness of the particles’ inertia. The phenomenological relaxation equation for \mathbf{M} which remains after this adiabatic substitution takes on the following form

$$\frac{d\mathbf{M}}{dt} - \boldsymbol{\Omega} \times \mathbf{M} = \frac{1}{\tau_B}(\mathbf{M}^{\text{eq}} - \mathbf{M}) - \frac{\mathbf{M} \times (\mathbf{M} \times \mathbf{H})}{6\eta_1\varphi}. \quad (20)$$

Here $(d/dt) \equiv \partial_t + (\mathbf{v} \cdot \nabla)$, τ_B is the Brownian relaxation time, and φ the volume concentration. As pointed out above and by other authors [2,4], the proper relaxation term being rather more in line with the construction rules of non-equilibrium thermodynamics is proportional to \mathbf{h} rather than $\delta\mathbf{M}$. This is what we have referred to as the *rectified* relaxation term. In the limit of small deviations from the magnetization equilibrium, we have a linear relationship between $\delta\mathbf{M}$ and \mathbf{h}

$$\mathbf{M} - \mathbf{M}^{\text{eq}} = \frac{M^{\text{eq}}}{H} \mathbf{h} + \left(\frac{\partial M^{\text{eq}}}{\partial H} - \frac{M^{\text{eq}}}{H} \right) \frac{\mathbf{M} \cdot \mathbf{h}}{(M^{\text{eq}})^2} \mathbf{M} + \mathcal{O}(h^2). \quad (21)$$

Replacing the leading order approximation of (21) into Eqs (7,18), we recover Shliomis’ *Debye theory* (20) by the following choice of the transport coefficients

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda_4 = \zeta_{\times} = 0, \quad (22)$$

$$\zeta = \frac{1}{\tau_B} \frac{M^{\text{eq}}}{H} + \frac{(M^{\text{eq}})^2}{6\eta_1\varphi}, \quad (23)$$

$$\zeta_{\parallel} (M^{\text{eq}})^2 = \frac{1}{\tau_B} \left(\frac{\partial M^{\text{eq}}}{\partial H} - \frac{M^{\text{eq}}}{H} \right) - \frac{(M^{\text{eq}})^2}{6\eta_1\varphi}. \quad (24)$$

4.2 Effective-Field Theory

On the basis of a kinetic equation for rotary diffusion, Martsenyuk et al. [16] constructed the Fokker-Planck equation for the probability distribution of the particle’s orientation. The authors relied on the idealizing assumptions that the ferrofluid is composed of (i) spherical (ii) mono-dispersed (iii) non-interacting (iv) rigid dipoles. From the resultant infinite hierarchy of equations for the momenta of \mathbf{M} , a separate equation for the magnetization is deduced by employing the method of the effective field. Thereby the magnetization

$$\mathbf{M} = M_s \mathcal{L}(\xi_e) \frac{\xi_e}{\xi_e} \quad (25)$$

is taken to be a function of the dimensionless, effective field $\xi_e = (m\mathbf{H}^{\text{eq}})/(k_B T)$, with M_s denoting the saturation magnetization of the ferrofluid, m the magnetic moment of an individual particle, $\mathcal{L}(x) = \coth x - 1/x$ the Langevin function and k_B the Boltzmann constant. In terms of the actual non-dimensional magnetic field $\xi = (m\mathbf{H})/(k_B T)$, the effective field is governed by the ordinary differential equation

$$\begin{aligned} \frac{d}{dt} \left[\mathcal{L}_e \frac{\xi_e}{\xi_e} \right] &= \boldsymbol{\Omega} \times \left[\mathcal{L}_e \frac{\xi_e}{\xi_e} \right] - \frac{1}{\tau_B} \frac{\mathcal{L}_e}{\xi_e} (\xi_e - \xi) - \\ &\frac{1}{2\tau_B \xi_e^2} \left(1 - \frac{3\mathcal{L}_e}{\xi_e} \right) \xi_e \times (\xi_e \times \xi), \end{aligned} \quad (26)$$

where $\mathcal{L}_e = \mathcal{L}(\xi_e)$. This equation has to be solved for ξ_e for given ξ . Then in a second step, the magnetization is to be deduced from ξ_e via (25).

We point out that this somewhat unwieldy two-step procedure can be circumvented. Without approximation Eq. (26) can be recast in the following, rather more explicit form

$$\begin{aligned} 2\tau_B \left\{ \frac{d}{dt} \mathbf{M} - \boldsymbol{\Omega} \times \mathbf{M} \right\} &= \\ - \left[3\chi - \frac{M}{H^{\text{eq}}} \right] \mathbf{h} - 3 \left[\frac{M}{H^{\text{eq}}} - \chi \right] \frac{\mathbf{M} \cdot \mathbf{h}}{M^2} \mathbf{M}. \end{aligned} \quad (27)$$

Here $\chi = mM_s/(3k_B T)$ denotes the initial Langevin susceptibility. It is noteworthy to point out that the *EFT* approach yields a relaxation term, which is proportional to \mathbf{h} rather than $\delta\mathbf{M}$, i.e. well in compliance with the *rectified Debye theory* outlined above. So it does not come as a surprise that Eq. (27) is recovered as a special case of the general structure of *FFD* as given by Eqs (7,18). The following particular parameter choice applies

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda_4 = \zeta_{\times} = 0, \quad (28)$$

$$\zeta = \frac{1}{2\tau_B} \left[3\chi - \frac{M}{H^{\text{eq}}} \right], \quad (29)$$

$$\zeta_{\parallel} = \frac{3}{2} \frac{1}{\tau_B} \frac{1}{M^2} \left[\frac{M}{H^{\text{eq}}} - \chi \right]. \quad (30)$$

Clearly, owing to its microscopic input the *EFT* provides a dependence for the transport coefficients ζ and ζ_{\parallel} on the strength of the magnetization, a feature which cannot be accomplished by the macroscopic *FFD*. That is why *EFT* is a complementary approach rather than being competitive. On the other hand, the disappearance of many of the transport coefficients [see Eq. (28)], an immediate consequence of the idealizing assumptions, reflects the limitations of *EFT*. Real ferrofluids generally do not meet these approximations. So one either has to develop a more elaborate theory, or – following the standard approach in macroscopic physics – to determine the set of transport coefficients by a series of appropriate experiments.

5 Conclusion

The general structure of the hydrodynamic equations for ferrofluids is derived here. The gain in rigour is paid by a loss of specific information on the transport parameters. We did not provide the numerical values of the transport coefficients here, nor their dependence on the thermodynamic variables. This task is left open for a series of experiments. An alternative way – albeit less reliable and less quantitative – is to derive this information from a microscopic theory such as *EFT*. Besides giving numerical estimates for the transport coefficients their primary advantage is to provide physical insight into their dependencies on the thermodynamic variables.

In spite of the complete lack of microscopic specifics in the present derivation, the resultant theory does have some restrictions that we need to keep in mind. They arise due to the assumption that a unique characteristic time τ is sufficient to characterize the magnetic relaxation process. As a result, any microscopic features (such as poly-dispersity) that influence this time are to be handled with some care. For instance, a ferrofluid consisting of two populations, each with a distinct relaxation time, will not be well accounted for at higher frequencies, outside the hydrodynamic regime.

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