Structure of ferrofluid dynamics

Hanns Walter Müller[1,*] and Mario Liu[2,†]
[1]*Max-Planck-Institut für Polymerforschung, D-55128 Mainz, Germany*
[2]*Institut für Theoretische Physik, Universität Hannover, 30167 Hannover, Germany*
(Received 29 June 2000; revised manuscript received 3 July 2001; published 27 November 2001)

The complete magnetodissipative structure of ferrofluid dynamics is derived from general principles, without reference to the angular momentum of the ferromagnetic grains. The results are independent of most microscopic details, and easily interpret two previous experiments. Both the Debye theory and the effective-field theory by Shliomis are shown to be special cases of the new set of equations.

DOI: 10.1103/PhysRevE.64.061405 PACS number(s): 47.10.+g, 75.50.Mm

I. INTRODUCTION

Since its inception about thirty years ago, ferrofluid physics has been very successful in obtaining a concise understanding of its varying phenomena [1,2]. There are broadly speaking three theories more widely applied to understanding ferrofluids: the *quasiequilibrium theory, Debye theory*, and EFT. The first was introduced by Rosensweig, who employed it in the first seven chapters of his book [1] to account for a wide range of interesting effects. In this theory, the magnetization $\boldsymbol{M}(\boldsymbol{r},t)$, being in steadfast equilibrium with the magnetic field, $\boldsymbol{M}(\boldsymbol{r},t)=\boldsymbol{M}^{\mathrm{eq}}[\boldsymbol{H}(\boldsymbol{r},t)]$, is not an independent variable.

With the detection of the enhanced shear viscosity in a static magnetic field [3], however, it became evident that the quasiequilibrium approximation is not always appropriate, even in stationary flow configurations at static applied fields. Starting from the intuitive picture of magnetic particles rotating against the viscosity of the carrier liquid as the actual source of dissipation, Shliomis [4] included both the magnetization **M** and the angular momentum density **S** as additional variables—though the latter is usually adiabatically eliminated afterwards. This theory accounts for magnetodissipation, and contains an extra term in the momentum flux,

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

which compensates the antisymmetric contribution from the term H_iB_j if **H** and **M** are nonparallel.

There are two versions for the temporal evolution of the magnetization, of which the first is a relaxation equation with a Debye-like relaxation term $\delta\mathbf{M}/\tau_{\mathrm{M}}\equiv(\mathbf{M}-\mathbf{M}^{\mathrm{eq}})/\tau_{\mathrm{M}}$. This is frequently referred to as the *Debye theory*. In combination with Eq. (1), many magnetodissipative phenomena, especially the elevated shear viscosity, were successfully explained. Later works [5,6] brought this equation more in line with the prescriptions of irreversible thermodynamics by substituting the term $\delta\mathbf{M}/\tau_{\mathrm{M}}$ with one proportional to the "effective field," $\boldsymbol{h}\equiv\partial u/\partial\boldsymbol{M}$, where u is the energy density [cf. the text around Eq. (3) for a more detailed discussion of $\boldsymbol{h}$]. We shall refer to this modification as the "*rectified Debye theory*."

When the "negative viscosity" experiment of Bacri *et al.* [7] contradicted the *Debye theory*, Shliomis referred to a more elaborate evolution equation for **M** [8], derived from a microscopic, statistical investigation of rotating magnetic particles. Since the equation was solved with the assistance of the effective field method, this second variant is commonly denoted as the EFT. The EFT improved the agreement to the "negative viscosity" experiment considerably.

Comparing both theories, and assuming that the EFT is the more rigorous one, valid for all experimentally relevant frequencies, Shliomis concluded that the *Debye theory* is adequate only for small deviations of the magnetization, $\delta M \ll M^{\mathrm{eq}}$, implying small frequencies, $\omega\tau_{\mathrm{M}}\ll 1$, of the magnetic field. In other words, it is valid only in the hydrodynamic regime. This conclusion is widely echoed in the ferrofluid community. For instance, when repeating the "negative viscosity" experiment in a more elaborate setup [9], it was deemed necessary to interpret the results in the context of the EFT—although it is (in its original form) rather more complicated and unwieldy than the *Debye theory*.

We do not think that this understanding of the respective range of validity does justice to the *Debye theory*. We believe that the proper macroscopic theory for ferrofluids is very similar to the *Debye theory*: As will be shown below, the *rectified Debye theory* is in fact well capable of accounting for the experimental data on "negative viscosities," somewhat better than EFT. We also believe that EFT is in its essence a microscopic theory, with necessarily rather specific inputs. In this case, they are: noninteracting, spherical, equal sized, and rigid dipoles. As a result, in spite of it being a rigorously valid theory, it is not always a realistic one.

Generally speaking, a macroscopic theory consists of two independent components. First is the structure as given by general principles and irreversible thermodynamics, and second is the set of the material-dependent parameters, i.e., the value of susceptibilities and transport coefficients. The main purpose of this paper is to specify the structure of a dynamic theory appropriate for ferrofluids. We shall not attempt to provide the value for the material-dependent parameters—as is the standard approach in macroscopic physics—leaving them to be determined by suitable experiments, one set for each type of ferrofluid.

*Email address: hwm@mpip-mainz.mpg.de
†Email address: liu@itp.uni-hannover.de

When comparing our results with EFT and the *rectified Debye theory*, we find both to be compatible with the general structure in the incompressible limit—although each possesses a set of transport coefficients that may be too specified, and, therefore, inappropriate for the special ferrofluid under consideration. Especially, all off-diagonal transport coefficients have been set to zero, a step that seems in need of scrutiny. We shall point to evidences from a previous experiment on magnetovortical resonance [10], which indicates that (at least) one such off-diagonal coefficient is finite. We shall also suggest experiments to directly measure some of these parameters.

In the compressible limit, the derived structure opens up new channels for magnetic dissipation: All three previous versions of ferrofluid dynamics (FFD) (i.e., *Debye*, *rectified Debye*, and EFT) predict magnetodissipative coupling to the flow only in situations where the deviation of the magnetization $\delta\mathbf{M}$ is perpendicular to the external field $\mathbf{H}$. Although this may appear intuitive from the picture of internal rotation, there is no convincing reason why magnetoviscous effects should not also occur when $\delta\mathbf{M}$ and $\mathbf{H}$ oscillate colinearly, with a temporal phase lag. We have obtained an off-equilibrium contribution to the total momentum flux tensor, which may be written as $\delta\mathbf{M}\cdot\mathbf{M}/\chi$. This is analogous to the term of Eq. (1), rewritable as $\delta\mathbf{M}\times\mathbf{H}$. Being a diagonal contribution to the stress, this term is associated with a normal traction and affects compressible flows such as sound propagation [11].

Next, we lay out our strategy for deriving the structure, a strategy motivated by the observation that hydrodynamic theories are successfully employed to account for slow, nonequilibrium phenomena of many condensed systems. The proper theory for any isotropic fluid has its conserved quantities as dynamic variables: the densities of energy, mass, and momentum. These are also its thermodynamic variables. If the fluids are magnetizable, the thermodynamic variables include the magnetic field, so one also needs to add it to the set of independent, dynamic variables. These are clearly the set of variables of the *quasiequilibrium theory* by Rosensweig. And indeed, as shown in Refs. [12,13], this theory is well capable of accounting for all low-frequency, nonequilibrium phenomena in ferrofluids if it is amended with the proper dissipative structure—call the result HMT, from *hydrodynamic Maxwell theory*. It accounts for many magnetodissipative phenomena, including field-enhanced viscosities [13] and the fluid's spin-up via a rotating field [12].

As in any hydrodynamic theory, the HMT is valid for small deviations of the implicit degrees of freedom from their equilibrium values, and in the low-frequency regime $\omega\tau_i \ll 1$, where τ_i denote their characteristic times. This includes especially the magnetization $\mathbf{M}$. So HMT is valid only for $\delta M \ll M^{\mathrm{eq}}$ and $\omega\tau_{\mathrm{M}} \ll 1$. This is the definition of the hydrodynamic regime. However, the magnetic relaxation time τ_{M} in ferrofluids is typically of order 10^{-4} s and is much larger than all the other τ_i ($\gtrsim 10^{-9}$ s), so the constraint $\omega\tau_{\mathrm{M}} \ll 1$ is the most severe and most easily violated one. When this happens (e.g., in the "negative viscosity" experiment), one has to include the magnetization as an independent variable to render the theory valid also for $\omega\tau_M \simeq 1$ and $\delta M/M^{\mathrm{eq}} \simeq 1$ (yet still $\omega\tau_i \ll 1$ for all the other τ_i). For these higher frequencies, and not in the hydrodynamic regime, is it necessary to introduce the magnetization as an independent variable. And this is also the reason why the *rectified Debye theory*, with the magnetization as an independent variable, has proven rather competent in accounting for the high-frequency experiment on "negative viscosities"—assuming that the off-diagonal transport coefficients mentioned above either vanish or do not couple in.

We shall derive both the equation of motion for the magnetization and the modifications in the other equations of motion due to the fact that the magnetization is turning independent. We do this by means of standard nonequilibrium thermodynamics, with the sole input of conservation laws, system symmetries, and the requirement that it reduces to the HMT for $\omega\tau_{\mathrm{M}} \ll 1$. (This is similar in its ideology to an earlier work, in which the electrical polarization and its temporal derivative were included as slow variables [14]). The chosen approach, in spite of the assumption of a single characteristic time associated with the slow variable, clearly lacks specifics and is, therefore, fairly general. There are a few noteworthy points as a result.

First, in contrast to all previous derivations, no reference was made with respect to the angular momentum $\boldsymbol{S}$ of the ferromagnetic grains. The result is, therefore, valid both for suspensions and for homogeneous magnetizable continua.

Second, the theory holds irrespective of the type of magnetic relaxation, whether the individual magnetic moments rotate freely against the crystal axis, or are fixed, and the particle has to rotate against the viscous torque of the carrier liquid ("Néel" versus "Brown").

Third, the equations of motion remain valid even if the magnetic particles interact appreciably with each other.

II. DERIVATION OF THE EQUATIONS

In this section the structure of ferrofluid dynamics is derived and presented. As outlined above, we the granularity of the suspension is coarse grained, and the ferrofluid is treated as a magnetizable continuum. The variables are the conserved quantities, the electromagnetic field, and the magnetization as the only one being nonhydrodynamic. As a conserved quantity, the concentration ρ_c (mass of magnetic particles over total volume) is a bona fide hydrodynamic variable, which must be included if the structure is to be complete. Because of the pronounced magnetophoresis and Soret effect, this remains so in spite of the long time needed to establish concentration gradients. In addition, the case of two conserved densities leads to surprising and little noted complications. For instance, the incompressible limit is no longer associated with $\nabla\cdot\boldsymbol{v}=0$, because the magnetic particles are much denser than the liquid, and changing the concentration will change the total density even if both constituent densities are constant. So the thermodynamic energy density u is taken as a function of the entropy density s, total density ρ, concentration ρ_c, magnetic field $\mathbf{B}$, magnetization $\mathbf{M}$, and the momentum density $\boldsymbol{g}=\rho\boldsymbol{v}$,

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

which defines the conjugate variables, especially $\mathbf{h}$. With $\mathbf{M} \equiv \mathbf{B}-\mathbf{H}$, or $\partial H_i/\partial M_j = -\delta_{ij}$ for given B, and the Maxwell relation, $\partial H_i/\partial M_j = \partial h_j/\partial B_i$, we have

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

In equilibrium, u is minimal with respect to $\mathbf{M}$, or $\mathbf{h} \equiv \partial u/\partial \mathbf{M} = 0$. So $\mathbf{B}^{\mathrm{eq}}(\mathbf{M})$ is the inverse function of the equilibrium magnetization curve $\mathbf{M}^{\mathrm{eq}}(\mathbf{B})$. Subtracting $\mathbf{M}$ from both $\mathbf{B}^{\mathrm{eq}}$ and $\mathbf{B}$, we may also write $\mathbf{h} = \mathbf{H}^{\mathrm{eq}} - \mathbf{H}$, where again $\mathbf{H}^{\mathrm{eq}}(\mathbf{M})$ (frequently referred to as the ''effective field'') is the inverse function of $\mathbf{M}^{\mathrm{eq}}(\mathbf{H})$.

The conserved variables satisfy continuity equations,

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

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

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

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

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

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 Refs. [12,14] for the cases where an external electric field is applied.) As result, we may use the Maxwell equations in the static approximation

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

The fluxes in Eqs. (4)–(7) still need to be derived—although the convective terms such as $\rho_c\boldsymbol{v}$ or $(\boldsymbol{v}\cdot\nabla)\mathbf{M} + \mathbf{M}\times\boldsymbol{\Omega}$ are already displayed, as they only redefine the unknown ones, being $\mathbf{j}^D$ and $\mathbf{X}^D$ in the present two examples. The fluxes are derived employing the so called standard procedure of hydrodynamics: Take the temporal derivative of Eq. (2), substitute $\dot{u}, T\dot{s}, \mu\dot{\rho}\cdots$ using the above equations of motion, and most importantly, require that the resultant equation to hold identically (cf Refs. [12,15] and references therein). This yields the energy flux $\mathbf{Q}$, the momentum flux Π_{ij}, and the entropy production R as

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

$$Q_i = A v_i - T f_i^D - \mu_c j_i^D - v_j \Pi_{ji}^D + \tfrac{1}{2}[\boldsymbol{v}\times(\boldsymbol{h}\times\boldsymbol{M})]_i, \tag{10}$$

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

where $A \equiv Ts + \mu\rho + \mu_c\rho_c + \boldsymbol{v}\cdot\boldsymbol{g}$, $v_{ij} \equiv \frac{1}{2}(\nabla_i v_j + \nabla_j v_i)$. This is the structure of ferrofluid dynamics. 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 $\boldsymbol{\nabla}T, \boldsymbol{\nabla}\mu_c, -\mathbf{h}, v_{ij}^0, v_{kk}$, 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.

A. Weak-field limit

If the applied magnetic field is weak, the system is almost isotropic and we have the usual relations of diffusive entropy and concentration current, viscous stress and especially the magnetic relaxation [16,5],

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

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

The transport coefficients $\kappa, \xi, \kappa\xi - \xi_1^2, \eta_1, \eta_2$, and ζ are positive functions of thermodynamic variables, in particular, of the magnitude of the magnetization M. Their actual values need to be determined either experimentally or on the basis of an appropriate microscopic model.

The relaxational term $\mathbf{X}^D$ in the magnetization dynamics is proportional to $\mathbf{h} = \mathbf{H}^{\mathrm{eq}} - \mathbf{H}$ (instead of to $\delta\boldsymbol{M}$, or what we have referred to as the *rectified Debye theory*). For small deviations from local equilibrium, it reduces to the Shliomis expression proportional to $\delta\mathbf{M} = \mathbf{M} - \mathbf{M}^{\mathrm{eq}}$, but not in situations where $\delta\mathbf{M}$ is large. The associated contribution to the entropy production, $-\mathbf{X}^D\cdot\mathbf{h}$, is in either case positive semidefinite.

When comparing our stress tensor with the traditional formulation we note that the last term in Eq. (9) is equivalent to the magnetodissipative element as given in Eq. (1). To facilitate further comparison we introduce the usual zero-field pressure $p_0(\rho, T)$ while employing the independent variables ρ, T, H, and M (assuming ρ_c is constant). Then the expression in the square bracket of Eq. (9) reads

$$p_0 + \frac{1}{2}H^2 + \int_0^{H^{\mathrm{eq}}} (1 - \rho\partial_\rho) M^{\mathrm{eq}}(H')\, dH' - \mathbf{h}\cdot\mathbf{M}. \tag{14}$$

The last term $\mathbf{h}\cdot\mathbf{M}$ is missing from previous works. It describes magnetodissipative effects if the off-equilibrium component $\mathbf{h}$ is parallel to the magnetization. This happens, for instance, when $\mathbf{M}$ and $\mathbf{H}$ oscillate parallel to each other with a temporal phase lag. While the antisymmetric element, Eq (1), implies a finite tangential traction, the term $\mathbf{h}\cdot\mathbf{M}$ is associated with a magnetodissipative normal force. This term may be probed by measuring the pressure drop across an interface between a ferrofluid and a nonmagnetic medium, if it is exposed to an oscillating magnetic field. The expected effect is maximized when the frequency approaches the in-

verse relaxation time $\tau_M \to \zeta/\chi$. The reason magnetodissipative normal stress has not been discussed until now may be due to the present focus on incompressible flow problems, for which a normal stress simply renormalizes the pressure while leaving the velocity profile unchanged. If, however, compressible flow profiles such as sound are considered, the coupling between density oscillations and magnetization will contribute appreciably to damping. This will be discussed in a forthcoming publication.

B. Strong magnetic fields

If the magnetic field is no longer weak, the symmetry characterizing the system is uniaxial, leading to a proliferation of transport coefficients. This is where experimental input becomes imperative. For instance, each of the coefficients of Eq. (12) turns into three, as in $\kappa \to \kappa\delta_{ij} + \kappa_\parallel M_i M_j + \kappa_\times \epsilon_{ijk} M_k$. Similarly, the two viscosities turn into seven. We shall not present all these complications here because the set of isotropic coefficients needs yet to be measured. (Strictly speaking, if the directions of **M** and **H** do not coincide, the system is biaxial, which represents an additional and considerable complication.) Nevertheless, we would like to consider the complete uniaxial form of $\mathbf{X}^D$, as $\dot{\mathbf{M}}$ belongs to the best studied aspects of ferrofluid physics. Due to the Onsager symmetry relation, counter terms necessarily appear in the stress,

$$X_i^D = -(\zeta\delta_{ij} + \zeta_\parallel M_i M_j + \zeta_\times \epsilon_{ijk} M_k) h_j + \lambda_1 M_i v_{kk} + \lambda_2 M_j v_{ij}^0 + \lambda_3 M_i M_j M_k v_{jk}^0 + \lambda_4 \epsilon_{ikj} M_k M_\ell v_{j\ell}^0, \tag{15}$$

$$\Pi_{ij}^D = \{\eta_2 v_{kk} + [\lambda_1 - \tfrac{1}{3}(\lambda_2 + M^2\lambda_3)] M_k h_k\}\delta_{ij} + 2\eta_1 v_{ij}^0 + \tfrac{1}{2}\lambda_2 (M_i h_j + M_j h_i) + \lambda_3 M_i M_j M_k h_k + \tfrac{1}{2}\lambda_4 [M_j (\boldsymbol{M}\boldsymbol{h})_i + (i \leftrightarrow j)]. \tag{16}$$

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 parameter $\zeta_\parallel$ in X_i^D implies different relaxation times for the parallel and perpendicular component of the magnetization. The value of the perpendicular time, for a series of five different ferrofluids, is provided in Ref. [17].

In both *Debye theories*, the EFT, or the isotropic case above, the only velocity gradient changing $\dot{\mathbf{M}}$ is $\boldsymbol{\Omega}$. In contrast, Eq. (15) shows that a compressional flow v_{kk}, or more importantly, an elongational one 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, because they do not enter the expression for the entropy production (11). Nevertheless, as these coefficients appear in combination either with velocity gradients [Eq. (15)] or with **h** [Eq. (16)], they can only be evaluated by an appropriate off-equilibrium experiment. It is noteworthy that the same term exists in the dynamics of nematic liquid crystals [18], where it is responsible for the well-known ''flow alignment'' of the director field in an applied shear flow.

III. COMPARISON WITH EXISTING THEORIES

The modifications of the stress tensor as compared to the standard expression have already been discussed at the end of Sec. II A. Here, the focus is on the relaxation equation for the magnetization. It will be shown that both the *Debye theory* and EFT can be embedded into the above formula, each with a specific choice of parameters. They may be taken as special cases of Eqs (7) and (15). (We are more precisely considering the *rectified Debye theory* which, however, reduces to the *Debye theory* for linear constitutive relations, or for small deviation of the magnetization from local equilibrium.)

A. The Debye theory

In the first variant of his description, Shliomis [4] introduced a phenomenological equation for **M**, with a linear Debye-like relaxation term. After elimination of the intrinsic angular momentum, this equation reads

$$\frac{d\mathbf{M}}{dt} - \boldsymbol{\Omega}\times\mathbf{M} = \frac{1}{\tau_B}(\mathbf{M}^{\mathrm{eq}} - \mathbf{M}) - \frac{\mathbf{M}\times(\mathbf{M}\times\mathbf{H})}{6\eta_1\varphi}, \tag{17}$$

where $(d/dt) \equiv \partial_t + (\mathbf{v}\cdot\nabla)$, τ_B is the Brownian relaxation time, and φ the volume concentration. Assuming small deviation of the magnetization from local equilibrium, $\delta M/M^{\mathrm{eq}} \ll 1$, one obtains to leading order

$$\mathbf{M} - \mathbf{M}^{\mathrm{eq}} = \frac{M^{\mathrm{eq}}}{H}\mathbf{h} + \left(\frac{\partial M^{\mathrm{eq}}}{\partial H} - \frac{M^{\mathrm{eq}}}{H}\right)\frac{\mathbf{M}\cdot\mathbf{h}}{(M^{\mathrm{eq}})^2}\mathbf{M}. \tag{18}$$

Using this relation in Eqs (7) and (15), the *Debye theory* (17) is recovered by the following choice:

$$\lambda_1 = \lambda_2 = \lambda_3 = \lambda_4 = \zeta_\times = 0, \tag{19}$$

$$\zeta = \frac{1}{\tau_B}\frac{M^{\mathrm{eq}}}{H} + \frac{(M^{\mathrm{eq}})^2}{6\eta_1\varphi}, \tag{20}$$

$$\zeta_\parallel (M^{\mathrm{eq}})^2 = \frac{1}{\tau_B}\left(\frac{\partial M^{\mathrm{eq}}}{\partial H} - \frac{M^{\mathrm{eq}}}{H}\right) - \frac{(M^{\mathrm{eq}})^2}{6\eta_1\varphi}. \tag{21}$$

B. Effective-field theory

On the basis of a kinetic equation for rotary diffusion, Martsenyuk, Raikher, and Shliomis [8] constructed the Fokker-Planck equation for the probability distribution of the particle's orientation. Thereby, the authors relied on the idealizing assumptions that the ferrofluid is composed of (i) spherical (ii) monodispersed (iii) noninteracting (iv) rigid dipoles. Form the resultant infinite hierarchy of equations for

the momenta of **M**, a separate equation for the magnetization is deduced by employing the method of the effective field. Thereby the magnetization

$$\mathbf{M}=M_s\mathcal{L}(\xi_e)\frac{\boldsymbol{\xi}_e}{\xi_e} \tag{22}$$

is taken to be a function of the dimensionless, effective field $\boldsymbol{\xi}_e=(m\mathbf{H}^{\rm eq})/(k_BT)$, 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 nondimensional magnetic field $\boldsymbol{\xi}=(m\mathbf{H})/(k_BT)$, the effective field is governed by the ordinary differential equation

$$\frac{d}{dt}\left[\mathcal{L}_e\frac{\boldsymbol{\xi}_e}{\xi_e}\right]=\boldsymbol{\Omega}\times\left[\mathcal{L}_e\frac{\boldsymbol{\xi}_e}{\xi_e}\right]-\frac{1}{\tau_B}\frac{\mathcal{L}_e}{\xi_e}(\boldsymbol{\xi}_e-\boldsymbol{\xi}) -\frac{1}{2\tau_B\xi_e^2}\left(1-\frac{3\mathcal{L}_e}{\xi_e}\right)\boldsymbol{\xi}_e\times(\boldsymbol{\xi}_e\times\boldsymbol{\xi}), \tag{23}$$

where $\mathcal{L}_e=\mathcal{L}(\xi_e)$. Solving this equation for $\boldsymbol{\xi}_e$ at given $\boldsymbol{\xi}$ determines the magnetization via Eq. (22) in parametric form. Eq. (23) can be recast, without approximation, in the following, rather more explicit form:

$$2\tau_B\left\{\frac{d}{dt}\mathbf{M}-\boldsymbol{\Omega}\times\mathbf{M}\right\}=-\left[3\chi-\frac{M}{H^{\rm eq}}\right]\mathbf{h}-3\left[\frac{M}{H^{\rm eq}}-\chi\right]\frac{\mathbf{M}\cdot\mathbf{h}}{M^2}\mathbf{M}, \tag{24}$$

with $\chi=mM_s/(3k_BT)$ as the initial susceptibility. Again, Eq. (24) is a special case of Eqs (7) and (15) with the following particular choice:

$$\lambda_1=\lambda_2=\lambda_3=\lambda_4=\zeta_\times=0, \tag{25}$$

$$\zeta=\frac{1}{2\tau_B}\left[3\chi-\frac{M}{H^{\rm eq}}\right], \tag{26}$$

$$\zeta_\parallel=\frac{3}{2}\frac{1}{\tau_B}\frac{1}{M^2}\left[\frac{M}{H^{\rm eq}}-\chi\right]. \tag{27}$$

IV. EXPERIMENTAL EVIDENCES

A. Negative viscosity

On the basis of the *Debye theory*, Shliomis and Morozov [19] predicted that a ferrofluid flow through a pipe may be accelerated under the influence of an oscillating magnetic field, by pumping energy from the electromagnetic field into the flow. The resulting enhanced through-flow rate was interpreted as a decrement $\Delta\eta_1$ of the effective shear viscosity, referred to as ''negative viscosity.'' This effect was later experimentally verified by Bacri *et al.* [7] and by Zeuner *et al.* [9]. When the measurements of $\Delta\eta_1$ did not agree with the prediction, Shliomis employed the EFT instead. We do not find this approach convincing: Although the rigid dipole approximation may be considered valid in the experiment (which uses cobalt particles), the neglect of particle interaction is certainly doubtful: It starts to become questionable at concentrations around $\varphi=3\%$, yet the negative viscosity experiment was carried out at $\varphi=20\%$.

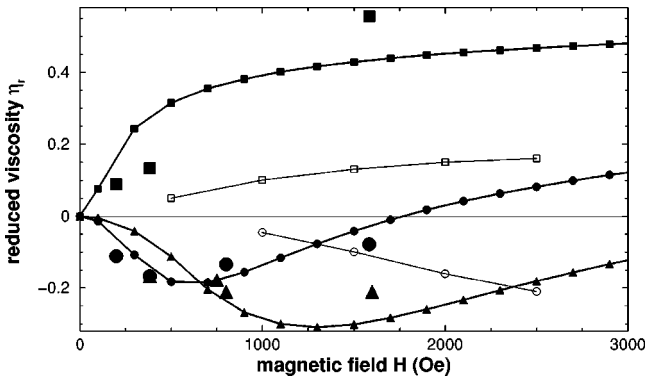

FIG. 1. Reduced viscosity $\eta_r=\Delta\eta_1(H,f)/\eta_1(0,0)$ at the field oscillation frequency $f=52$ Hz (squares), 345 Hz (circles), and 645 Hz (triangles). Large black symbols denote the experimental data as measured in Ref. [7], open symbols are effective-field theory as gleaned from Fig. 4 of Bacri *et al.* [7]; small black symbols are calculated from Eqs. (7) and (13).

Employing expressions from the weak-field case of Sec. II A, we reevaluated the experiment and found convincing agreement, see Fig. 1. We took $\mathbf{X}^D=-\zeta\mathbf{h}$, and 1.6 ms for the coefficient ζ/χ – as given in Ref. [7] and independent of H or M. Furthermore, for lack of pertinent ferrofluid specifications, we also took the $M^{\rm eq}(H)$ as given by the Langevin function, used the saturation magnetization $M_s=127$ G, and the initial susceptibility $\chi=1$ to fit the data (small black symbols). For the sake of comparison we also provide the outcome of the EFT as gleaned from Ref. [7]. To that end we used their expression $\eta_r=(3/2)\varphi g$ for the reduced viscosity. The necessary values for $g=g(\xi_0,\omega\tau_B)$ were compiled from Fig. 4 of Ref. [7] with $\xi_0=5.25\times10^{-3}H$ (Oe) and $\omega\tau_B=10^{-2}f$ (Hz).

A few points need emphasizing here. First, we freely admit that modifying some of the above parameters would make EFT appear better, or the *(rectified) Debye theory* worse. But engaging in a lengthy quibbling would miss the actual and rather more important message, namely, that the original experimental reason to mistrust the *Debye theory* is false. (Theoretically, there never was any reason to give Debye less credit than EFT.)

In fact, the more serious criticism of the above fits is not in a specific value chosen for any parameter. Rather, it must be reserved for the sweeping approximation inherent both in the weak-field case and in EFT. For the given elevated field strength, we need to justify why we did not used the expression of Sec. II B instead, especially the λ_2 term. The reason is simply that most of the additional parameters do not as yet have a known value.

More generally speaking, it is important to be aware that we have at our hand a healthy macroscopic theory capable of accounting for all phenomena of ferrofluids. The structure of the theory is given in Sec. II, its parameters need to be measured, ferrofluid for ferrofluid.

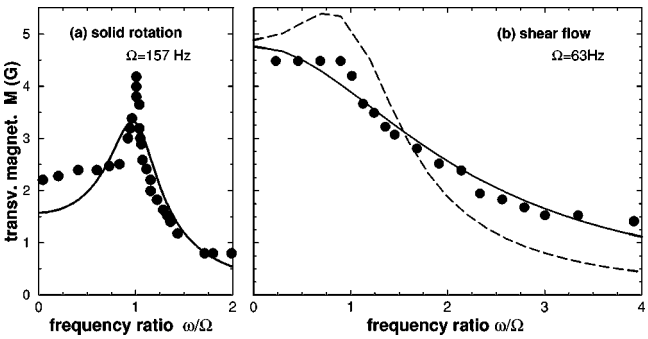

FIG. 2. Black circles denote measured transverse magnetization [10]; the solid lines are computed from Eq. (15) with $\lambda_2=2.54$, and the dashed line with $\lambda_2=0$ (traditional approach). Both lines necessarily coincide in the left picture as $v_{ij}^0=0$ there.

B. Magnetovortical resonance

Equation (15) shows that in addition to the vorticity $\mathbf{\Omega}$, compressional and elongational flow may also contribute to the dynamics of $\mathbf{M}$. For a complete theory, we still need an estimate of the coefficients λ_i, most reliably via experimental input. One such measurement for λ_2 already exists, which is the experiment on the magnetovortical resonance [10]. In this experiment, a ferrofluid under solid body rotation, and another under shear, are exposed to an oscillating magnetic field, while $M_\perp$, the component of the magnetization transverse to the field, is recorded. In the case of the solid body rotation ($\Omega\neq 0, v_{ij}^0=0$), a sharp resonance is observed, see Fig. 2(a); while the signal drastically flattens out for the shear flow case ($\Omega\neq 0, v_{ij}^0\neq 0$), see Fig. 2(b). The difference between them is clearly the finite elongational flow v_{ij}^0. Fitting the decay of $M_\perp$ as shown in Fig. 2(b) with Eqs. (7) and (15) yields $\lambda_2=2.54$ for the ferrofluid at hand.

Since both the *Debye theory* and EFT set $\lambda_2=0$, the above explanation was not available, so an auxiliary and microscopic explanation was given in Ref. [10], which relies on a flow induced modification of the relaxation time τ_M: Shear flow induces fracture of dynamical particle chains, which leads to a reduced effective dipolar interaction between the particles. This implies that ζ_i (and with it τ_M) are functions of v_{ij}^0, cf. Eq. (15). In contrast to the macroscopic, linear explanation given by λ_2, this one here is a quadratic effect that exists only if both thermodynamic forces h and v_{ij}^0 are finite. And it amounts to claiming that although X^D does not depend on v_{ij}^0 linearly, it does so nonlinearly, cf. Eq (15). It appears prudent to exhaust all linear explanations first, before postulating a nonlinear one. Besides, both theories are in fact different otherwise, and should be checked against further experiments.

One such experiment, which is at the same time a direct evaluation of λ_2, is given by measuring the off-equilibrium magnetization $M_\perp$ in a Taylor-Couette apparatus, exposed to a static magnetic field perpendicular to the rotation axis. If both cylinders are rotated independently with angular frequencies Ω_1 and Ω_2, one may perform a continuous transition from a rigid rotation ($\Omega_1=\Omega_2$, i.e., $v_{ij}^0=0$) to a simple shear ($\Omega_1\neq\Omega_2$, i.e., $v_{ij}^0\neq 0$) while keeping the vorticity $\mathbf{\Omega}$ constant. That way the recorded value of $M_\perp$ vs $(\Omega_1-\Omega_2)$ yields the coefficient λ_2.

Alternatively, information on λ_2 can be obtained from the counter terms in the stress tensor, see Eq. (16), e.g., in the experiment suggested below Eq. (14), or the one in Ref. [20].

V. CONCLUSION

The general structure of the hydrodynamic equations for ferrofluids is derived here, with the gain in rigor 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. To complete the theory, therefore, they must be determined by a series of experiments. An alternative way is to calculate them from an appropriate microscopic model, such as the EFT within its specified range of validity. Consequently, the macroscopic theory presented here is not a competitor of EFT, as both theories are complementary to each other.

The validity of our approach is corroborated by the ease with which two previous experiments associated with magnetodissipation:''negative viscosity'' and ''magnetovortical resonance,'' are interpreted. Predicted phenomena include magnetodissipative normal traction, and dependence of the magnetization dynamics on elongational flows.

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 the back of our mind. They arise due to the assumption we made of a unique characteristic time associated with the slow variable when generalizing the HMT. As a result, any microscopic features (such as polydispersity) 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. (At lower frequencies, FFD is completely equivalent to HMT [13], which we know is meant to accommodate arbitrarily diverse characteristic times of all the implicit degrees of freedom. Nevertheless, one may no longer interpret τ_{M} as a unique relaxation time, as it then contains contributions from all populations present.)

[1] R.E. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, 1985).
[2] M.I. Shliomis, J. Magn. Magn. Mater. **159**, 236 (1996).
[3] J.P. McTague, J. Chem. Phys. **51**, 133 (1969).
[4] M.I. Shliomis, Sov. Phys. Usp. **17**, 153 (1974).
[5] E. Blums, A. Cebers, and M.M. Maiorov, *Magnetic Fluids* (Walter de Gruyter, Berlin, 1997).
[6] U. Felderhof and B. Kroh, J. Chem. Phys. **110**, 7403 (1999).

[7] J.-C. Bacri, R. Perzynski, M.I. Shliomis, and G.I. Burde, Phys. Rev. Lett. **75**, 2128 (1995).
[8] M.A. Martsenyuk, Y.L. Raikher, and M.I. Shliomis, Sov. Phys. JETP **38**, 413 (1974); Y.L. Raikher and M.I. Shliomis, in *Relaxation Phenomena in Condensed Matter*, edited by W. Coffey, Advances in Chemical Physics Series 87 (Wiley, New York, 1994).
[9] A. Zeuner, R. Richter, and I. Rehberg, Phys. Rev. E **58**, 6287 (1998).
[10] F. Gazeau, B.M. Heegaard, J.C. Bacri, A. Cebers, and R. Perzynski, Europhys. Lett. **35**, 609 (1996); F. Gazeau, C. Baravian, J.C. Bacri, R. Perzynski, and M.I. Shliomis, Phys. Rev. E **56**, 614 (1997).
[11] H.W. Müller and M. Liu (unpublished).
[12] M. Liu, Phys. Rev. Lett. **70**, 3580 (1993); **74**, 4535 (1995); **80**, 2937 (1998).
[13] S. Lissek, H.W. Müller, and M. Liu (unpublished).
[14] Y.M. Jiang and M. Liu, Phys. Rev. Lett. **77**, 1043 (1996); Phys. Rev. E **58**, 6685 (1998).
[15] K. Henjes and M. Liu, Ann. Phys. (Leipzig) **223**, 243 (1992); M. Liu and K. Stierstadt, e-print cond-mat/0010261.
[16] L.D. Landau and E.M. Lifshitz, *Fluid Mechanics* (Pergamon, Oxford, 1987).
[17] J.P. Embs, H.W. Müller, C. Wagner, K. Knorr, and M. Lücke, Phys. Rev. E **61**, R2196 (2000).
[18] P.G. de Gennes and J. Prost, *The Theory of Liquid Crystals* (Clarendon, Oxford, 1983).
[19] M.I. Shliomis and K.I. Morozov, Phys. Fluids **6**, 2855 (1994).
[20] H.W. Müller and A. Engel, Phys. Rev. E **60**, 7001 (1999).