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Comment on “Magnetoviscosity and relaxation in ferrofluids”

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It is shown and discussed how the conventional system of hydrodynamic equations for ferrofluids was derived. The set consists of the equation of fluid motion, the Maxwell equations, and the magnetization equation. The latter was recently revised by Felderhof [Phys. Rev. E **62**, 3848 (2000)]. His phenomenological magnetization equation looks rather like our corresponding equation, but leads to wrong consequences for the dependence of ferrofluid viscosity and magnetization relaxation time on magnetic field.

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I. INTRODUCTION: EQUATION OF FLUID MOTION

In a recent paper [1], Felderhof made an attempt to revise the conventional hydrodynamic equations for ferrofluids. He proposed some modification in the equation of ferrofluid magnetization. A complete set of ferrohydrodynamic equations was presented in our paper [2] 30 years ago. In this Comment, we will consider the object of Felderhof’s criticism, analyze his proposition, and explain why we feel it is wrong.

The main peculiarity of ferrofluids is a specific relation between the magnetic and rotational degrees of freedom of suspended magnetic grains of which the fluids are composed. Therefore the concept of *internal rotation* first applied to ferrofluids in [2] has proved to be very fruitful. The model [2] takes into account that the volume density of the angular momentum of ferrofluids consists of both the visible (“orbital”) and the internal (“spin”) parts. The former, $\mathbf{L}=\rho(\mathbf{r}\times\mathbf{v})$, is associated with the translational motion of magnetic grains and molecules of the solvent. The latter, $\mathbf{S}$, is caused by the rotation of the grains themselves and should be treated as an independent variable along with the fluid velocity $\mathbf{v}$, density ρ, and pressure p. However, an appropriate thermodynamic coordinate is the difference $\mathbf{S}-I\boldsymbol{\Omega}$, where $\boldsymbol{\Omega}=\frac{1}{2}\operatorname{curl}\mathbf{v}$ is the local angular velocity of the fluid and I means the volume density of the particles moment of inertia. For a suspension of spherical particles $I=\rho_s\phi d^2/10$ where ϕ is the volume fraction of the dispersed phase, ρ_s the particles material density, and d the mean particle diameter. In this case it is convenient to set $\mathbf{S}=I\boldsymbol{\omega}_p$ where $\boldsymbol{\omega}_p$ is the macroscopic (i.e., averaged over physically small volume) angular velocity of the particles. Any deviation of $\boldsymbol{\omega}_p$ from $\boldsymbol{\Omega}$ gives rise to dissipation processes due to redistribution of angular momentum between $\mathbf{L}$ and $\mathbf{S}$ forms. (The angular momentum conservation law refers, to the total angular momentum $\mathbf{L}+\mathbf{S}$.) These processes contribute the stress tensor σ_{ik}. For an ordinary (nonmagnetic) suspension, the tensor has been derived by the methods of irreversible thermodynamics in [3]:

$$\sigma_{ik}=-p\,\delta_{ik}+\eta\left(\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}\right)+\frac{1}{2\tau_s}(S_{ik}-I\Omega_{ik}), \tag{1}$$

where

$$S_{ik}=\epsilon_{ikl}S_l,\quad \Omega_{ik}=(\partial v_k/\partial x_i-\partial v_i/\partial x_k)/2=\epsilon_{ikl}\Omega_l,$$

and ϵ_{ikl} stands for antisymmetric unit tensor. Apart from the viscosity η, Eq. (1) contains once more kinetic coefficient: the spin relaxation time $\tau_s=I/6\eta\phi=\rho_s d^2/60\eta$. For $d=10$ nm and $\eta=10^{-2}$ P this formula gives $\tau_s\sim10^{-11}$ s(!). Thus, the difference $\boldsymbol{\omega}_p-\boldsymbol{\Omega}$ instantly decays whereupon the hydrodynamic description is reduced to the common set of hydrodynamic equations. Ferrofluids, however, give us an opportunity to maintain this difference by an extraneous magnetic torque that acts directly upon the particle rotation

$$6\eta\phi(\boldsymbol{\omega}_p-\boldsymbol{\Omega})=\mathbf{M}\times\mathbf{H}. \tag{2}$$

Here $\mathbf{H}$ is the magnetic field within the fluid and $\mathbf{M}$ is the ferrofluid magnetization. At the *equilibrium* in a stationary field, $\mathbf{M}$ is described well by the Langevin formula

$$\mathbf{M}_0=nmL(\xi)\frac{\mathbf{H}}{H},\quad \xi=\frac{mH}{k_BT},\quad L(\xi)=\coth\xi-\xi^{-1}, \tag{3}$$

where m is the magnetic moment of a single particle and n the number density of the particles. Eliminating the last term in Eq. (1) with the aid of the torque balance equation (2) and including in σ_{ik} the Maxwell tensor of magnetic field, one gets [2,4]

$$\sigma_{ik}=-p\,\delta_{ik}+\eta\left(\frac{\partial v_i}{\partial x_k}+\frac{\partial v_k}{\partial x_i}\right)+\frac{1}{2}(M_iH_k-M_kH_i)+\frac{1}{4\pi}\left(H_iB_k-\frac{1}{2}H^2\delta_{ik}\right). \tag{4}$$

On substitution $B_k=H_k+4\pi M_k$ in this tensor, we are convinced of its *symmetry*. Equation (4) and the momentum conservation law

$$\rho\frac{dv_i}{dt}=\frac{\partial\sigma_{ik}}{\partial x_k},\quad \frac{d}{dt}=\frac{\partial}{\partial t}+(\mathbf{v}\cdot\boldsymbol{\nabla}),$$

determine the equation of ferrofluid motion

$$\rho\frac{d\mathbf{v}}{dt}=-\boldsymbol{\nabla}p+\eta\boldsymbol{\nabla}^2\mathbf{v}+(\mathbf{M}\cdot\boldsymbol{\nabla})\mathbf{H}+\tfrac{1}{2}\operatorname{curl}(\mathbf{M}\times\mathbf{H}). \tag{5}$$

In the calculation of the divergence of the stress tensor we have used the equations

$$\operatorname{div} \mathbf{v} = 0, \quad \operatorname{curl} \mathbf{H} = 0, \quad \operatorname{div} \mathbf{B} = 0, \tag{6}$$

i.e., the ferrofluid is considered to be incompressible and nonconducting.

The system of equations (5)–(6) is still not complete since it does not determine the ferrofluid magnetization. The latter influences the fluid motion [see Eq. (5)] and depends itself on the motion as well. There are two basic ways to derive the missing magnetization equation. Both the ways have been proposed by the author with co-workers [2,5] and discussed in reviews [4,6,7].

II. PHENOMENOLOGICAL MAGNETIZATION EQUATION

Originally the magnetization equation was derived phenomenologically [2] as a modification of the Debye relaxation equation [8]. To get the generalized equation, one should introduce a local reference frame $\mathbf{\Sigma}'$, in which the suspended particles are quiescent *on the average*, i.e., $\boldsymbol{\omega}_p' = 0$. It is natural to assume that the magnetization relaxation is described in the system by the simplest Debyelike equation

$$\frac{d'\mathbf{M}}{dt} = -\frac{1}{\tau}(\mathbf{M} - \mathbf{M}_0), \tag{7}$$

with $\mathbf{M}_0$ from Eq. (3). In other words, it assumes that any deviation (either in direction or magnitude) of $\mathbf{M}$ from its equilibrium value $\mathbf{M}_0$ decays according to the simple exponential law $(\mathbf{M} - \mathbf{M}_0) \sim \exp(-t/\tau)$. Here $\tau = 3\eta V/k_B T$ stands for the Brownian time of rotational particle diffusion ($V = \pi d^3/6$) since the particles are assumed to be rigid magnetic dipoles whose reorientation is possible only with rotation of the particles themselves. The frame of reference Σ' rotates with respect to the fixed ("laboratory") system Σ with the angular velocity $\boldsymbol{\omega}_p$. The rates of change of any vector $\mathbf{A}$ in systems Σ and Σ' are related by the kinematic expression

$$\frac{d\mathbf{A}}{dt} = \boldsymbol{\omega}_p \times \mathbf{A} + \frac{d'\mathbf{A}}{dt}. \tag{8}$$

Substituting here $\mathbf{A} = \mathbf{M}$, $\boldsymbol{\omega}_p$ from Eq. (2), and $d'\mathbf{M}/dt$ from Eq. (7), we obtain the equation sought

$$\frac{d\mathbf{M}}{dt} = \mathbf{\Omega} \times \mathbf{M} - \frac{1}{\tau}(\mathbf{M} - \mathbf{M}_0) - \frac{1}{6\eta\phi}\mathbf{M} \times (\mathbf{M} \times \mathbf{H}) \tag{9}$$

(Shliomis [2]). The last (relaxation) term in this equation describes a process of approach of the vector $\mathbf{M}$ to its equilibrium orientation without change of the length of this vector. Equations (5), (6), and (9) constitute the complete set of conventional ferrohydrodynamic equations.

Let us compare Eq. (9) with the Felderhof's equation [1]

$$\frac{d\mathbf{M}}{dt} = \mathbf{\Omega} \times \mathbf{M} - \gamma_H(\mathbf{H}_l - \mathbf{H}) - \frac{1}{6\eta\phi}\mathbf{M} \times (\mathbf{M} \times \mathbf{H}). \tag{10}$$

Here γ_H is a positive phenomenological constant and "$\mathbf{H}_l = \mathbf{M}C(M)$ is expressed in terms of the local magnetization" [1], that requires an introduction of a very inconvenient notation $C(M) = (k_B T/mM)L^{-1}(M/nm)$, where $L^{-1}(x)$ means the function inverse to Langevin function (3). On the face of it, Eq. (10) is only much less convenient than Eq. (9) since the left- and right-hand sides of Eq. (10) contain *different* relaxing values: $\mathbf{M}$ and $\mathbf{H}_l(\mathbf{M})$. Felderhof claims, however, that his "relaxation equation was *derived* from irreversible thermodynamics (IT), and differs from that *postulated* by Shliomis. The two relaxation equations lead to a different dependence of viscosity on magnetic field." Let us consider both these statements.

From the point of view of IT, the relaxation term $(\mathbf{M}_0 - \mathbf{M})/\tau$ in Eq. (9) is neither more nor less "postulated" than the term $\gamma_H(\mathbf{H} - \mathbf{H}_l)$ in Eq. (10). It is worth to remind, there are two methods of IT, and both were proposed by Landau. The first of two, $L1$, based on conservation laws and the condition of positive entropy production, was applied for the first time to the building of hydrodynamics of helium [9], then—hydrodynamics of fluids with internal rotation [3], liquid paramagnets [10], and some other liquids. Relaxation equation (10) has been also derived by that method. One has to be skillful enough to use this cumbrous method because it does not lead to the one and only form of sought equations. In this sense the second method, $L2$, is much more definite, simple, and direct than method $L1$. It was first applied just to the description of relaxation of the order parameter in a nonequilibrium system [11]. An equilibrium value of the parameter ($\mathbf{M}_0$ in our case) corresponds to the minimum of an appropriate thermodynamic potential Φ (usually the Gibbs or Helmholtz free energy) depending on the magnetization $\mathbf{M}$ and other thermodynamic variables. Thus, at the equilibrium $\partial\Phi/\partial\mathbf{M} = 0$. Out of equilibrium this condition is not satisfied, so the relaxation process occurs: $\mathbf{M}$ changes in time approaching $\mathbf{M}_0$. For small deviations from equilibrium, the derivative $\partial\Phi/\partial\mathbf{M}$ and the relaxation rate $d\mathbf{M}/dt$ are small. The relation between the two derivatives in the Landau theory is reduced to simple proportionality

$$\frac{d\mathbf{M}}{dt} = -\gamma\frac{\partial\Phi}{\partial\mathbf{M}}, \tag{11}$$

with a constant coefficient $\gamma > 0$. Hence we have

$$\frac{d\Phi}{dt} = \frac{\partial\Phi}{\partial\mathbf{M}}\frac{d\mathbf{M}}{dt} = -\gamma\left(\frac{\partial\Phi}{\partial\mathbf{M}}\right)^2 < 0, \tag{12}$$

as it should be: when a system moves to equilibrium, its free energy decreases. In the case of a weakly nonequilibrium state of the system, one can substitute in Eqs. (11) and (12) the expansion

$$\frac{\partial\Phi}{\partial\mathbf{M}} = \left(\frac{\partial\Phi}{\partial\mathbf{M}}\right)_0 + \left(\frac{\partial^2\Phi}{\partial\mathbf{M}^2}\right)_0 (\mathbf{M} - \mathbf{M}_0) + \cdots,$$

where subscript 0 marks the point of equilibrium. As the first derivative in this point is equal to zero and the second one is positive, Eq. (11) turns into Eq. (7) with $\tau^{-1}=\gamma(\partial^2\Phi/\partial\mathbf{M}^2)_0$ and Eq. (12) takes the form

$$\frac{d\Phi}{dt}=-\frac{(\mathbf{M}-\mathbf{M}_0)^2}{\gamma\tau^2}. \tag{13}$$

Thus, Eq. (7) and hence Eq. (9) are well corroborated by the method of IT. Equation (10) does also not conflict with IT. Nevertheless, in my opinion it is wrong. As we show below, it leads to anomalous result for ferrofluid viscosity and magnetization relaxation time. The pitfall of IT is discussed in Sec. IV.

The Einstein formula for viscosity of suspension $\eta=\eta_0(1+2.5\phi)$ was obtained without taking into account the rotational motion of suspended particles relative to carrier liquid. If, however, the particles angular velocity $\boldsymbol{\omega}_p$ does not coincide with the angular velocity of the fluid $\boldsymbol{\Omega}$, there arise frictional forces that manifest themselves in an additional (so-called *rotational*) viscosity η_r. As the difference $\boldsymbol{\omega}_p-\boldsymbol{\Omega}$ is maintained by the magnetic torque [see Eq. (2)], rotational viscosity turns out to be a function of the dimensionless field strength ξ. In a stationary field, the steady solution of Eq. (9) yields in the linear order in $\Omega\tau$,

$$\mathbf{M}-\mathbf{M}_0=\tau_\perp(\boldsymbol{\Omega}\times\mathbf{M}_0),\qquad \tau_\perp=\frac{2\tau}{2+\xi L(\xi)}, \tag{14}$$

where $\tau_\perp$ is the relaxation time of the transverse (to the field) component of the magnetization. For the Poiseuille flow or the planar Couette flow under the field directed along the flow (i.e., $\mathbf{H}\perp\boldsymbol{\Omega}$), we find

$$\mathbf{M}\times\mathbf{H}=-\tau_\perp M_0 H\boldsymbol{\Omega}, \tag{15}$$

while for arbitrary orientation of magnetic field the right-hand side of the expression should be multiplied by $\sin^2\alpha$ where α is the angle between vectors $\mathbf{H}$ and $\boldsymbol{\Omega}$. Let us substitute the magnetic torque (15) in Eq. (5). When the field $\mathbf{H}$ is homogeneous, the magnetic force $(\mathbf{M}\cdot\nabla)\mathbf{H}$ in the right-hand side of Eq. (5) vanishes, while two other terms of the equation may be grouped

$$\eta\nabla^2\mathbf{v}+\tfrac{1}{2}\,\mathrm{curl}(\mathbf{M}\times\mathbf{H})=(\eta+\tfrac{1}{4}\tau_\perp M_0H)\nabla^2\mathbf{v}.$$

The quantity added here to the ordinary viscosity should be regarded as rotational viscosity

$$\eta_r=\tfrac{1}{4}\tau_\perp M_0 H. \tag{16}$$

Substituting here M_0 from Eq. (3) and $\tau_\perp$ from Eq. (14), we derive the formula [2]

$$\eta_r(\xi)=\frac{3}{2}\eta\phi\frac{\xi L(\xi)}{2+\xi L(\xi)}=\frac{3}{2}\eta\phi\frac{\xi-\tanh\xi}{\xi+\tanh\xi}. \tag{17}$$

In the absence of magnetic field an individual particle ''rolls'' freely along corresponding shear surface with angular velocity $\boldsymbol{\omega}_p$ equal to $\boldsymbol{\Omega}$, so that $\eta_r(0)=0$. Conversely, $\eta_r(\xi)$ attains its limiting value

$$\eta_r(\infty)=3\eta\phi/2 \tag{18}$$

(the saturation) when *rolling* of the particle is replaced by *slipping*: the field of sufficiently large intensity guarantees constancy of the particle's orientation, not allowing it to twist with the fluid. Note that the result (18) does *not depend* on a concrete form of the magnetization equation but follows directly from the equation of fluid motion (5). Actually, in the limit under consideration $\boldsymbol{\omega}_p=\mathbf{0}$, so that Eq. (2) takes the form $\mathbf{M}\times\mathbf{H}=-6\eta\phi\boldsymbol{\Omega}$. Substituting this torque in Eq. (5), we immediately arrive at Eq. (18). Indeed, this value was obtained by Hall and Busenberg [12] as early as 1969 *without the use* of any magnetization equation. In any case, however, such an equation must not contradict the saturation value (18). Our formula (17) does satisfy the limit (18), whereas Felderhof's equation (10) leads to a quite different result. His final formula in Ref. [1] gives the value

$$\eta_r^F(\infty)=\frac{3}{2}\eta\phi\frac{(nm)^2}{6\eta\phi\gamma_H+(nm)^2}, \tag{19}$$

which is *evidently less* than the correct value (18). According to Ref. [1], $\gamma_H=\chi/\tau$, where $\chi=nm^2/3k_BT$ is the initial magnetic susceptibility. Substituting the γ_H and $\phi=nV$ in Eq. (19) we find $6\eta\phi\gamma_H=2(nm)^2/3$, afterwards Eq. (19) yields $\eta_r^F(\infty)=9\eta\phi/10$. Thus the ratio of the Felderhof's limiting value of viscosity to the correct value (18) is equal to 0.6. In other words, in the limit $\xi=\infty$ Felderhof's equation (10) predicts $\omega_p=0.4\Omega$ instead of $\omega_p=0$ as it should be.

III. MAGNETIZATION EQUATION DERIVED MICROSCOPICALLY

Both the above-mentioned phenomenological methods allow to obtain *linear* relaxation terms in hydrodynamic equations [such as $(\mathbf{M}_0-\mathbf{M})/\tau$ in Eq. (9)] and corresponding quadratic terms for the rate of the entropy growth or the free energy diminution (such as that in Eq. (13)). It is clear that such terms are valid only for small departures from equilibrium. Indeed, Eq. (9) describes well the rotational viscosity for arbitrary intensity of a stationary magnetic field but small values of $\Omega\tau$ (see, e.g., a good agreement between McTague's experiment [13] and our theory [2]), or for small dimensionless amplitude ξ or frequency $\omega\tau$ of an alternating magnetic field (see, e.g., experiments on the *negative viscosity* and their explanation in Ref. [14]). Meanwhile, to describe successfully the negative ferrofluid viscosity at finite values of the parameters, we did need to use in Refs. [15,16] a more precise magnetization equation. Such a *macroscopic* equation should be derived from the kinetic Fokker-Planck equation that provides the *microscopic* description of part icle diffusion in colloids. The program was realized by Martsenyuk, Raikher, and Shliomis [5] soon after the phenomenological magnetization equation (9) was derived in Ref. [2].

The Fokker-Planck equation for a ferrofluid moving in a field **H** has the form [7]

$$2\tau\frac{\partial W}{\partial t}=\widehat{\mathbf{R}}\cdot(\hat{\mathbf{R}}-2\tau\boldsymbol{\Omega}-\mathbf{e}\times\boldsymbol{\xi})W, \tag{20}$$

where $\mathbf{e}=\mathbf{m}/m$ is a unit vector along a particle magnetic moment, $\boldsymbol{\xi}=m\mathbf{H}/k_BT$, and $\hat{\mathbf{R}}=\mathbf{e}\times\partial/\partial\mathbf{e}$ is the infinitesimal rotation operator. Equation (20) determines the orientational distribution function $W(\mathbf{e},t)$ of particles magnetic moments. The macroscopic magnetization is determined by the relation $\mathbf{M}(t)=nm\langle\mathbf{e}\rangle$ where angular brackets denote statistical averaging with the distribution function. Multiplying Eq. (20) by **e** and integrating over the angles, we arrive at the equation

$$2\tau\frac{d\langle\mathbf{e}\rangle}{dt}=2\tau\boldsymbol{\Omega}\times\langle\mathbf{e}\rangle-2\langle\mathbf{e}\rangle-\langle\mathbf{e}\times(\mathbf{e}\times\boldsymbol{\xi})\rangle, \tag{21}$$

which, however, is not closed. Indeed, along with the first moment of the distribution function, $\langle\mathbf{e}\rangle$, Eq. (21) contains the second moment (the last term in the equation). It is easy to make sure that the equation for the second moment includes the third one, and so on, thus there is the infinite chain of cross-linked equations. Ideally, however, one would like to have only one equation since only the first moment—magnetization—has a clear physical meaning. An original scheme of closure of the first-moment equation (21), titled the *effective field method*, has been proposed in Ref. [5]. Let us explain the fruitful physical idea.

In equilibrium ($\boldsymbol{\Omega}=\mathbf{0}$) under a constant magnetic field the stationary solution of Eq. (20) is the Gibbs distribution

$$W_0(\mathbf{e})=\frac{\xi}{4\pi\sinh\xi}\exp(\boldsymbol{\xi}\cdot\mathbf{e}). \tag{22}$$

An averaging of the vector **e** with function (22) gives expression (3) for the equilibrium magnetization

$$\mathbf{M}_0=nmL(\xi)\boldsymbol{\xi}/\xi. \tag{23}$$

Only in true equilibrium the magnetization is one or another function of the field. In a nonequilibrium state there is *no connection* between **M** and **H**: any arbitrary magnetization may be created, in principle, even in the absence of the field. Nevertheless, one may consider any value of **M** as an equilibrium magnetization in a certain—specially prepared —magnetic field. This *effective field* $\mathbf{H}_e$ is related to the *nonequilibrium* magnetization by the *equilibrium* relation

$$\mathbf{M}=nmL(\xi_e)\boldsymbol{\xi}_e/\xi_e\,. \tag{24}$$

During the equilibrium settling process, the dimensionless effective field $\boldsymbol{\xi}_e=m\mathbf{H}_e/k_BT$ tends to the true field $\boldsymbol{\xi}$, so the magnetization (24) relaxes to its equilibrium value (23). Comparing Eqs. (23) and (24), we see that the latter is obtained by averaging of **e** with the distribution function

$$W_e(\mathbf{e})=\frac{\xi_e}{4\pi\sinh\xi_e}\exp(\boldsymbol{\xi}_e\cdot\mathbf{e}), \tag{25}$$

which differs from the Gibbs distribution (22) by replacement of the true field by the effective one. Carrying out the averaging in Eq. (21) with the function (25), we find the sought equation [5]

$$\frac{d}{dt}\left[L(\xi_e)\frac{\boldsymbol{\xi}_e}{\xi_e}\right]=\boldsymbol{\Omega}\times\left[L(\xi_e)\frac{\boldsymbol{\xi}_e}{\xi_e}\right]-\frac{L(\xi_e)}{\tau\xi_e}(\boldsymbol{\xi}_e-\boldsymbol{\xi})-\frac{\xi_e-3L(\xi_e)}{2\tau\xi_e^3}\boldsymbol{\xi}_e\times(\boldsymbol{\xi}_e\times\boldsymbol{\xi}). \tag{26}$$

This equation defines the dependence of the effective field $\boldsymbol{\xi}_e$ upon time, true field $\boldsymbol{\xi}$, and the fluid vorticity $\boldsymbol{\Omega}$. Its solution $\boldsymbol{\xi}_e$ being substituted into Eq. (24) determines the magnetization of a moving fluid. In the case of small departures from equilibrium, the effective field might be represented as a sum of the true field and some small correlation: $\boldsymbol{\xi}_e=\boldsymbol{\xi}+\boldsymbol{\nu}$. Then from Eqs. (23) and (24) in the linear approximation in $\boldsymbol{\nu}$ we get

$$\mathbf{M}-\mathbf{M}_0=nm[L'(\xi)\boldsymbol{\nu}_\parallel+L(\xi)\boldsymbol{\nu}_\perp], \tag{27}$$

where the components

$$\boldsymbol{\nu}_\parallel=\boldsymbol{\xi}(\boldsymbol{\nu}\cdot\boldsymbol{\xi})/\xi^2,\qquad \boldsymbol{\nu}_\perp=\boldsymbol{\xi}\times(\boldsymbol{\nu}\times\boldsymbol{\xi})/\xi^3,$$

are parallel and perpendicular to the true field, respectively. Employing the relation (27), one can reduce Eq. (26) to the linear magnetization equation

$$\frac{d\mathbf{M}}{dt}=\boldsymbol{\Omega}\times\mathbf{M}-\frac{\mathbf{H}[\mathbf{H}\cdot(\mathbf{M}-\mathbf{M}_0)]}{\tau_\parallel H^2}-\frac{\mathbf{H}\times(\mathbf{M}\times\mathbf{H})}{\tau_\perp H^2}, \tag{28}$$

where relaxation times of the components of magnetization are

$$\tau_\parallel=\frac{d\ln L(\xi)}{d\ln\xi}\tau,\qquad \tau_\perp=\frac{2L(\xi)}{\xi-L(\xi)}\tau. \tag{29}$$

Substituting $\tau_\perp$ from Eq. (29) in Eq. (16), we obtain [5]

$$\eta_r(\xi)=\frac{3}{2}\eta\phi\frac{\xi L^2(\xi)}{\xi-L(\xi)}. \tag{30}$$

In the same approximation our phenomenological equation (9) also takes the form (28) but with other relaxation times: $\tau_\parallel=\tau$ and $\tau_\perp$ is defined in Eq. (14).

Figure 1 shows that though at first sight functions (17) and (30) do not appear alike, they agree fairly closely in the entire range of their argument. Both are in a good agreement with experimental data of many authors and with computational results provided by direct numerical integration of the Fokker-Planck equation in linear approximation in $\Omega\tau$ [17]. Quite recently, Felderhof [18] solved this linearized equation by the Galerkin method using a large number of trial functions (the associated Legendre functions). Comparing his "exact result" for the rotational viscosity with Eqs. (30) and (17), he wrote that "the result of Martsenyuk, Raikher, and Shliomis [5] is quite a good approximation, but the result of Shliomis [2] deviates up to 17%". We note that Felderhof

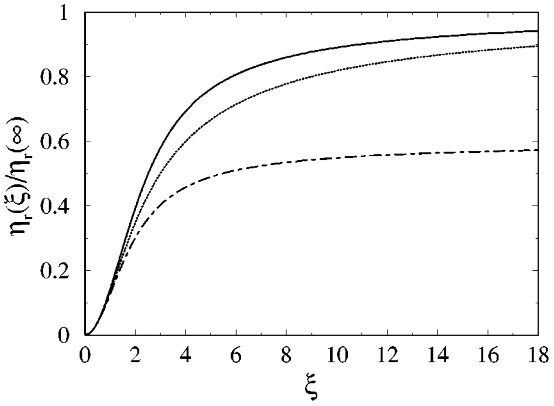

FIG. 1. Reduced rotational viscosity $2\eta_r(\xi)/3\eta\phi$ as a function of ξ given by the effective field method [5] [Eq. (30), solid curve], by the phenomenological approach [2] [Eq. (17), dotted curve], and by Felderhof's approximation [1] [Eq. (32), dash-dotted curve].

''forgot'' to mention in Ref. [18] his own prediction [1] — see the lower curve in Fig. 1— which deviates up to 40%.

IV. DISCUSSION

It is easy to see that Felderhof's ''local field'' $\mathbf{H}_l$ in Eq. (10) is the same as our effective field $\mathbf{H}_e$ determined by Eq. (24). Hence one can use the relationship (27) for a linear analysis of Eq. (10). Substituting in (27) $\boldsymbol{\nu}=\boldsymbol{\xi}_e-\boldsymbol{\xi}=(m/k_BT)(\mathbf{H}_e-\mathbf{H})$, we find

$$(\mathbf{H}_e-\mathbf{H})_\parallel=\frac{(\mathbf{M}-\mathbf{M}_0)_\parallel}{3\chi L'(\xi)},\quad (\mathbf{H}_e)_\perp=\frac{\xi\mathbf{M}_\perp}{3\chi L(\xi)}. \tag{31}$$

Let us substitute these relations in Felderhof's equation (10) and put there $\gamma_H=\chi/\tau$: with such a choice his equation coincides with Eq. (9) in the limit $\xi\ll 1$ as it should be. Then for arbitrary ξ we obtain from Eq. (10), making use of Eqs. (31) and (16),

$$\tau_\perp^F=\frac{6L(\xi)\tau}{\xi[2+3L^2(\xi)]},\quad \eta_r^F=\frac{9}{2}\eta\phi\frac{L^2(\xi)}{2+3L^2(\xi)}. \tag{32}$$

Both the relaxation time and viscosity, in my opinion, are wrong. Indeed, in a strong field $\xi\gg 1$ they take the magnitudes $\tau_\perp^F=6\tau/5\xi$ and $\eta_r^F=9\eta\phi/10$, while it should be $\tau_\perp=2\tau/\xi=6\eta V/mH$ and $\eta_r=3\eta\phi/2$. The dependence $\eta_r^F(\xi)$ shown in Fig. 1 strongly differs from two other curves.

Let us give consideration to the question, why does Felderhof's equation lead to the anomalous results. We have shown above how the Debye equation (7) originates from the potential $\Phi(\mathbf{M})$. One can choose, however, as an independent variable the effective field and introduce the potential $\tilde{\Phi}(\mathbf{H}_e)$. Then instead of Eq. (11) we obtain in similar fashion

$$\frac{d\mathbf{H}_e}{dt}=-\tilde{\gamma}\frac{\partial\tilde{\Phi}}{\partial\mathbf{H}_e},\quad \tilde{\gamma}>0.$$

Acting further by the $L2$ method, we arrive at the equation [cf. Eq. (7)]

$$\frac{d'\mathbf{H}_e}{dt}=-\frac{1}{\tau}(\mathbf{H}_e-\mathbf{H}), \tag{33}$$

where we set $\tilde{\gamma}^{-1}=(\partial^2\tilde{\Phi}/\partial\mathbf{H}_e^2)\tau$. With this choice, Eq. (33) turns into Eq. (7) in the low field limit.

Equations (7) and (33) satisfy the principal propositions of the theory of *linear response* according to which the time rate $\dot{x}$ of change of a value x at each a moment is determined by the value x at the same moment: $\dot{x}=\dot{x}(x)$. Then, if x weakly deviates from its equilibrium value x_0, one can expand $\dot{x}(x)$ over x and confine oneself to the linear term: $\dot{x}=-\lambda(x-x_0)$, where λ is a positive constant. Thus, τ in Eqs. (7) and (33) should be considered as a *constant*. This inference seems important because the method $L1$ of irreversible thermodynamics does not allow, *in principle*, to determine the field dependence of kinetic coefficients such as γ_H in Eq. (10). In the rotating reference frame Σ' the equation reads

$$\frac{d'\mathbf{M}}{dt}=-\gamma_H(\mathbf{H}_e-\mathbf{H}).$$

In contrast to Eqs. (7) and (33), this equation relates one value $(\mathbf{H}_e)$ with time rate of change of another one $(\mathbf{M})$. Therefore, under the nonlinear magnetization law (24), the coefficient γ_H wittingly cannot be constant but represents an *unknown function* of ξ.

Equation (33) has been written out in a coordinate system Σ'. Reverting to the immobile system Σ by the general formula (8) and eliminating $\boldsymbol{\omega}_p$ with the aid of Eq. (2), we obtain [19]

$$\frac{d\mathbf{H}_e}{dt}=\boldsymbol{\Omega}\times\mathbf{H}_e-\frac{1}{\tau}(\mathbf{H}_e-\mathbf{H})-\frac{1}{6\eta\phi}\mathbf{H}_e\times(\mathbf{M}\times\mathbf{H}). \tag{34}$$

This equation determines together with Eq. (24) the magnetization $\mathbf{M}$ in an implicit form, effective field $\mathbf{H}_e$ being the parameter. In the case of small departures from equilibrium, Eq. (34) can be linearized with respect to $\mathbf{H}_e-\mathbf{H}$ and $\mathbf{M}-\mathbf{M}_0$. Using relationships (31) and

$$\frac{d\mathbf{M}}{dt}=\frac{d\mathbf{M}}{d\mathbf{H}_e}\frac{d\mathbf{H}_e}{dt}=3\chi\left[L'(\xi)\frac{d(\mathbf{H}_e)_\parallel}{dt}+\frac{L(\xi)}{\xi}\frac{d(\mathbf{H}_e)_\perp}{dt}\right]$$

we turn to Eq. (28) with $\tau_\parallel=\tau$ and $\tau_\perp$ from Eq. (14). Thus, in linear approximation Eqs. (9) and (34) *coincide* with each other. As a result, both the equations yield *the same* relationship (17) for the rotational viscosity of ferrofluids.

Perhaps if Felderhof had used $\mathbf{H}_e$ as an independent variable *correctly*, he would have arrived at Eq. (34).

V. CONCLUSION

Thus, our theory consists of hydrodynamic and Maxwell equations (5)–(6) plus a magnetization equation. There are three kinds of the latter: Eqs. (9), (26), and (34). It is well established that Eq. (26) derived by the effective field method from the Fokker-Planck equation yields quite accurate results for real ferrofluids. Indeed, a direct numerical simulation of the magnetic moment Brownian dynamics performed by Cebers [20,21] in the mid-1980s has indicated that Eq. (26) describes perfectly the fluid magnetization in a wide range of parameters ξ and $\Omega\tau$. The same conclusion has been made in Ref. [6] by comparing the solution of Eq. (26) with the results of numerical integration of the nonstationary Fokker-Planck equation (20). At the same time, the calculations [20,6] have shown that the phenomenological equation (9) is valid for any field magnitudes ξ but only small enough fluid vorticities: $\Omega\tau\leqslant 1$. Hence Eq. (9) can be recommended for the description of weakly nonequilibrium situations, as the equation is far simpler for analysis than Eq. (26). The latter, however, guarantees the correct quantitative description of magnetization processes even if deviations from the state of equilibrium are large, $\Omega\tau\gg 1$, that is, when Eq. (9) leads to erroneous results. Interestingly, our calculations have shown that the equation for the effective field (34) is free from such a shortcoming: it is valid even far from equilibrium. Therefore, taking into account that Eq. (34) is nevertheless simpler than Eq. (26), one should use Eq. (34) for a wide range of applications.

As for the Felderhof's equation (10), it does not stand up to comparison with our phenomenological equation (9) nor the microscopically derived Eq. (26). We have shown that an incorrectly derived Eq. (10) leads to anomalous results (19) and (32) (see also Fig. 1), which is why we feel it should be rejected.

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