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 corresponding Shliomis’ 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 worded for the first time in our paper [2] almost 30 years ago. In the Comment, we will consider the object of Felderhof’s criticism, analyze his proposition, and explain why 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 \( \rho \), and pressure \( p \).

However, an appropriate thermodynamic coordinate is the difference \( \mathbf{S} - f \mathbf{\Omega} \) where \( \mathbf{\Omega} = \frac{1}{2} \text{curl} \mathbf{v} \) is the local angular velocity of the fluid and \( f \) means the volume density of the particles moment of inertia. For a suspension of spherical particles \( f = \rho_s \phi d^2/10 \) where \( \phi \) is the volume fraction of the dispersed phase, \( \rho_s \) the particles material density, and \( d \) the mean particle diameter. In this case it is convenient to set \( \mathbf{S} = f \mathbf{\omega}_p \) where \( \mathbf{\omega}_p \) is the macroscopic (i.e., averaged over physically small volume) angular velocity of the particles. Any deviation of \( \mathbf{\omega}_p \) from \( \mathbf{\Omega} \) gives rise to dissipation processes due to redistribution of angular momentum between \( \mathbf{L} \) and \( \mathbf{S} \) forms. (The angular momentum conservation law refers, sure, to the total angular momentum \( \mathbf{L} + \mathbf{S} \)). These processes contribute the stress tensor \( \sigma_{ik} \). For an ordinary (nonmagnetic) suspension the tensor has been derived by the methods of irreversible thermodynamics in [3]:

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

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 \( \epsilon_{ikl} \) stands for antisymmetric unit tensor. Apart from the viscosity \( \eta \), Eq. (1) contains once more kinetic coefficient: the spin relaxation time \( \tau_s \).

For \( d = 10 \text{ nm} \) and \( \eta = 10^{-2} \text{ Ps} \) this formula gives \( \tau_s \sim 10^{-11} \text{ s} \). Thus, the difference \( \mathbf{\omega}_p - \mathbf{\Omega} \) 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 which acts directly upon the particles rotation:

\[
6\eta \phi (\mathbf{\omega}_p - \mathbf{\Omega}) = \mathbf{M} \times \mathbf{H}.
\]

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

\[
\mathbf{M}_0 = n m L(x) \frac{\mathbf{H}}{H}, \quad \xi = \frac{m H}{k_B T}, \quad L(x) = \coth \xi - \xi^{-1},
\]

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

\[
\sigma_{ik} = -p \delta_{ik} + \eta \left( \frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right) + \frac{1}{2} \left( M_i H_k - M_k H_i \right) + \frac{1}{4\pi} \left( H_i B_k - H_k B_i \right) \delta_{ik}.
\]

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

\[
\rho \frac{dv_i}{dt} = \frac{\partial \sigma_{ik}}{\partial x_k}, \quad \frac{d}{dt} = \frac{\partial}{\partial t} + (\mathbf{v} \nabla),
\]
determine the equation of ferrofluid motion

$$\frac{d\mathbf{v}}{dt} = -\nabla p + \eta \nabla^2 \mathbf{v} + (\mathbf{M}\mathbf{v})\mathbf{H} + \frac{1}{2} \mathbf{curl} (\mathbf{M} \times \mathbf{H}). \quad (5)$$

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

$$\text{div} \mathbf{v} = 0, \quad \text{curl} \mathbf{H} = 0, \quad \text{div} \mathbf{B} = 0, \quad (6)$$
i.e., the ferrofluid is considered to be incompressible and non-conducting.

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 (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 has been derived phenomenologically [2] as a modification of the Debye relaxation equation [8]. To get the generalized equation, one should introduce a local reference frame \( \Sigma' \), in which the suspended particles are quiescent on the average, i.e., \( \omega'_p = 0 \). It is natural to assume that the magnetization relaxation is described in the system by the simplest Debye-like equation

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

with \( \mathbf{M}_0 \) from (3). 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 \( \tau = 3\eta V/k_BT \) 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 \( \Sigma' \) rotates with respect to the fixed (“laboratory”) system \( \Sigma \) with the angular velocity \( \omega_p \). The rates of change of any vector \( \mathbf{A} \) in systems \( \Sigma \) and \( \Sigma' \) are related by the kinematic expression

$$\frac{dA}{dt} = \omega_p \times \mathbf{A} + \frac{d'A}{dt}. \quad (8)$$

Substituting here \( \mathbf{A} = \mathbf{M}, \omega_p \) from (2), and \( d'M/dt \) from (7), we obtain the equation sought:

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

(Shliomis, 1972). 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 equation [1]

$$\frac{dM}{dt} = \Omega \times \mathbf{M} - \gamma_H (\mathbf{H}_i - \mathbf{H}) - \frac{1}{6\eta\phi} \mathbf{M} \times (\mathbf{M} \times \mathbf{H}) \quad (10)$$

(Felderhof, 2000). Here \( \gamma_H \) is a positive phenomenological constant and \( \mathbf{H}_i = \mathbf{MC}(\mathbf{M}) \) is expressed in terms of the local magnetization [1], that requires an introduction of a very inconvenient notation \( \mathbf{C}(\mathbf{M}) = (k_B T/m \mathbf{M}) L^{-1}(\mathbf{M}/nm) \), 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 (9) since the left- and right-hand sides of (10) contain different relaxing values: \( \mathbf{M} \) and \( \mathbf{H}_i(\mathbf{M}) \). 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 (9) is neither more nor less “postulated” than the term \( \gamma_H (\mathbf{H}_i - \mathbf{H}) \) in (10). It is worth to remind, there are two methods of IT, and the both was 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 the method. One has to be skilful enough to use this cumbersome 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 L1. It was first applied just to the description of relaxation of the order parameter in a non-equilibrium system [11]. An equilibrium value of the parameter (\( \mathbf{M}_0 \) in our case) corresponds to the minimum of an appropriate thermodynamic potential \( \Phi \) (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:

$$\frac{d\mathbf{M}}{dt} = -\gamma \frac{\partial \Phi}{\partial \mathbf{M}} \quad (11)$$

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

$$\frac{d\Phi}{dt} = \frac{\partial \Phi}{\partial \mathbf{M}} \frac{d\mathbf{M}}{dt} = -\gamma (\frac{\partial \Phi}{\partial \mathbf{M}})^2 < 0 \quad (12)$$
as it should be: when a system moves to equilibrium, its free energy decreases. In the case of a weakly non-equilibrium state of the system, one can substitute in (11) and (12) the expansion
\[
\frac{\partial \Phi}{\partial \mathbf{M}} = \left( \frac{\partial \Phi}{\partial \mathbf{M}_0} \right) + \left( \frac{\partial^2 \Phi}{\partial \mathbf{M}^2} \right)_0 (\mathbf{M} - \mathbf{M}_0) + \ldots,
\]
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 the first derivative in this point is equal to zero and the subscript 0 marks the point of equilibrium. As the difference \(\mathbf{M} - \mathbf{M}_0\) leads to anomalous result for ferrofluid viscosity and magnetization relaxation time. The pitfall of IT is discussed in Sec. IV.

Thus, Eq. (7) and hence Eq. (9) are well corroborated by the method of IT. Equation (10) does also not conflict with IT. Nevertheless 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 \(\omega_p\) does not coincide with the angular velocity of the fluid \(\Omega\), there arise friction forces which manifest themselves in an additional (so-called rotational) viscosity \(\eta_r\). As the difference \(\omega_p - \Omega\) is maintained by the magnetic field, (see (2)), rotational viscosity turns out to be a function of the dimensionless field strength \(\xi\). In a stationary field, the steady solution of Eq. (9) yields in the linear order in \(\Omega\)
\[
\mathbf{M} - \mathbf{M}_0 = \tau_\perp (\Omega \times \mathbf{M}_0), \quad \tau_\perp = \frac{2 \tau}{2 + \xi \Omega (\xi)} ,
\]
(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., \(\mathbf{H} \perp \Omega\)), we find
\[
\mathbf{M} \times \mathbf{H} = -\tau_\perp \mathbf{M}_0 H \Omega ,
\]
(15)
while for arbitrary orientation of magnetic field the right-hand side of the expression should be multiplied by \(\sin^2 \alpha\) where \(\alpha\) is the angle between vectors \(\mathbf{H}\) and \(\Omega\). Let us substitute the magnetic torque (15) in (5). When the field \(\mathbf{H}\) is homogeneous, the magnetic force \((\mathbf{M} \mathbf{V}) \mathbf{H}\) in the right-hand side of Eq. (5) vanishes, while two other terms of the equation may be grouped:
\[
\eta \nabla^2 \mathbf{v} + \frac{1}{2} \text{curl} (\mathbf{M} \times \mathbf{H}) = (\eta + \frac{1}{4} \tau_\perp \mathbf{M}_0 H) \nabla^2 \mathbf{v} .
\]
The quantity added here to the ordinary viscosity should be regarded as rotational viscosity
\[
\eta_r = \frac{\tau_\perp}{4} \mathbf{M}_0 H .
\]
(16)
Substituting here \(\mathbf{M}_0\) from (3) and \(\tau_\perp\) from (14), we derive the formula [2]
\[
\eta_r (\xi) = \frac{3}{2} \eta \phi \xi L (\xi) + \frac{3}{2} \eta \phi \xi - \tanh \xi \xi + \tanh \xi \xi .
\]
(17)
In the absence of magnetic field an individual particle “rolls” freely along corresponding shear surface with angular velocity \(\omega_p\) equal to \(\Omega\), so that \(\eta_r (0) = 0\). Conversely, \(\eta_r (\xi)\) attains its limiting value
\[
\eta_r (\xi) = 3 \eta \phi / 2
\]
(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 \(\omega_p = \omega\), so that Eq. (2) takes the form \(\mathbf{M} \times \mathbf{H} = -6 \eta \phi \Omega\). Substituting this torque in (5), we immediately arrive at (18). Indeed, the value was obtained by Hall and Busenberg [12] as early as 1969 without 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 the quite different result. His final formula in [1] gives the value
\[
\eta_r (\xi) = \frac{3}{2} \eta \phi \frac{(nm)^2}{6 \eta \phi \gamma H + (nm)^2} ,
\]
(19)
which is evidently less than the correct value (18). According to [1], \(\gamma_H = \chi / \tau\) where \(\chi = nm^2 / 3 k_B T\) is the initial magnetic susceptibility. Substituting the \(\gamma_H = \phi = n V\) in (19) we find \(6 \eta \phi \gamma H = 2 (nm)^2 / 3\), afterwards Eq. (19) yields \(\eta_r (\xi) = 9 \eta \phi / 10\). Thus the ratio of the Felderhof’s limiting value of viscosity to the correct value (18) is equal to 0.6. Other words, in the limit \(\xi = \infty\) Felderhof’s equation (10) predicts \(\omega_p = 0.4 \Omega\) (!!) instead of \(\omega_p = 0\) as it must be.

III. MAGNETIZATION EQUATION DERIVED MICROSCOPICALLY

Both the above-mentioned phenomenological methods allow to obtain linear relaxation terms in hydrodynamic equations [like \((\mathbf{M}_0 - \mathbf{M}) / \tau\) in (9)] and corresponding quadratic terms for the rate of the entropy growth or the free energy diminution (like that in (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 \(\tau r\) (see, e.g., a good agreement between McTague’s experiment [13] and Shliomis’ theory [2]), or for small dimensionless amplitude \(\xi\) or frequency \(\omega r\) of an alternating magnetic field (see, e.g., experiments on the negative viscosity and their explanation...
in [14]). Meanwhile, to describe successfully the negative ferrofluid viscosity at finite values of the parameters, we did need to use in [15,16] a more precise magnetization equation. Such a macroscopic equation should be derived from the kinetic Fokker–Planck equation which provides the microscopic description of particle diffusion in colloids. The program was realized by Martsenyuk, Raikher and Shliomis [5] soon after the phenomenological magnetization equation (9) was derived in [2].

The Fokker–Planck equation for a ferrofluid moving in a field \( \mathbf{H} \) has the form [7]
\[
2\tau \frac{\partial W}{\partial t} = \hat{\mathbf{R}} \cdot (\hat{\mathbf{R}} - 2\tau \mathbf{\Omega} - \mathbf{e} \times \mathbf{e}) W, \tag{20}
\]
where \( \mathbf{e} = \mathbf{m}/m \) is the unit vector along a particle magnetic moment, \( \mathbf{\xi} = m\mathbf{H}/k_B T \), 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 \( \mathbf{M}(t) = nm(\mathbf{e}) \) where angular brackets denote statistical averaging with the distribution function. Multiplying Eq. (20) by \( \mathbf{e} \) and integrate over the angles, we arrive at the equation
\[
2\tau \frac{d(\mathbf{e})}{dt} = 2\tau \mathbf{\Omega} \langle \mathbf{e} \rangle - 2(\mathbf{e}) - \langle \mathbf{e} \times (\mathbf{e} \times \mathbf{e}) \rangle, \tag{21}
\]
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 [5]. Let us explain the fruitful physical idea.

In equilibrium (\( \mathbf{\Omega} = 0 \)) under a constant magnetic field the stationary solution of Eq. (20) is the Gibbs distribution
\[
W_0(\mathbf{e}) = \frac{\xi}{4\pi \sinh \xi} \exp(\xi \mathbf{e}). \tag{22}
\]
An averaging of the vector \( \mathbf{e} \) with function (22) gives expression (3) for the equilibrium magnetization:
\[
\mathbf{M}_0 = nmL(\xi) \frac{\mathbf{\xi}}{\xi}. \tag{23}
\]

Only in true equilibrium the magnetization is one or another function of the field. In a non-equilibrium state there is no connection between \( \mathbf{M} \) and \( \mathbf{H} \): any arbitrary magnetization may be created – in principle – even in the absence of the field. Nevertheless, one may consider any value of \( \mathbf{M} \) as an equilibrium magnetization in a certain – specially prepared – magnetic field. This effective field \( \mathbf{H}_e \) is related to the non-equilibrium magnetization by the equilibrium relation:
\[
\mathbf{M} = nmL(\xi) \mathbf{\xi}/\xi. \tag{24}
\]

During the equilibrium settling process, the dimensionless effective field \( \xi_e = mH_e/k_B T \) tends to the true field \( \xi_e \) so the magnetization (24) relaxes to its equilibrium value (23). Comparing (23) and (24), we see that the latter is obtained by averaging of \( \mathbf{e} \) with the distribution function
\[
W_e(\mathbf{e}) = \frac{\xi_e}{4\pi \sinh \xi_e} \exp(\xi_e \mathbf{e}), \tag{25}
\]
which differs from the Gibbs distribution (22) by replacement of the true field by the effective one. Carrying out the averaging in (21) with the function (25), we find the sought equation [5]
\[
\frac{d}{dt} [L(\xi_e) \frac{\mathbf{\xi}_e}{\xi_e}] = \mathbf{\Omega} \times \left[ L(\xi_e) \frac{\mathbf{\xi}_e}{\xi_e} - \frac{L(\xi_e)}{\tau \xi_e} (\xi_e - \mathbf{\xi}) \right] - \frac{\mathbf{\xi}_e - 3L(\xi_e)}{2\tau \xi^3} \xi_e \times (\mathbf{\xi}_e \times \mathbf{\xi}). \tag{26}
\]

This equation defines the dependence of the effective field \( \xi_e \) upon time, true field \( \xi \), and the fluid vorticity \( \mathbf{\Omega} \). Its solution \( \xi_e \) being substituted into (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: \( \xi_e = \xi + \nu \). Then from (23) and (24) in the linear approximation in \( \nu \) we get
\[
\mathbf{M} - \mathbf{M}_0 = nm \left[ nL(\nu_\parallel) + L(\nu) \nu_\perp \right], \tag{27}
\]
where the components
\[\nu_\parallel = \xi(\nu \mathbf{\xi})/\xi^2, \quad \nu_\perp = \mathbf{\xi} \times (\nu \mathbf{\xi})/\xi^3\]
are parallel and perpendicular to the true field, respectively. Employing the relation (27), one can reduce Eq. (26) to the linear magnetization equation
\[
\frac{d\mathbf{M}}{dt} = \mathbf{\Omega} \times \mathbf{M} - \mathbf{H}[\mathbf{H}(\mathbf{M} - \mathbf{M}_0)] - \frac{\mathbf{H} \times (\mathbf{M} \times \mathbf{H})}{\tau \nu_\perp H^2}, \tag{28}
\]
where relaxation times of the components of magnetization are
\[
\tau_\parallel = \frac{d \ln L(\xi)}{d \ln \xi} \tau, \quad \tau_\perp = \frac{2L(\xi)}{\xi - L(\xi)} \tau. \tag{29}
\]
Substituting \( \tau_\perp \) from (29) in (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 (14).
IV. DISCUSSION

It is easy to see that Felderhof’s “local field” $H_e$ in (10) is none other than our effective field $H_e$ determined by (24). Hence one can use the relationship (27) for a linear analysis of Eq. (10). Substituting in (27) $\nu = \xi_e - \xi = (m/k_BT)(H_e - H)$, we find

$$
(H_e - H) = \frac{(M - M_0)}{3\chi L'(\xi)}, \quad (H_e) = \frac{\xi M}{3\chi L(\xi)}.
$$

(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 (9) in the limit $\xi \ll 1$ as it should be. Then for arbitrary $\xi$ we obtain from (10), making use of (31) and (16),

$$
\tau_\perp^\xi = \frac{6L(\xi)}{\xi[2 + 3L^2(\xi)]}, \quad \eta_\parallel^\xi = \frac{9}{2} \frac{\eta}{3L^2(\xi)}.
$$

(32)

Both the relaxation time and viscosity are wrong. Indeed, in a strong field, $\xi \gg 1$, they take the magnitudes $\tau_\perp^\xi = 6\tau/5\xi$ and $\eta_\parallel^\xi = 9\eta/10$, while it should be $\tau_\perp = 2\tau/\xi = 6\etaV/mH$ and $\eta_\parallel = 3\eta/2$. The dependence $\eta_\parallel^\xi(\xi)$ 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 does Debye equation (7) originate from the potential $\Phi(M)$. One can choose, however, as an independent variable the effective field and introduce the potential $\Phi(H_e)$. Then instead of (11) we obtain in similar fashion

$$
\frac{dH_e}{dt} = -\gamma \frac{\partial}{\partial H_e} \Phi, \quad \gamma > 0.
$$

(33)

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

$$
\frac{dH_e}{dt} = -\frac{1}{\tau}(H_e - H),
$$

(34)

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

Equations (7) and (33) satisfy the principal propositions of the theory of linear response according to which the rate $\dot{x}$ of change of a value $x$ at each a moment is determined by the value $x$ at the same moment: $\dot{x} = \lambda x_0$. 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 $\lambda$ is a positive constant. Thus, $\tau$ in (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 $\gamma_H$ in (10). In the rotating reference frame $\Sigma'$ the equation reads

$$
\frac{dM}{dt} = -\gamma_H (H_e - H).
$$

In contrast with (7) and (33), this equation relates one value $H_e$ with time rate of change of another one $M$. Therefore, under the nonlinear magnetization law (24), the coefficient $\gamma_H$ writeingly cannot be constant but represents a unknown function of $\xi$. Equation (33) has been written out in a coordinate system $\Sigma'$. Reverting to the immobile system $\Sigma$ by the general formula (8) and eliminating $\omega_p$, the aid of (2), we obtain [19]

$$
\frac{dH_e}{dt} = \Omega \times H_e - \frac{1}{\tau} (H_e - H) - \frac{1}{6\eta_\perp} H_e \times (M \times H).
$$

(34)

This equation determines together with (24) the magnetization $M$ in an implicit form, effective field $H_e$ being the
parameter. In the case of small departures from equilibrium, Eq. (34) can be linearized with respect to $H_e - H$ and $M - M_0$. Using relationships (31) and

$$\frac{dM}{dt} = \frac{dM}{dH_e} \frac{dH_e}{dt} = 3\lambda \left[ L' (\xi) \frac{d(H_e)}{dt} + L (\xi) \frac{d(H_e)}{d\tau} \right]$$

we turn to Eq. (28) with $\tau = \tau$ and $\tau_1$ from (14). Thus, in linear approximation Eqs. (9) and (34) coincide with each other. As the result, both the equations yield the same relationship (17) for the rotational viscosity of ferrofluids.

It is worth to note, if Felderhof had used $H_e$ as an independent variable correctly, he would have arrived at Eq. (34). However, he has missed the opportunity.

V. CONCLUSION

Thus, Shliomis’ theory consists of hydrodynamic and Maxwell equations (5)-(6) plus a magnetization equation. There are three kinds of the latter: (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 middle of 80th has indicated that Eq. (26) describes perfectly the dynamics performed by Cebers [20,21] in the middle of 80th. At the same time, the calculations [20,6] have shown that the phenomenological equation (9) is valid for any field magnitudes $\xi$ but only small enough fluid vorticities: $\Omega \tau \leq 1$. Hence Eq. (9) can be recommended to 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 latest calculations have shown that the new equation for the effective field (34) is free from such a shortcoming: it is valid even far from equilibrium. Therefore, taking into account that (34) is nevertheless simpler than (26), one should recommend Eq. (34) to the most wide applications.

As for the Felderhof’s equation (10), it does not stand up to comparison even with our phenomenological equation (9) to say nothing of the microscopically derived Eq. (26). We have shown that incorrectly derived Eq. (10) leads to anomalous results (19) and (32) – see also Fig. 1 – and that is why it should be rejected.

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