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# Reply to "Comment on 'Magnetoviscosity and relaxation in ferrofluids'"

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The relation between the macroscopic theory of dense ferrofluids and the microscopic theory of dilute ferrofluids is discussed. It is shown that the dense and dilute regimes must be carefully distinguished. Shliomis's approximate theory for dilute ferrofluids does not apply in the dense regime, and has limited validity in the dilute regime.

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## I. DYNAMICS OF FERROFLUIDS

In his Comment [1] on my paper [2] Shliomis does not recognize that the dynamics of ferrofluids must be described by different methods in different regimes of density. My paper was concerned with dense ferrofluids. In the dense regime the suspended ferromagnetic particles interact strongly by direct and hydrodynamic interactions. On a slow timescale, macroscopic behavior of the suspension may be described by Maxwell's equations of magnetostatics, thermodynamics, and an extension of hydrodynamics. The thermodynamic equation of state and the transport coefficients of hydrodynamics are difficult to calculate, and must be obtained from experiment or computer simulation. On the other hand, at sufficiently low density interactions between particles can be neglected. The particles perform individual Brownian motion of position and orientation. On the slow timescale of diffusion particle inertia can be neglected. Statistically the system is described by a single-particle distribution function. If the spatial distribution in a volume element is uniform, it suffices to consider the orientational distribution function. Its time evolution is governed by a Smoluchowski equation, called Fokker-Planck equation by Shliomis [1].

Shliomis claims that the relaxation of magnetization of a dense suspension can be described by his Eq. (26), derived from an effective field approximation to the Smoluchowski equation, and that the macroscopic equation (26) guarantees a correct description of magnetization processes even for large deviations from equilibrium. I take issue with both claims. First, there is no guarantee that an equation derived as an approximation for the dilute regime has any validity in the dense regime. Second, in the dilute regime it is necessary to consider the full distribution function, and a relaxation equation for the magnetization can only be approximate. On occasion, the equation may describe the time dependence of the magnetization fairly well, but it can also be substantially wrong.

The situation is somewhat analogous to the theory of gases. Flow phenomena of a Knudsen gas must be described by the full single-particle distribution function. For a dense fluid one uses thermodynamics and hydrodynamic equations with phenomenological transport coefficients that are difficult to calculate from microscopic theory.

## II. MACROSCOPIC THEORY

Within the framework of macroscopic theory Kroh and I derived an expression for the rate of entropy production consistent with Maxwell's equations, equilibrium thermodynamics, and hydrodynamics [3]. With the expression firmly established, it is natural to explore the consequences of the corresponding phenomenological relaxation equation for the simplest case of a variable-independent relaxation time. The equation had been proposed earlier on more intuitive grounds [4,5].

In the following I indicate Shliomis' equations [1] by a prefix *S*, and the equations of my paper [2] by a prefix *F*. Since Shliomis in Eq. (S10) quotes my Eq. (F2.15) incorrectly, I repeat it here:

$$\frac{\partial \boldsymbol{M}}{\partial t}+\boldsymbol{\nabla}\cdot(\boldsymbol{v}\cdot\boldsymbol{M})-\boldsymbol{\Omega}\times\boldsymbol{M}=\gamma_H(\boldsymbol{H}-\boldsymbol{H}_\ell)-\frac{1}{4\zeta}\boldsymbol{M}\times(\boldsymbol{M}\times\boldsymbol{H}). \tag{1}$$

First of all, I did not assume $\boldsymbol{\nabla}\cdot\boldsymbol{v}=0$. Second, I did not replace the vortex viscosity $\zeta$ by $\frac{3}{2}\eta\phi$, an expression valid only for dilute ferrofluids. Third, I did not call $\boldsymbol{H}_\ell$ the "local field," as Shliomis does in his Discussion in Ref. [1]. The subscript $\ell$ stands for "local equilibrium." The name "effective field" seems rather less appropriate.

Constant $\gamma_H$ is the simplest possible behavior, but is not required by irreversible thermodynamics. Following Landau and Khalatnikov [6], Shliomis assumes constant $\gamma_H$ below Eq. (S11). His thermodynamic potential $\Phi(\boldsymbol{M})$ reads in my notation, cf. Eq. (F2.12),

$$\Phi(\boldsymbol{M})=\varphi(M)-\boldsymbol{M}\cdot\boldsymbol{H}, \tag{2}$$

where $\boldsymbol{H}$ is the local Maxwell field. At the equilibrium point $\boldsymbol{M}_0=\boldsymbol{M}_{eq}$ corresponding to $\boldsymbol{H}$, the derivative $\partial\Phi/\partial\boldsymbol{M}$ vanishes, and $\boldsymbol{H}$ equals $\boldsymbol{H}_\ell(\boldsymbol{M}_0)=(\partial\varphi/\partial\boldsymbol{M})_0$. From Eq. (F2.11) one finds the derivative $\partial\varphi/\partial M=MC(M)$, and Eq. (F2.9) can be expressed as

$$\boldsymbol{H}-\boldsymbol{H}_\ell=-\left(\frac{\partial^2\Phi}{\partial\boldsymbol{M}^2}\right)_0\cdot(\boldsymbol{M}-\boldsymbol{M}_0)+O((\boldsymbol{M}-\boldsymbol{M}_0)^2). \tag{3}$$

Note that $(\partial^2\Phi/\partial\boldsymbol{M}^2)_0$ is a second-rank tensor that is not proportional to the unit tensor, so Shliomis' Eq. (S11) does not turn into Eq. (S7), even for small deviations from equilibrium, and Eq. (S13) is wrong.

Thus Shliomis' Eq. (S7) with constant $\tau$, as formulated originally [8], is not corroborated by irreversible thermodynamics in an obvious way. On the other hand, since $\boldsymbol{H}_{\ell} = \partial\varphi/\partial \boldsymbol{M}$ by definition, his Eq. (S11) with constant $\gamma$ turns into Eq. (1) with constant $\gamma_H = \gamma$.

As noted above, the assumption that $\gamma_H$ is a constant adopts the simplest possibility, but is not a necessary consequence of irreversible thermodynamics. However, Einstein argued the assumption in his second paper on Brownian motion [7]. Einstein called the coefficient $\gamma_H$ for general macroscopic variable $\alpha$ the "mobility of the system in respect to $\alpha$," and extended the relaxation equation to a diffusion equation. The assumption of constant mobility is often made, and it is part of Landau theory [6,9]. It is also part of the general formulation of irreversible thermodynamics of Onsager and Machlup [10]. It is the first statement in Becker's treatment of the subject [11], and it is commonly made in the theory of dynamical critical phenomena [12]. It has been shown by Meixner [13] that it can serve as a basis for the derivation of various "kinetic" equations for the motion in an "internal coordinate space." Various examples are treated in the book of de Groot and Mazur [14]. In particular, it is noteworthy that the Smoluchowski equation for the orientational distribution function of a dilute dipolar suspension has been derived by Prigogine and Mazur [15] in this manner. They also proposed a generalization of the equation to higher density. For a recent discussion on the relaxation equation with constant mobility see Adelman and Ravi [16], who ascribe the theory to Onsager [10], rather than Einstein [7].

Shliomis claims that the relaxation term $\gamma_H(\boldsymbol{H}-\boldsymbol{H}_{\ell})$ with constant $\gamma_H$ in Eq. (1) is wrong. However, his claim is based on a comparison with results for dilute suspensions. As argued above, the macroscopic theory is not designed for dilute suspensions.

At the beginning of his Sec. III, Shliomis states that the phenomenological methods allow one to obtain only linear relaxation laws. The Einstein theory equation Eq. (S11) is clearly nonlinear. Conversely, if the linear relaxation behavior is known at each equilibrium point, then the field-dependence of the relaxation time can be deduced, and one can formulate the nonlinear relaxation equation for large deviations. Shliomis suggests that in nonlinear situations the relaxation equation (S26), derived from Brownian motion theory for dilute suspensions, should be used. This ignores again the fact that dense suspensions are qualitatively different from dilute ones.

At the end of his Sec. 4, Shliomis proposes yet another relaxation equation, Eq. (S34). His starting point above Eq. (S33) ignores the tenet of irreversible thermodynamics that on the left-hand side of a phenomenological rate equation the rate of change of an extensive or additive variable should appear [10,17,18]. It was argued already by Onsager [19] that the right-hand side should be expressed in terms of thermodynamic forces. Thus the canonical form is $\dot{a}_i = F_i(\{X_j\})$, where $\{a_i\}$ are additive variables, and $\{X_j\}$ the conjugate thermodynamic forces. The use of additive variables on the left is essential in the derivation of the equation from statistical foundations [20–22]. Thus Eq. (S34) does not seem plausible. Its agreement with Eq. (S9) for small departures from equilibrium does not make it more so.

Thus I maintain that for dense ferrofluids Eq. (F2.15) with constant $\gamma_H$ is a plausible conjecture, worth exploring. The actual variation of the transport coefficient, and its possible extension to a tensor property, must be found from experiment or computer simulation.

One of the goals of my paper was to investigate how the modified relaxation equation affects the field dependence of magnetoviscosity. Its second goal was to show that the conventional calculation of magnetoviscosity, as proposed by Shliomis [8], is not correct for dense suspensions. It is necessary to take collective interactions into account via Maxwell's equations. The grouping of terms carried out by Shliomis [1] following Eq. (S15) is misleading. It suggests that one is dealing with a modification of the transport coefficient viscosity. Moreover, it suggests that the magnetoviscosity derives from an antisymmetric stress tensor [23]. In planar Couette flow both curl ($\boldsymbol{M}\times\boldsymbol{H}$) and the Kelvin force density $(\boldsymbol{M}\cdot\nabla)\boldsymbol{H}$ vanish. In Poiseuille flow with applied field along the tube both differ from zero. Actually, the contribution to magnetoviscosity under consideration is only an apparent viscosity. It is merely a way of expressing the effect of the magnetic forces and torques on the flow of the suspension. Note that the resulting magnetic force density is the divergence of a symmetric stress tensor, the sum of $\mathsf{T}_a$ and $\mathsf{T}_m$ in Rosensweig's notation [23]. A second contribution to magnetoviscosity comes from the influence of the magnetic field on the average hydrodynamic stress tensor via the microstructure of the suspension. This contribution is a genuine local transport coefficient. It vanishes for a dilute suspension of spherical particles.

It remains to discuss the limiting value of magnetoviscosity at high field. As shown in Eq. (F7.5), the relaxation equation (1) with constant $\gamma_H$ leads to a value $\eta_r(\infty)$ less than $\zeta$, whereas Shliomis' relaxation equation leads to the value $\frac{3}{2}\eta\phi$, the value of the vortex viscosity $\zeta$ for low volume fraction. His argument why this must be so on the basis of Eq. (S5) is incorrect. As shown in an earlier paper with Kroh [24], one should regard Eq. (F2.14) as a means of calculating the average angular velocity of particles from the known vorticity, magnetization, and magnetic field. In the fast rotational relaxation approximation, the mean angular velocity becomes a dependent variable. Logically one is not allowed to fix its value. The limiting value of the magnetoviscosity must be obtained from the equations for $\boldsymbol{v}$, $\boldsymbol{M}$, and $\boldsymbol{H}$, including the relaxation equation. A different relaxation equation can yield a different value.

## III. MICROSCOPIC THEORY

For an explanation of the dynamics of dilute ferrofluids, a microscopic theory is required. Since interactions can be neglected, it suffices to consider a single particle. A first theory based on hydrodynamics and magnetostatics, but omitting the effect of Brownian motion, was constructed by Hall and Busenberg [25]. They used an incorrect expression for the

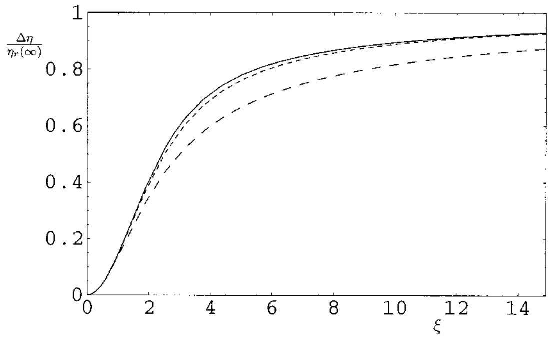


FIG. 1. Plot of the reduced magnetoviscosity $\Delta\eta_\| / \eta_r(\infty)$ of a dilute ferrofluid, as a function of the variable $\xi = mH_0/k_BT$ as calculated from the exact solution for the orientational distribution function (solid curve), from Shliomis' approximation [8] (long dashes), and from the approximation of Martsenyuk *et al.* [28] (short dashes).

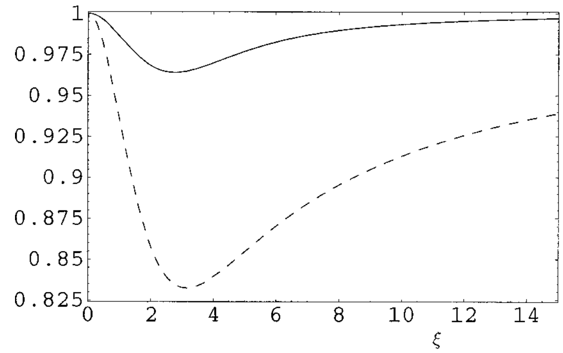


FIG. 2. Ratio of the approximate result of Shliomis [8] for the magnetoviscosity $\Delta\eta_\|$ to the exact value as a function of $\xi$ (long dashes). Similarly the ratio of the approximate result of Martsenyuk *et al.* [28] to the exact value (solid curve).

entropy production, cf. Eq. (F2.16), and their result for the magnetoviscosity is correct only in the high-field limit, $\eta_r(\infty) = \frac{3}{2}\eta\phi$. The reason why the limiting value is correct is evident from Eq. (F6.1).

It is preferable to calculate the magnetoviscosity from the stress tensor [2], rather than from the entropy production. For Poiseuille or planar Couette flow with applied field parallel to the tube or the plates, one can argue [2] that it suffices to evaluate the transverse component of the magnetization. The effect of Brownian motion was studied independently by Shliomis [8] and by Brenner and Weissman [26]. In the theory of Shliomis the effect was included via the relaxation equation Eq. (S7). Brenner and Weissman solved the steady-state Smoluchowski equation for the orientational distribution function numerically for a variety of flow situations. A similar numerical scheme was proposed by Levi *et al.* [27]. Martsenyuk *et al.* [28] used the Smoluchowski equation to derive an approximate magnetic relaxation equation, and hence found Eq. (S30). Incidentally, the limiting value $\eta_r(\infty) = \frac{3}{2}\eta\phi$ follows straightforwardly from the behavior of the steady-state orientational distribution function at high field.

Recently I have shown that for a dilute suspension the magnetoviscosity can be evaluated exactly from a simple scheme [29]. Considering the case of Poiseuille flow with applied magnetic field $\boldsymbol{H}_0$ along the axis of the tube we find from Eq. (F5.6) $\Delta\eta_\| = \frac{1}{2}Q_\| B_{eq}$, where $Q_\| = m_\rho/(2\Omega)$, with $m_\rho$ the component of magnetization transverse to the tube axis. This can be calculated to first order in the vorticity from the Smoluchowski equation for the orientational distribution function. For a dilute suspension the equilibrium magnetic induction $B_{eq}$ may be replaced by $H_0$. The value $\frac{1}{2}Q_\| H_0$ may be compared with the expressions for $\eta_r$ given by Eqs. (S14) and (S30) found from the approximations of Shliomis [8] and Martsenyuk *et al.* [28]. In Fig. 1 we plot the exact result, as well as the two approximate expressions, as a function of $\xi$. In Fig. 2 we plot the ratio of the two approximate expressions to the exact result. This shows that the approximate result of Martsenyuk *et al.* [28] is quite good, but that Shliomis' result [8] deviates up to 17%.

At the end of his Sec. 3, Shliomis comments on my solution of the Smoluchowski equation [29]. Contrary to his suggestion, the method used leads to rapid convergence to the exact result. I did not "forget" to mention the result of Ref. [2]. There is no point in the comparison, since the relaxation equation (1) cannot be used in the dilute regime, as explained at length above.

For a dilute suspension the behavior of the magnetization after a sudden change of field can also be calculated exactly [30,31]. The result can be compared with the approximate relaxation equations (S9) and (S26). If the final field vanishes, then the decay is exponential for arbitrary value of the initial field, and this is reproduced precisely by both approximate equations. If the initial field is suddenly reversed, then the decay is more complicated. For initial field $\xi = 15$ the mean relaxation time, calculated from the integral of the relaxation function

$$\Gamma_1(t) = \frac{M(t)/M_s + L(\xi)}{2L(\xi)}, \tag{4}$$

is $\tau_M = 0.2309\tau$. The approximate Eq. (S9) yields $\tau_M = \tau$, and Eq. (S26) yields $\tau_M = 0.2406\tau$. At $t = 1.5\tau_M$ the exact relaxation function equals 0.186, and the approximate relaxation function found from Eq. (S26) equals 0.220, overestimating the exact value by 18.5%.

The above-mentioned results of the microscopic theory show that for dilute ferrofluids approximate relaxation equations for the magnetization must be used with caution. In any case, it is preferable to solve the Smoluchowski equation for the distribution function. How a calculation valid for the dilute regime can be extended into the dense regime remains a difficult question. It is not clear at which density and at which timescale the microscopic theory can be replaced by the macroscopic one. The calculation of transport coefficients occurring in the macroscopic equations for dense suspensions from the microscopic foundations remains a challenge.

[1] M.I. Shliomis, Phys. Rev. E. **64**, 063501 (2001).
[2] B.U. Felderhof, Phys. Rev. E **62**, 3848 (2000).
[3] B.U. Felderhof and H.J. Kroh, J. Chem. Phys. **110**, 7403 (1999).
[4] J.T. Jenkins, J. Phys. (France) **32**, 931 (1971).
[5] E. Blums, A. Cebers, and M.M. Maiorov, *Magnetic Fluids* (de Gruyter, Berlin, 1996), p. 142.
[6] L.D. Landau and I.M. Khalatnikov, Dokl. Akad. Nauk SSSR **96**, 469 (1954).
[7] A. Einstein, Ann. Phys. (Leipzig) **19**, 371 (1906); reprinted in the English translation in *Investigations on the Theory of the Brownian Movement*, edited by R. Fürth (Dover, New York, 1956).
[8] M.I. Shliomis, Sov. Phys. JETP **34**, 1291 (1972).
[9] E.M. Lifshitz and L.P. Pitaevskii, *Physical Kinetics* (Pergamon, Oxford, 1981), Chap. 12.
[10] L. Onsager and S. Machlup, Phys. Rev. **91**, 1505 (1953).
[11] R. Becker, *Theory of Heat*, 2nd ed. (Springer, Berlin, 1967), p. 344.
[12] P.C. Hohenberg and B.I. Halperin, Rev. Mod. Phys. **49**, 435 (1977).
[13] J. Meixner, Z. Phys. **149**, 624 (1957).
[14] S.R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics* (North-Holland, Amsterdam, 1962), p. 229.
[15] I. Prigogine and P. Mazur, Physica (Utrecht) **19**, 241 (1953).
[16] S.A. Adelman and R. Ravi, Adv. Chem. Phys. **115**, 181 (2000).
[17] Ref. [14], p. 85.
[18] N.G. van Kampen, Physica (Utrecht) **67**, 1 (1973).
[19] L. Onsager, Phys. Rev. **37**, 405 (1931); **38**, 2265 (1931).
[20] N.G. van Kampen, Physica (Utrecht) **23**, 707 (1957); **23**, 816 (1957).
[21] Ref. [14], Chap. 6.
[22] N.G. van Kampen, *Stochastic Processes in Physics and Chemistry* (North-Holland, Amsterdam, 1992), Chap. 10.
[23] R.E. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, 1985), p. 265.
[24] H.J. Kroh and B.U. Felderhof, Z. Phys. B: Condens. Matter **66**, 1 (1987).
[25] W.F. Hall and S.N. Busenberg, J. Chem. Phys. **51**, 137 (1969).
[26] H. Brenner and M.H. Weissman, J. Colloid Interface Sci. **41**, 499 (1972).
[27] A.C. Levi, R.F. Hobson, and F.R. McCourt, Can. J. Phys. **51**, 180 (1973).
[28] M.A. Martsenyuk, Yu.L. Raikher, and M.I. Shliomis, Zh. Eksp. Teor. Fiz. **65**, 834 (1973) [Sov. Phys. JETP **38**, 413 (1974)].
[29] B.U. Felderhof, Magnetohydrodynamics (N.Y.) **36**, 396 (2000).
[30] J.L. Déjardin, P.M. Déjardin, Yu.P. Kalmykov, and S.V. Titov, Phys. Rev. E **60**, 1475 (1999).
[31] B.U. Felderhof and R.B. Jones, J. Chem. Phys. **115**, 4444 (2001).