Magnetoviscosity and relaxation in ferrofluids

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The increase in viscosity of a ferrofluid due to an applied magnetic field is discussed on the basis of a phenomenological relaxation equation for the magnetization. The relaxation equation was derived earlier from irreversible thermodynamics, and differs from that postulated by Shliomis. The two relaxation equations lead to a different dependence of viscosity on magnetic field, unless the relaxation rates are related in a specific field-dependent way. Both planar Couette flow and Poiseuille pipe flow in parallel and perpendicular magnetic field are discussed. The entropy production for these situations is calculated and related to the magnetoviscosity.

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I. INTRODUCTION

The flow of a ferrofluid can be manipulated by application of a magnetic field. A locally nonuniform field leads to a force density acting on the fluid. Besides the usual viscosity, two dissipative processes govern the dynamics, namely, rotational friction of ferromagnetic particles against the suspending fluid, and magnetic relaxation [1,2]. For sufficiently large particles magnetic relaxation is due to orientational Brownian motion of the permanent magnetic dipoles. For a dilute ferrofluid in weak magnetic field this leads to a simple relation between the two transport coefficients. For dense ferrofluids the transport coefficients are modified by hydrodynamic, magnetic, and other interactions between particles, and are not easily calculated. For such systems one is forced to take a more phenomenological point of view.

Recently we have studied the irreversible thermodynamics of ferrofluids on the basis of hydrodynamics and the full set of Maxwell equations [3]. The analysis led to an expression for the entropy production and phenomenological relaxation equations for internal rotation and magnetization. The relaxation equation for magnetization is closely related, but not identical to the equation postulated earlier by Shliomis [4]. In the following we explore the consequences for the dependence of viscosity on magnetic field, and compare them with the predictions made on the basis of Shliomis' relaxation equation [2,4,5].

We consider both planar Couette flow and Poiseuille pipe flow in parallel and perpendicular magnetic fields. For Couette flow the magnetoviscosity is calculated from the magnetic stress tensor. For Poiseuille flow it follows from the flow pattern for given applied pressure gradient. We show that in both cases the magnetoviscosity can be calculated alternatively from the entropy production.

The magnetoviscosity shows a dependence on magnetic field which agrees with that calculated from Shliomis' relaxation equation only if the ratio of relaxation rates for the two equations depends on magnetic field in specific fashion, determined by the equilibrium equation of state. We compare predictions following from the assumption that the two rates do not depend on magnetic field.

The analysis suggests that relaxation of magnetization in a ferrofluid should be analyzed critically on the basis of experiment and computer simulation. Both the dependence of magnetoviscosity on magnetic field and the relaxation of magnetization after the field is turned off are of interest. Theoretical analysis of dense ferrofluids in the framework of nonequilibrium statistical mechanics is difficult, but in principle can be based on the generalized Smoluchowski equation for Brownian motion [6].

II. RELAXATION EQUATIONS

We study steady state flow situations of a ferrofluid displaced slightly from thermal equilibrium due to an imposed shear flow. In thermal equilibrium the fluid is at rest everywhere. The local magnetization $\mathbf{M}_{\mathrm{eq}}(\mathbf{r})$ and the local magnetic field $\mathbf{H}_{\mathrm{eq}}(\mathbf{r})$ are then related by the equilibrium equation of state, which we write in the form

$$\mathbf{M}_{\mathrm{eq}}=\mathbf{H}_{\mathrm{eq}}A(H_{\mathrm{eq}}), \tag{2.1}$$

where $A(H)$ is a known function of magnetic field. For numerical purposes we shall use the expression

$$A(H)=\frac{M_s}{H}L\left(\frac{3\chi_0 H}{M_s}\right) \tag{2.2}$$

with the Langevin function $L(\xi)=\coth\xi-\xi^{-1}$. The saturation magnetization M_s and the initial susceptibility χ_0 enter as parameters. For a dilute ferrofluid $M_s=n\mu$ and $\chi_0=n\mu^2/(3k_BT)$, where n is the number density of Brownian particles, μ is the size of the magnetic moment of a particle, and T is the temperature. We shall also use Eq. (2.1) in the inverted form

$$\mathbf{H}_{\mathrm{eq}}=\mathbf{M}_{\mathrm{eq}}C(M_{\mathrm{eq}}). \tag{2.3}$$

In a nonequilibrium situation the magnetization will tend to relax to the equilibrium value corresponding to the local value of the magnetic field. Shliomis [4] has postulated the relaxation equation

$$\frac{d\mathbf{M}}{dt}-\boldsymbol{\omega}\times\mathbf{M}=-\gamma_M(\mathbf{M}-\mathbf{M}_0(\mathbf{H})), \tag{2.4}$$

where $d/dt=\partial/\partial t+\mathbf{v}\cdot\nabla$ is the substantial derivative for flow velocity $\mathbf{v}$, and $\boldsymbol{\omega}$ is the mean rate of rotation of the suspended particles. Furthermore $\mathbf{M}_0(\mathbf{H})=\mathbf{H}A_0(H)$ depends on the local value of the magnetic field according to Eq. (2.1) with the Langevin expression Eq. (2.2) for a dilute ferrofluid. Martsenyuk, Raikher, and Shliomis [7] have justified Eq. (2.4) for a dilute suspension on the basis of Brownian motion theory. The relaxation rate γ_M is composed of both Brownian relaxation and Néel relaxation [7]. For sufficiently large Brownian particles Néel relaxation may be neglected. An approximate calculation [7] for a dilute ferrofluid on the basis of Brownian motion theory shows that the rate coefficient γ_M depends on the field, and increases in proportion to H for large field.

We have shown [3] that irreversible thermodynamics in combination with Maxwell's equations leads to the relaxation equation

$$\frac{d\mathbf{M}}{dt}-\boldsymbol{\omega}\times\mathbf{M}+\mathbf{M}\nabla\cdot\mathbf{v}=\gamma_H(\mathbf{B}-\mathbf{B}_l(\mathbf{M})), \tag{2.5}$$

where $\mathbf{B}$ is the magnetic induction given by

$$\mathbf{B}=\mathbf{H}+4\pi\mathbf{M} \tag{2.6}$$

in Gaussian units, and the field $\mathbf{B}_l(\mathbf{M})$ is

$$\mathbf{B}_l(\mathbf{M})=\mathbf{H}_l(\mathbf{M})+4\pi\mathbf{M}, \tag{2.7}$$

with $\mathbf{H}_l(\mathbf{M})=\mathbf{M}C(M)$ expressed in terms of the local magnetization by Eq. (2.3). The third term on the left of Eq. (2.5) accounts for compressibility of the ferrofluid, usually a quite small effect. Subtracting Eqs. (2.6) and (2.7) we can write Eq. (2.5) in the alternative form

$$\frac{d\mathbf{M}}{dt}-\boldsymbol{\omega}\times\mathbf{M}+\mathbf{M}\nabla\cdot\mathbf{v}=\gamma_H(\mathbf{H}-\mathbf{H}_l(\mathbf{M})). \tag{2.8}$$

Shliomis' relaxation equation, Eq. (2.4), is linear in $\mathbf{M}$ and is intended to hold for small deviations from local equilibrium. Let $\mathbf{M}_l(\mathbf{H})=\mathbf{H}A(H)$ be the magnetization corresponding to local equilibrium in the field $\mathbf{H}$. To first order in the deviation $\mathbf{m}_l=\mathbf{M}-\mathbf{M}_l$ we have

$$\mathbf{H}-\mathbf{H}_l(\mathbf{M})=-\mathbf{m}_lC(M_l)-\frac{\mathbf{m}_l\cdot\mathbf{M}_l}{M_l}\mathbf{M}_lC'(M_l)+O(m_l^2). \tag{2.9}$$

Thus Eqs. (2.4) and (2.8) agree for small deviations from equilibrium, apart from the compressibility term and the more general equation of state in Eq. (2.8), provided the relaxation rates γ_M and γ_H are related by

$$\gamma_M=\gamma_HC(M_l), \tag{2.10}$$

and provided the deviation $\mathbf{m}_l$ is perpendicular to the direction of the local field $\mathbf{H}$.

The relaxation equation Eq. (2.8) also describes relaxation of large deviations from equilibrium. For simplicity we shall assume γ_H to be a scalar. According to irreversible thermodynamics it is a positive function of $\mathbf{M}$ and $\mathbf{H}$. Microscopic theory is required for a more precise determination of the transport coefficient. With free energy density

$$\varphi(M)=\varphi_0+\int_0^M M'C(M')dM' \tag{2.11}$$

we have the thermodynamic force

$$\mathbf{H}-\mathbf{H}_l(\mathbf{M})=\frac{\partial}{\partial\mathbf{M}}[\mathbf{M}\cdot\mathbf{H}-\varphi(M)], \tag{2.12}$$

which suggests that γ_H does not depend strongly on $\mathbf{M}$ and $\mathbf{H}$.

The mean rotation rate $\boldsymbol{\omega}$ in Eqs. (2.4) and (2.8) satisfies the relaxation equation [1,2]

$$\rho I\frac{d\boldsymbol{\omega}}{dt}=2\zeta(\nabla\times\mathbf{v}-2\boldsymbol{\omega})+\mathbf{M}\times\mathbf{H}, \tag{2.13}$$

where I is the moment of inertia per unit mass and ζ is the vortex viscosity. Typically the relaxation time $\rho I/\zeta$ is quite short, and the rate of change may be neglected. In this approximation of fast rotational relaxation the mean rate of rotation is expressed in terms of the local fluid vorticity $\boldsymbol{\Omega}=\frac{1}{2}\nabla\times\mathbf{v}$ by

$$\boldsymbol{\omega}=\boldsymbol{\Omega}+\frac{1}{4\zeta}\mathbf{M}\times\mathbf{H}. \tag{2.14}$$

Substituting in Eq. (2.8) we obtain

$$\frac{\partial\mathbf{M}}{\partial t}+\nabla\cdot(\mathbf{v}\mathbf{M})-\boldsymbol{\Omega}\times\mathbf{M}=\gamma_H(\mathbf{H}-\mathbf{H}_l)-\frac{1}{4\zeta}\mathbf{M}\times(\mathbf{M}\times\mathbf{H}). \tag{2.15}$$

We recall that the field $\mathbf{H}(\mathbf{r},t)$ must be calculated self-consistently from the magnetization everywhere in space via Maxwell's equations of magnetostatics.

We have shown in Ref. [3] that for a ferrofluid of shear viscosity η and bulk viscosity ζ_v at constant temperature T the local rate of entropy production is given by

$$T\sigma=\eta\sum_{\alpha\beta}\left(\partial_\alpha v_\beta+\partial_\beta v_\alpha-\frac{2}{3}\nabla\cdot\mathbf{v}\delta_{\alpha\beta}\right)^2+\zeta_v(\nabla\cdot\mathbf{v})^2$$
$$+4\zeta(\boldsymbol{\omega}-\boldsymbol{\Omega})^2+\gamma_H(\mathbf{H}-\mathbf{H}_l)^2. \tag{2.16}$$

It will be of interest to calculate the entropy production for typical flow situations.

III. FORCE DENSITY AND STRESS

The fluid equation of motion is postulated as

$$\rho\frac{d\mathbf{v}}{dt}=\nabla\cdot\boldsymbol{\sigma}_{\text{hyd}}+\mathbf{F}_m, \tag{3.1}$$

where $\boldsymbol{\sigma}_{\text{hyd}}$ is the hydrodynamic stress tensor and $\mathbf{F}_m$ is the magnetic force density. The hydrodynamic stress tensor is given by

$$\sigma_{\text{hyd}\alpha\beta}=-p\,\delta_{\alpha\beta}+\eta[\partial_\alpha v_\beta+\partial_\beta v_\alpha-\tfrac{2}{3}(\nabla\cdot\mathbf{v})\delta_{\alpha\beta}]$$
$$+\zeta_v(\nabla\cdot\mathbf{v})\delta_{\alpha\beta}+\zeta\varepsilon_{\alpha\beta\gamma}(\nabla\times\mathbf{v}-2\boldsymbol{\omega})_\gamma, \tag{3.2}$$

where p is the pressure. The magnetic force density is

$$\mathbf{F}_m=(\nabla\mathbf{B})\cdot\mathbf{M}. \tag{3.3}$$

From Maxwell's equations of magnetostatics

$$\nabla\cdot\mathbf{B}=0,\quad \nabla\times\mathbf{H}=0, \tag{3.4}$$

one derives

$$\mathbf{F}_m=\nabla\cdot\boldsymbol{\sigma}_m \tag{3.5}$$

with the magnetic stress tensor

$$\boldsymbol{\sigma}_m=\frac{1}{4\pi}\mathbf{B}\mathbf{H}+\left(\frac{B^2}{8\pi}-\mathbf{M}\cdot\mathbf{B}\right)\mathbf{1}. \tag{3.6}$$

With these definitions we adhere closely to the derivation including the full set of Maxwell equations of Ref. [3].

We note that the equation $\nabla\times\mathbf{H}=0$ can be used to rewrite the force density as

$$\mathbf{F}_m=\mathbf{F}'_m+2\pi\nabla M^2. \tag{3.7}$$

with the Kelvin force density

$$\mathbf{F}'_m=\mathbf{M}\cdot(\nabla\mathbf{H}). \tag{3.8}$$

This can be written as

$$\mathbf{F}'_m=\nabla\cdot\boldsymbol{\sigma}'_m \tag{3.9}$$

with the modified magnetic stress tensor

$$\boldsymbol{\sigma}'_m=\frac{1}{4\pi}\mathbf{B}\mathbf{H}+\frac{1}{8\pi}H^2\mathbf{1}. \tag{3.10}$$

The equation of motion Eq. (3.1) can be written with $\mathbf{F}'_m$ instead of $\mathbf{F}_m$ provided the term $2\pi M^2$ in Eq. (3.7) is absorbed in the pressure p. This is the form used by Shliomis [1] and Rosensweig [2]. The equation of state for the pressure is not relevant in the flow situations considered below.

Using Eq. (3.5) we can rewrite the fluid equation of motion Eq. (3.1) in the form

$$\rho\frac{d\mathbf{v}}{dt}=\nabla\cdot(\boldsymbol{\sigma}_{\rm hyd}+\boldsymbol{\sigma}_m). \tag{3.11}$$

This shows that the acceleration of a fluid element is due to the sum of hydrodynamic and magnetic stress.

In the approximation of fast rotational relaxation the antisymmetric part of the total stress tensor vanishes, as follows from Eqs. (2.14), (3.2), and (3.6). Hence in this approximation the equation of motion simplifies to

$$\rho\frac{d\mathbf{v}}{dt}=\nabla\cdot(\boldsymbol{\sigma}^S_{\rm hyd}+\boldsymbol{\sigma}^S_m). \tag{3.12}$$

Only the symmetric part of the total stress tensor is relevant for the translational motion of the fluid. For certain flow situations the contribution from the magnetic stress tensor can be interpreted as resulting from an additional viscosity.

Below we consider several steady state flow situations with small deviations from thermal equilibrium. We write

$$\mathbf{B}=\mathbf{B}_{\rm eq}+\mathbf{b},\quad \mathbf{H}=\mathbf{H}_{\rm eq}+\mathbf{h},\quad \mathbf{M}=\mathbf{M}_{\rm eq}+\mathbf{m}, \tag{3.13}$$

and calculate to first order in the small quantities $\mathbf{b}$, $\mathbf{h}$, $\mathbf{m}$, and $\mathbf{v}$. The entropy production of Eq. (2.16) is calculated to second order. In all situations considered the relaxation equation Eq. (2.15) becomes to first order

$$\boldsymbol{\Omega}\times\mathbf{M}_{\rm eq}=-\gamma_H\left[\mathbf{h}-\mathbf{m}C(M_{\rm eq})-\mathbf{h}\cdot\frac{\mathbf{M}_{\rm eq}\mathbf{M}_{\rm eq}}{M_{\rm eq}}C'(M_{\rm eq})\right]+\frac{1}{4\zeta}[\mathbf{M}_{\rm eq}\times(\mathbf{m}\times\mathbf{H}_{\rm eq})+\mathbf{M}_{\rm eq}\times(\mathbf{M}_{\rm eq}\times\mathbf{h})]. \tag{3.14}$$

It turns out that in all cases $\mathbf{h}\cdot\mathbf{M}_{\rm eq}=0$, so that the term with $C'(M_{\rm eq})$ vanishes.

IV. PLANAR COUETTE FLOW

We consider a ferrofluid between two parallel plates at $z=\pm L$ in the presence of a uniform applied field $\mathbf{B}_0$. In equilibrium the fluid is at rest and uniformly magnetized with equilibrium magnetization $\mathbf{M}_{\rm eq}$. The fluid is sheared by moving the plates with opposite velocity in the x direction. The flow velocity $\mathbf{v}$ satisfies stick boundary conditions at the plates.

We shall consider two flow situations in which the magnetic field and magnetization are uniform. The shear flow is $\mathbf{v}=(Uz/L,0,0)$, where U is the velocity of the upper plate. Hence $\boldsymbol{\Omega}=\Omega\mathbf{e}_y$ with $\Omega=U/2L$. The xz component of the change in the total stress tensor is

$$\delta[\boldsymbol{\sigma}^S_{\rm hyd}+\boldsymbol{\sigma}^S_m]_{xz}=\eta\left(\frac{\partial v_x}{\partial z}+\frac{\partial v_z}{\partial x}\right)+\frac{1}{8\pi}\delta(B_xH_z). \tag{4.1}$$

We can omit the term $\delta(B_zH_x)$ because of the magnetic boundary conditions at the plates and the uniformity of the fields. Explicitly to first order

$$\delta[\boldsymbol{\sigma}^S_{\rm hyd}+\boldsymbol{\sigma}^S_m]_{xz}=2\Omega\eta+\tfrac{1}{2}(m_xH_{{\rm eq}\,z}-m_zB_{{\rm eq}\,x}). \tag{4.2}$$

The change of viscosity is therefore

$$\Delta\eta=\frac{m_xH_{{\rm eq}\,z}-m_zB_{{\rm eq}\,x}}{4\Omega}. \tag{4.3}$$

Consider first the simplest situation, where the applied field $\mathbf{B}_0$ is in the x direction. Then $H_{{\rm eq}\,x}=B_0$, since $\mathbf{H}_0=\mathbf{B}_0$ outside the plates. The equilibrium magnetization is in the x direction with $M_{{\rm eq}\,x}=B_0A(B_0)$, and $B_{{\rm eq}\,x}=B_0(1+4\pi A(B_0))$. In the imposed shear flow one finds from the boundary conditions at $z=L$ that the uniform perturbed fields $\mathbf{b}$ and $\mathbf{h}$ satisfy $b_z=0$ and $h_x=h_y=0$. From Eq. (3.14) one finds $m_x=m_y=0$ and

$$m_z=-\frac{4\zeta\Omega}{B_{\rm eq}}\frac{M^2_{\rm eq}}{4\zeta\gamma_H+M^2_{\rm eq}}. \tag{4.4}$$

The change of viscosity is therefore

$$\Delta\eta_\parallel=\zeta\frac{P_H}{1+P_H} \tag{4.5}$$

with the dimensionless ratio

$$P_H = M_{\rm eq}^2/(4\zeta\gamma_H). \tag{4.6}$$

Next we consider the situation where the applied field is perpendicular to the x direction. Then $H_{\rm eq\,y} = B_{0y}$ and $B_{\rm eq\,z} = B_{0z}$, so that the equilibrium magnetization is directed in the yz plane with components $M_{\rm eq\,y}$, $M_{\rm eq\,z}$, which must be found from the coupled equations

$$M_{\rm eq\,y} = \frac{B_{0y}}{C(M_{\rm eq})},$$

$$M_{\rm eq\,z} = \frac{B_{0z}}{4\pi + C(M_{\rm eq})}. \tag{4.7}$$

Hence one calculates $H_{\rm eq\,z} = M_{\rm eq\,z}C(M_{\rm eq})$ and the angle θ defined by

$$\mathbf{H}_{\rm eq} = H_{\rm eq}[\cos\theta\mathbf{e}_y + \sin\theta\mathbf{e}_z]. \tag{4.8}$$

In the imposed shear flow one finds from the boundary conditions at $z = L$ that the uniform perturbed fields $\mathbf{b}$ and $\mathbf{h}$ satisfy $b_z = 0$ and $h_x = h_y = 0$. From Eq. (3.14) one finds $m_y = m_z = 0$ and

$$m_x = 4\zeta\Omega\frac{M_{\rm eq}\sin\theta}{4\zeta\gamma_H C(M_{\rm eq}) + M_{\rm eq}H_{\rm eq}}. \tag{4.9}$$

The change of viscosity is therefore

$$\Delta\eta_\perp = \zeta\frac{P_H}{1+P_H}\sin^2\theta \tag{4.10}$$

with coefficient P_H given by Eq. (4.6). If the rate γ_H is related to the coefficient γ_M by Eq. (2.10), and the equation of state Eq. (2.2) is used, then the expressions Eqs. (4.5) and (4.10) reduce to those derived by Shliomis [4]. Our derivation is somewhat more general, and it is evident that demagnetization effects are properly accounted for.

V. POISEUILLE FLOW

The dependence of viscosity of a ferrofluid on magnetic field was first investigated by McTague [8] by use of a capillarimeter. In the absence of the magnetic field the viscosity follows from the Poiseuille flow pattern for given pressure gradient. The dependence on magnetic field, found by McTague, has been explained by use of the expressions for planar Coulette flow [2] [4]. For magnetic field parallel to the tube the change of viscosity was calculated from Eq. (4.5). For magnetic field perpendicular to the tube it was calculated from Eq. (4.10) with angular average $\langle\sin^2\theta\rangle = \frac{1}{2}$. We show below that the same expressions can be derived from a complete discussion of the actual flow situation in cylindrical geometry.

In the absence of a pressure gradient the flow velocity vanishes and the magnetic field and magnetization are uniform. We calculate the flow velocity and the perturbed magnetization to first order in the applied pressure gradient. It turns out that for magnetic field both parallel and perpendicular to the tube the flow pattern retains the Poiseuille form. The viscosity follows from the proportionality to the pressure gradient.

Consider first the situation with applied magnetic field parallel to the tube of radius R. We choose the z axis along the axis of the tube. In equilibrium the magnetic field $\mathbf{H}_{\rm eq} = H_{\rm eq}\mathbf{e}_z$ and the magnetization $\mathbf{M}_{\rm eq} = M_{\rm eq}\mathbf{e}_z$ are uniform. We assume that an applied pressure gradient causes a flow pattern which in cylindrical coordinates (ρ,φ,z) takes the form

$$\mathbf{v}(\mathbf{r}) = f(\rho)\mathbf{e}_z, \quad p(\mathbf{r}) = -kz \tag{5.1}$$

with the property $f(R) = 0$. The magnetic induction $\mathbf{B} = B_0\mathbf{e}_z$ remains uniform, but the magnetic field $\mathbf{H}$ and the magnetization $\mathbf{M}$ acquire radial components. Using the boundary condition on B_ρ at $\rho = R$ we conclude that $h_\rho = -4\pi m_\rho$ for all ρ. From Eqs. (3.14) and (5.1) we find

$$m_\rho = Q_\parallel\frac{df}{d\rho} \tag{5.2}$$

with coefficient

$$Q_\parallel = \frac{2\zeta}{B_{\rm eq}}\frac{P_H}{1+P_H}. \tag{5.3}$$

The symmetric part of the first order magnetic stress tensor is

$$\boldsymbol{\sigma}_{m1}^S = \frac{1}{8\pi}[\mathbf{h}\mathbf{B}_{\rm eq} + \mathbf{B}_{\rm eq}\mathbf{h}], \tag{5.4}$$

since $\mathbf{b} = 0$ and $\mathbf{m}\cdot\mathbf{B}_{\rm eq} = 0$. The z component of the stationary equation of motion

$$\eta\nabla^2\mathbf{v} + \nabla\cdot\boldsymbol{\sigma}_{m1}^S - \nabla p = 0 \tag{5.5}$$

can now be expressed as

$$\left(\eta + \frac{1}{2}Q_\parallel B_{\rm eq}\right)\left[\frac{d^2f}{d\rho^2} + \frac{1}{\rho}\frac{df}{d\rho}\right] = k. \tag{5.6}$$

Hence we deduce that $f(\rho)$ has the Poiseuille form $f(\rho) = A(\rho^2 - R^2)$ with prefactor $A = \frac{1}{4}k/(\eta + \Delta\eta_\parallel)$ corresponding to the viscosity change $\Delta\eta_\parallel = \frac{1}{2}Q_\parallel B_{\rm eq}$. From Eq. (5.3)

$$\Delta\eta_\parallel = \zeta\frac{P_H}{1+P_H}, \tag{5.7}$$

as in Eq. (4.5).

Next we consider applied magnetic field $\mathbf{B}_0 = B_0\mathbf{e}_x$ in the x direction. The equilibrium magnetic field $\mathbf{H}_{\rm eq}$ and the magnetization $\mathbf{M}_{\rm eq}$ are then also in the x direction. If a pressure gradient is imposed we again obtain a flow pattern of the form Eq. (5.1). In this case the magnetic field $\mathbf{H} = B_0\mathbf{e}_x$ remains unchanged, but the magnetic induction and the magnetization acquire axial components b_z and m_z, related by $b_z = 4\pi m_z$. From Eqs. (3.14) and (5.1) we find

$$m_z = Q_\perp\cos\varphi\frac{df}{d\rho} \tag{5.8}$$

with coefficient

$$Q_\perp = \frac{2\zeta}{H_{\rm eq}}\frac{P_H}{1+P_H}. \tag{5.9}$$

The symmetric part of the first order magnetic stress tensor is

$$\boldsymbol{\sigma}^S_{m1}=\frac{1}{8\pi}[\mathbf{b}\mathbf{H}_{\mathrm{eq}}+\mathbf{H}_{\mathrm{eq}}\mathbf{b}], \tag{5.10}$$

since $\mathbf{b}\cdot\mathbf{B}_{\mathrm{eq}}=0$ and $\mathbf{b}\cdot\mathbf{M}_{\mathrm{eq}}=0$. The function $f(\rho)$ in Eq. (5.1) has again the Poiseuille form $f(\rho)=A(\rho^2-R^2)$ with prefactor $A=\frac{1}{4}k/(\eta+\Delta\eta_\perp)$. The z component of the stationary equation of motion Eq. (5.5) yields

$$\Delta\eta_\perp=\frac{1}{2}\zeta\frac{P_H}{1+P_H}, \tag{5.11}$$

which agrees with Eq. (4.10) if there the factor $\sin^2\theta$ is replaced by its angular average $\frac{1}{2}$. This shows that the method used earlier [2,4], based on such a replacement, yielded the correct result.

VI. ENTROPY PRODUCTION

It is of interest to calculate the entropy production for each of the flow situations considered above. The calculation shows that the viscosity increase $\Delta\eta$ due to the presence of the applied magnetic field can be found alternatively from the additional entropy production. For each of the four situations the dimensionless parameter P_H, defined in Eq. (4.6), is just the ratio of the last two terms in Eq. (2.16). Thus defining σ_R as the entropy production due to rotational friction, and σ_M as the entropy production due to magnetic relaxation, we have

$$\frac{\sigma_R}{\sigma_M}=P_H. \tag{6.1}$$

Consider first the planar Couette flow with applied magnetic field parallel to the plates. In this situation the torque $\mathbf{M}\times\mathbf{H}$ is to first order $m_zB_{\mathrm{eq}}\mathbf{e}_y$. The difference $\mathbf{H}-\mathbf{H}_l$ is to first order

$$\mathbf{H}-\mathbf{H}_l\approx\mathbf{h}-\mathbf{m}C(M_{\mathrm{eq}}), \tag{6.2}$$

since $\mathbf{m}\cdot\mathbf{M}_{\mathrm{eq}}=0$. As shown in Sec. IV both $\mathbf{h}$ and $\mathbf{m}$ are in the z direction and $h_z=-4\pi m_z$, so that $\mathbf{H}-\mathbf{H}_l\approx-\mathbf{m}B_{\mathrm{eq}}/M_{\mathrm{eq}}$. The additional entropy production $\Delta\sigma$ is given by the sum of the last two terms in Eq. (2.16). Using the expression Eq. (4.4) for m_z one finds $T\Delta\sigma=4\Omega^2\Delta\eta_\parallel$, with $\Delta\eta_\parallel$ given by Eq. (4.5).

For the planar Couette flow with applied field perpendicular to the plates the torque $\mathbf{M}\times\mathbf{H}$ is to first order $m_xH_{\mathrm{eq}}[-\sin\theta\mathbf{e}_y+\cos\theta\mathbf{e}_z]$. The difference $\mathbf{H}-\mathbf{H}_l$ to first order is again given by Eq. (6.2), but now $\mathbf{h}=0$ and $\mathbf{m}$ is in the x direction. Using the expression Eq. (4.9) for m_x one finds $T\Delta\sigma=4\Omega^2\Delta\eta_\perp$ with $\Delta\eta_\perp$ given by Eq. (4.10).

For the Poiseuille flow with applied field in the direction of flow the torque $\mathbf{H}-\mathbf{H}_l$ is to first order $-m_\rho B_{\mathrm{eq}}\mathbf{e}_\rho$. The difference $\mathbf{H}-\mathbf{H}_l$ is to first order $-\mathbf{m}B_{\mathrm{eq}}/M_{\mathrm{eq}}$ with $\mathbf{m}$ in the radial direction. For the local additional entropy production one finds

$$T\Delta\sigma=\left(\frac{df}{d\rho}\right)^2\Delta\eta_\parallel \tag{6.3}$$

with $\Delta\eta_\parallel$ given by Eq. (5.7). Comparing this with the local entropy production for the Poiseuille flow without magnetic field one sees that $\Delta\eta_\parallel$ can be identified with the additional viscosity.

For the Poiseuille flow with applied field perpendicular to the tube the torque $\mathbf{M}\times\mathbf{H}$ is to first order $m_zH_{\mathrm{eq}}\mathbf{e}_y$. The difference $\mathbf{H}-\mathbf{H}_l$ is to first order $-\mathbf{m}H_{\mathrm{eq}}/B_{\mathrm{eq}}$ with $\mathbf{m}$ in the axial direction. For the local additional entropy production one finds

$$T\Delta\sigma=2\cos^2\varphi\left(\frac{df}{d\rho}\right)^2\Delta\eta_\perp \tag{6.4}$$

with $\Delta\eta_\perp$ given by Eq. (5.10). Integrating over the azimuthal direction one sees that $\Delta\eta_\perp$ can be identified with the additional viscosity.

VII. FRICTION AND RELAXATION

In the expression Eq. (2.16) for the entropy production rotational friction and magnetic relaxation appear as independent dissipative processes, each characterized by its own transport coefficient. For a dilute ferrofluid in which Néel relaxation can be neglected and for vanishing magnetic field the two transport processes are intimately related. Then the relaxation is due to orientational Brownian motion of individual particles in zero field, and the relaxation rate is given by $\gamma_M=2D_R$ with rotational diffusion coefficient f_R given by the Einstein relation $D_R=k_BT/f_R$. For particles of radius a the rotational friction coefficient is $f_R=8\pi\eta a^3$. In a dilute ferrofluid the vortex viscosity is $\zeta=\frac{1}{4}nf_R$, so that the product of transport coefficients is simply $\zeta\gamma_M=\frac{1}{2}nk_BT$.

In dense ferrofluids the transport coefficients ζ and γ_M or γ_H should be regarded as independent quantities. For a ferrofluid disturbed slightly from equilibrium the value of the transport coefficients in the equilibrium situation is relevant. Due to the effect of the magnetic field on the microstructure the coefficients will depend on the field H_{eq}. The microscopic calculation of the transport coefficients is difficult, since it involves the many-body hydrodynamic interaction, the anisotropic magnetic interaction, and the anisotropic microstructure of the suspension.

We have argued that the relation Eq. (2.10) provides the correspondence between Shliomis' relaxation equation Eq. (2.4), with $\mathbf{M}_0$ replaced by $\mathbf{M}_l(\mathbf{H})$, and our relaxation equation (2.8). Since for the calculation of viscosity the transport coefficients are needed only in equilibrium we put

$$\gamma_M(H_{\mathrm{eq}})=\gamma_H(H_{\mathrm{eq}})C(M_{\mathrm{eq}})=\gamma_H(H_{\mathrm{eq}})/A(H_{\mathrm{eq}}). \tag{7.1}$$

Shliomis' expressions [4] for the magnetoviscosity $\Delta\eta$ in planar Couette flow take the same form as Eqs. (4.5) and (4.10), except that the coefficient P_H is replaced by

$$P=M_{\mathrm{eq}}H_{\mathrm{eq}}/(4\zeta\gamma_M). \tag{7.2}$$

With the relation Eq. (7.1) our expressions for the magnetoviscosity are therefore identical to those of Shliomis [4], except that we allow a more general equation of state and field-dependent transport coefficients.

We have remarked following Eq. (2.12) that the form of our relaxation equation suggests that the coefficient γ_H does

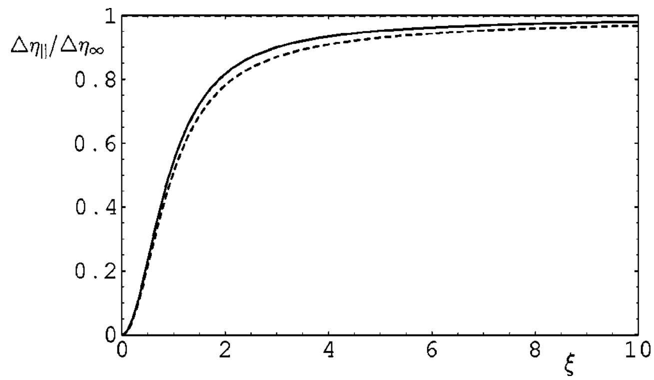

FIG. 1. Plot of magnetoviscosity $\Delta\eta_\|/\Delta\eta_\infty$ in parallel field as a function of $\xi=3\chi_0 H/M_s$ as calculated from Shliomis' relaxation equation Eq. (2.4) (dashed curve with $\Delta\eta_\infty=\zeta$), and as calculated from our relaxation equation Eq. (2.8) [solid curve with $\Delta\eta_\infty=\Delta\eta_{\|F}(\infty)$] for parameter values quoted in Sec. VII.

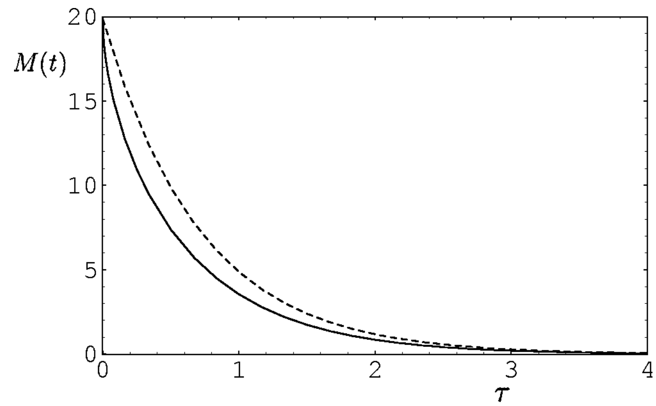

FIG. 2. Plot of magnetization $M(t)$ (in G) after a magnetic field of 10 kG is suddenly turned off, as a function of reduced time $\tau=\gamma_M t$, as calculated from Shliomis' relaxation equation Eq. (2.4) (dashed curve), and as calculated from our relaxation equation Eq. (2.8) (solid curve) for parameter values quoted in Sec. VII.

not depend strongly on the field. For large field the ratio $A(H_{\rm eq})=M_{\rm eq}/H_{\rm eq}$ behaves as $A(H_{\rm eq})\approx M_s/H_{\rm eq}$. If γ_H is taken to be a constant, then according to Eq. (7.1) the rate coefficient $\gamma_M(H_{\rm eq})$ must behave as $\gamma_M(H_{\rm eq})\approx\gamma_H H_{\rm eq}/M_s$ for large field. This agrees with the behavior found by Martsenyuk, Raikher, and Shliomis [7] for dilute ferrofluids.

Therefore it is of interest to consider the dependence on magnetic field of the viscosity under the assumption that the transport coefficients ζ and γ_H do not depend on the field. In the analysis of experimental data [2,5] it has been assumed that the coefficients ζ and γ_M do not depend on the field and can be varied independently. Shliomis' relaxation equation leads to the expression

$$\Delta\eta_{\|S}=\zeta\frac{M_s^2\xi L(\xi)}{12\chi_0\zeta\gamma_M+M_s^2\xi L(\xi)},\quad \xi=\frac{3\chi_0 H}{M_s} \tag{7.3}$$

if the equation of state Eq. (2.2) is adopted. If the relation $6\zeta\gamma_M=M_s^2/\chi_0$ is used, then this reduces to the expression derived originally by Shliomis [4]. Our relaxation equation leads to

$$\Delta\eta_{\|F}=\zeta\frac{M_s^2L^2(\xi)}{4\zeta\gamma_H+M_s^2L^2(\xi)} \tag{7.4}$$

if the same equation of state is used. In Eqs. (7.3) and (7.4) the coefficients γ_M and γ_H will be regarded as constants. The two expressions agree for small ξ, independent of the value of ζ, provided γ_M and γ_H are related by $\gamma_H=\gamma_M\chi_0$. The second expression tends to

$$\Delta\eta_{\|F}(\infty)=\zeta\frac{M_s^2}{4\zeta\gamma_H+M_s^2} \tag{7.5}$$

for large ξ. In Fig. 1 we plot $\Delta\eta_{\|S}/\zeta$ and $\Delta\eta_{\|F}/\Delta\eta_{\|F}(\infty)$ as functions of ξ for $M_s=20\,{\rm G}$, $\chi_0=0.1$, $\zeta=0.001\,{\rm P}$, and $\gamma_M=10^5\,{\rm Hz}$, assuming $\gamma_H=\gamma_M\chi_0$. The curves nearly coincide, but note that $\Delta\eta_{\|F}(\infty)/\zeta=0.909$ for this choice of parameters. This suggests that the dependence of viscosity on magnetic field can yield information on the relaxation behavior.

The difference between the two relaxation equations under the assumption of constant γ_M and constant γ_H, respectively, also becomes manifest if we consider relaxation from an equilibrium state after an applied field is switched off. We consider a spherical sample of radius R in vacuum, magnetized up to $t=0$ by an applied field $\mathbf{H}_0=H_0\mathbf{e}_z$. At time $t=0$ the applied field is suddenly switched off. By spherical symmetry the magnetization remains uniform across the sample, but its amplitude diminishes. The fluid remains at rest, so that the vorticity $\mathbf{\Omega}$ vanishes, and the magnetization $\mathbf{M}$ is always parallel to the magnetic field $\mathbf{H}$. Hence from Eq. (2.14) the mean particle rotation $\boldsymbol{\omega}$ vanishes, and Eqs. (2.4) and (2.8) simplify accordingly.

In Fig. 2 we plot the decay of magnetization according to Eq. (2.4) with constant γ_M and according to Eq. (2.8) with constant γ_H for the equation of state Eq. (2.2), the same parameter values as before, and for an initial applied field $H_0=10\,{\rm kG}$. Note that both decays are nonexponential. For long times both decays become exponential with the same rate $(1+4\pi\chi_0/3)\gamma_M$. The plots show a distinct difference in relaxation behavior. One can define a mean relaxation time τ_M from the integral of the reduced magnetization $M(t)/M(0)$ over time. By numerical integration one finds for relaxation according to Eq. (2.4) the value $\gamma_M\tau_M=0.709$, whereas $\gamma_M\tau_M=0.545$ according to Eq. (2.8). Both values are to be compared with $3/(3+4\pi\chi_0)=0.705$. The difference in relaxation behavior suggests that the chosen geometry may be suitable for a study of nonlinear magnetic relaxation in experiment or computer simulation.

VIII. DISCUSSION

We have studied the dynamics of ferrofluids using two different equations for the relaxation of magnetization. The first equation was postulated many years ago by Shliomis [4], and has been used extensively in the literature [1] [2]. The equation was justified for dilute ferrofluids on the basis of Brownian motion theory [7]. Recently we derived an alternative relaxation equation on the basis of irreversible thermodynamics in combination with the full set of Maxwell equations [3]. In the preceding we discussed the dependence of magnetoviscosity on magnetic field for typical flow situations on the basis of the two relaxation equations. It turns out that the two equations lead to identical results for the magnetoviscosity, provided the relaxation rates are related in a particular fashion, determined by the equilibrium equation of state.

It is plausible that the relaxation rate in the equation derived from irreversible thermodynamics depends only weakly on the field. We have contrasted the implications for magnetoviscosity of the assumption of constant rate in both relaxation equations. The two equations lead to a different field dependence of the magnetoviscosity. This may be of relevance for the interpretation of experiments.

The analysis suggests that the nature of magnetic relaxation in ferrofluids should be carefully studied. Data on magnetoviscosity should be analyzed in combination with the equilibrium equation of state. Also it would be useful to study directly the time dependence of nonlinear relaxation of magnetization after the applied magnetic field is suddenly turned off.

Finally we note that the theory developed above can be transposed to electrostatics by a replacement of the induction **B**, magnetic field **H**, and magnetization **M**, by the corresponding electric displacement **D**, electric field **E**, and polarization **P**. Shliomis' relaxation equation was postulated independently in electrostatics by Hubbard and Onsager [9] in the weak field limit and in the approximation of fast rotational relaxation. The relaxation equation was extended beyond the latter approximation by Hubbard and Kayser [10]. These authors also postulated a corresponding expression for the entropy production. The relation to the theory of magnetic ferrofluids was discussed by Hubbard and Stiles [11]. Our derivation from irreversible thermodynamics [3] includes electrostatics and leads to a relaxation equation analogous to Eq. (2.8). The analysis developed above for ferrofluids applies equally to electrostatics.

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