Stationary Off-Equilibrium Magnetization in Ferrofluids under Rotational and Elongational Flow

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The magnetization of a ferrofluid, which is exposed to a flow, was recently proposed to depend on the symmetric velocity gradients (elongational flow). This is demonstrated by an experimental setup, which allows one to evaluate the transport coefficient associated with the elongational flow contribution.

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Ferrofluids [1] are colloidal suspensions of mono- or subdomain ferrimagnetic nanosized particles suspended in a carrier liquid. Under the influence of an external magnetic field the fluid behaves paramagnetically. In time-dependent external magnetic fields or in the presence of a flow (stationary or oscillatory) the local magnetization $\mathbf{M}(\mathbf{r}, t)$ may be off from the equilibrium value $\mathbf{M}^{\mathrm{eq}}(\mathbf{H})$, which belongs to the local magnetic field $\mathbf{H}(\mathbf{r}, t)$. Perceptible deviations $\delta\mathbf{M} = (\mathbf{M} - \mathbf{M}^{\mathrm{eq}})$ occur when the inverse magnetic relaxation time τ^{-1} compares to the frequency scale of the hydrodynamic motion (e.g., the oscillation frequency ω of an external ac magnetic field or the characteristic gradient $|\nabla_i v_j|$ of a flow). The microscopic mechanism underlying the magnetic relaxation is due to either particle rotation against the viscosity of the liquid carrier (Brownian rotational diffusion) or reorientation of the magnetic moments relative to the crystallographic orientation of the ferromagnetic grains (Néel relaxation). Regardless of the microscopic origin there is a feedback of $\delta\mathbf{M}$ to the macroscopic flow dynamics, provided τ is large enough to compare with the hydrodynamic time scale of interest. This gives rise to phenomena commonly denoted as magnetodissipative or magnetoviscous effects. Among the more remarkable ones there is the enhanced effective shear viscosity observed when a tube flow is exposed to an axis parallel static magnetic field [2,3] or the flow acceleration in response to an ac field [4–6]. The intuitive idea is that the suspended particles try to follow the local vorticity $\mathbf{\Omega} = \nabla \times \mathbf{v}/2$ of the flow, thus being hampered by a static magnetic field but eventually being accelerated by an oscillatory one. To account for the magnetodissipative effect a separate evolution equation for $\mathbf{M}$ was introduced in Ref. [3] (referred to here as the traditional approach), which necessarily contains the flow vorticity $\mathbf{\Omega}$. Let us consider the simplest example when a uniformly magnetized sample is exposed to a flow: Following [3] the time evolution of $\mathbf{M}$ does not distinguish whether the vorticity results from a solid rotation (purely antisymmetric velocity gradient) or a shear (combination between symmetric and antisymmetric velocity gradients, i.e., rotational and elongational flow components both being nonzero).

Quite recently a novel macroscopic ferrofluid dynamics (FFD) [7] suggested that the relaxation equation for M_i entails—besides $(\mathbf{\Omega} \times \mathbf{M})_i$—also a term of the form $\lambda_2 M_j v_{ij}$, where $v_{ij} = (\nabla_i v_j + \nabla_j v_i)/2$ is the symmetric part of the velocity gradient. Such a contribution is analogous to a term appearing in the director dynamics of nematic liquid crystals, which is known to induce the flow alignment effect [8]. As a rigorous *macroscopic* theory, which does not rely on microscopic details of the ferrofluid suspension, FFD suggests the possible existence of such a v_{ij} coupling, though it is unable to estimate whether it is of quantitative significance for a given ferrofluid (i.e., whether the associated transport coefficient λ_2 has a perceptible size). However, a recent experiment on magnetovortical resonance [9] indicates that this term might indeed be important [7]: A ferrofluid either in solid rotation ($\mathbf{\Omega} \neq 0, v_{ij}^0 = 0$) or under shear ($\mathbf{\Omega} \neq 0, v_{ij}^0 \neq 0$) was exposed to a homogeneous magnetic field, perpendicular to $\mathbf{\Omega}$. While the field was oscillating with a frequency ω, the amplitude of the transverse off-equilibrium component of the magnetization was recorded. In the case of the rigid rotation a sharp peak at a turning rate $\Omega = \omega$ was observed, whereas the resonance drastically flattened out in the shear flow configuration. The explanation given in Ref. [9] relies on a flow-induced modification of the relaxation time τ: Shear flow was argued to induce fracture of dynamical particle chains, leading to smaller effective particle sizes, thus implying a reduced relaxation time τ. We do not state that this explanation is incorrect but we point out that this effect is of *higher order* in the thermodynamic nonequilibrium forces, as it requires both $\delta\mathbf{M}$ and v_{ij} to be nonzero. Contrarily the explanation advocated in Ref. [7] is based on the term $M_j v_{ij}$, which is a *first order* nonequilibrium effect.

This unresolved issue is motivation enough for a more careful and direct investigation of the magnetization dynamics, with the aim to quantify the role of v_{ij} in a simple stationary flow configuration. To that end a Couette apparatus was constructed with both cylinders rotating independently of each other. This feature allows a continuous and well-controllable transition from a rigid rotation ($v_{ij} = 0$)

to a simple shear ($v_{ij} \neq 0$) while keeping the overall vorticity $\mathbf{\Omega}$ constant. In this setup, the deflection of the magnetization in a field perpendicular to the axis is recorded. Our experimental results reveal that the symmetric velocity gradient, i.e., the elongational flow component, significantly affects the magnetization vector in the ferrofluid. Moreover, the apparatus provides a simple experimental tool for a quantitative evaluation of the transport coefficients λ_2.

We now consider a ferrofluid within a gap of a Couette apparatus (see Fig. 1). A homogeneous stationary magnetic field $\mathbf{H}_{\rm ext}$ perpendicular to the axis is applied. The two concentric cylinders with inner and outer radii R_1 and R_2 can be rotated with independent angular frequencies Ω_1 and Ω_2, respectively. This allows them to pass over from a rigid rotation (with equal turning frequencies) to a flow with a finite-shear rate ($\Omega_1 \neq \Omega_2$). It is important that the present setup allows a continuous transition between the two distinct flow characteristics *without* changing the geometry. Difficulties with the evaluation of distinct and sometimes complicated demagnetization factors are thus circumvented.

As a consequence of the applied flow the magnetization vector is deflected out of the equilibrium direction, thus also deforming the magnetic field outside of the sample. A Hall detector positioned in the center of the apparatus (see Fig. 1) records the magnetic induction perpendicular to the applied field. To the leading order of the magnetodissipative effect to be considered here, the magnetic field does not change the flow profile. Accordingly, the velocity $\mathbf{v}(\mathbf{r}) = v_\varphi(r)\mathbf{e}_\varphi$ exhibits a pure azimuthal component [10]

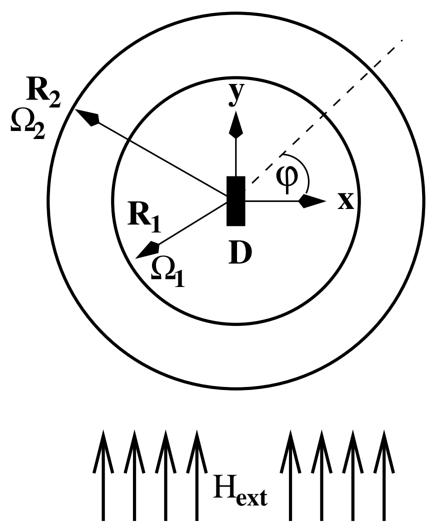

FIG. 1. The ferrofluid is located within a gap between two rotating cylinders with radii R_1 and R_2 rotating, respectively, with the angular velocities Ω_1 and Ω_2. A stationary homogeneous magnetic field $\mathbf{H}_{\rm ext}$ is applied in the y direction. The Hall detector D in the center records the off-equilibrium component of the magnetization transverse to $\mathbf{H}_{\rm ext}$.

$$v_\varphi(r) = \Omega(r + sR_2^2/r). \tag{1}$$

Here $\mathbf{\Omega} = \Omega\,\mathbf{e}_z = \nabla \times \mathbf{v}/2$ is the vorticity with

$$\Omega = \frac{\Omega_2 R_2^2 - \Omega_1 R_1^2}{R_2^2 - R_1^2}. \tag{2}$$

In the present setup, $\mathbf{\Omega}$ is uniform over the gap. The dimensionless second control parameter

$$s = \frac{R_1^2}{R_2^2 - R_1^2}\left(\frac{\Omega_1 - \Omega_2}{\Omega}\right) \tag{3}$$

measures the amount of shear stress (elongational flow). Evaluating the symmetric velocity gradient at the inside of the outer cylinder next to the detector gives

$$v_{ij} = \frac{1}{2}(\nabla_i v_j + \nabla_j v_i) = -s\Omega\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{4}$$

Following [7] the evolution equation for the magnetization in an incompressible flow field $\mathbf{v}(\mathbf{r})$ reads as follows:

$$\partial_t M_i + v_j \nabla_j M_i - \lambda_2 v_{ij} M_j - (\mathbf{\Omega} \times \mathbf{M})_i = -\tfrac{1}{\tau}(M_i - M_i^{\rm eq}). \tag{5}$$

In writing Eq. (5) we have assumed that the magnetic field strength is weak so that terms of higher than second order in $H_{\rm ext}$ can be omitted. The third term on the left-hand side reflects the coupling to the elongational flow. Its strength is weighted by the, as yet unknown, transport coefficient λ_2. The relationship $\mathbf{M}^{\rm eq} = \chi\mathbf{H}$ gives the equilibrium magnetization (fluid at rest), with $\mathbf{H}(\mathbf{r}, t)$ being the local magnetic field inside the sample and χ the magnetic susceptibility. Although the applied external field is homogeneous the annular geometry enforces a complicated demagnetization, resulting in a nonuniform dependence $\mathbf{M}^{\rm eq}(x, y)$. Assuming that the axial extension of the cylinders is much larger than the diameter, the equilibrium magnetization within the gap is

$$\mathbf{M}^{\rm eq} \simeq \chi H_{\rm ext}\begin{pmatrix} \frac{b}{r^2}\sin 2\varphi \\ -a - \frac{b}{r^2}\cos 2\varphi \end{pmatrix}, \tag{6}$$

where φ is the azimuthal angle measured relative to the x axis, and $r^2 = x^2 + y^2$ is the radius. The coefficients a and b are given by

$$a = \frac{-2(2 + \chi)}{4(1 + \chi) + \chi^2(1 - R_1^2/R_2^2)};$$

$$b = a\frac{\chi}{2 + \chi}R_1^2. \tag{7}$$

We now turn to the stationary off-equilibrium magnetization component occurring as a result of the applied flow. With the inequality $\tau|\nabla_i v_j| \ll 1$ it is legal to replace $\mathbf{M}$ on the left-hand side of Eq. (5) by $\mathbf{M}^{\rm eq}$. Solving the full boundary value problem for the magnetic field distribution inside and outside of the sample, we obtain, for the transverse off-equilibrium magnetic field component at the location of the detector,

$$H_x = \tau\Omega H_{\mathrm{ext}} \frac{4\chi^2(2+\chi)R_2^2(R_2^2-R_1^2)}{[4R_2^2(1+\chi)+\chi^2(R_2^2-R_1^2)]^2}\left[1+s\left(\frac{R_1^2+R_2^2}{2R_1^2}-\lambda_2\frac{4R_2^2(1+\chi)+\chi^2(R_2^2-R_1^2)}{2\chi(2+\chi)R_1^2}\right)\right]. \quad (8)$$

In the experiment H_x is measured as a function of the two available control parameters Ω and s. Relating $H_x(\Omega, s)$ to the zero-shear reference value $H_x^0 = H_x(\Omega, s = 0)$ allows us to determine the coefficient λ_2 from the measured slope of H_x drawn as a function of the shear rate s.

To that end a cylindrical Couette apparatus was set up (Fig. 2). The inner cylinder has a radius of 9 mm while the radius of the outer cylinder equals 10 mm. Both cylinders have a height of 60 mm; they can be rotated independently, driven by computer controlled electromotors. The range of angular velocities of both driving units reaches from 0 to 100 s^{-1}. With the geometrical data at hand this interval also coincides with the accessible vorticity range at zero-shear rate. The available range for s depends on the actual vorticity and can be varied maximally from -2.4 to 4.7. The frequencies of the motors can be maintained to an accuracy of about 1%, resulting in an error of less than 2% in Ω and s.

A Hall detector is positioned in the center of the inner cylinder to record the x component of the magnetic field. The sensor is connected with an electronic amplification allowing a resolution of the measured magnetization component of 8 A/m. A second Hall sensor is used to measure the strength of the applied magnetic field $0 < \mathbf{H}_{\mathrm{ext}} < 20$ kA/m produced by a Fanselau coil arrangement. During the observation time the field strength was held constant with an accuracy better than 0.1%. With this device we have performed experiments in which the shear rate s was changed in discrete steps, as shown in Fig. 3, at constant vorticity Ω. For each s-Ω combination the Hall voltage of the sensor was averaged over a recording time of 70 s in order to reduce the electronic noise and other fluctuations due to variations of the motor frequencies. A typical plot of the Hall voltage measured during such a run is presented in Fig. 3. The data reveal an experimental resolution better than 10 A/m. The magnetic fluid used in all experiments was APG513A, an ester-based commercial ferrofluid containing approximately 7 vol % of magnetite particles giving a magnetic susceptibility of $\chi = 1.44$.

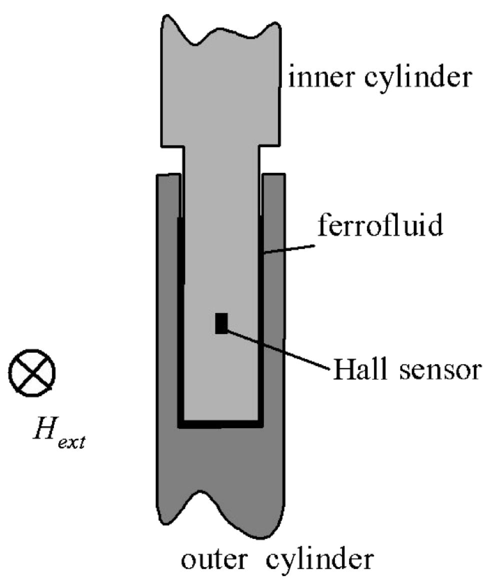

FIG. 2. Schematic sketch of the experimental setup. Details are given in the text.

We first start with a check of the performance of the system and determine the relaxation time of the magnetization. This is accomplished by studying the rigidly rotating flow configuration, where $s = v_{ij} = 0$. Clearly, since the λ_2 term in Eq. (5) is inoperative in this situation, the present measurement is not yet suitable to discriminate between the traditional approach and FFD. From Eq. (8) we get the following linear relationship between Ω and the off-equilibrium magnetic field component H_x^0,

$$\frac{H_x^0}{H_{\mathrm{ext}}} = \tau\Omega \frac{4\chi^2(2+\chi)R_2^2(R_2^2-R_1^2)}{[4R_2^2(1+\chi)+\chi^2(R_2^2-R_1^2)]^2}. \quad (9)$$

Fitting the measured slope with Eq. (9) yields (see Fig. 4), the relaxation time of the ferrofluid, $\tau = 1.8$ ms. This value is well in the range expected for a fluid with a kinematic viscosity of about 100 mm^2/s.

We turn now to the experimental determination of the transport coefficient λ_2. To that end Fig. 5 shows the measured ratio H_x/H_x^0 as a function of the elongational flow parameter s. The data were obtained for a magnetic field of $H_{\mathrm{ext}} = 20$ kA/m. The predicted linear relationship [see Eq. (8)] is confirmed over the whole range of vorticities studied. Similar linear relations are found for other applied field strengths' and values of Ω. From the slope of the measured relation shown in Fig. 5, one fits $\lambda_2 = 0.2 \pm 0.05$. This value is found to be constant throughout the whole investigated range of magnetic field

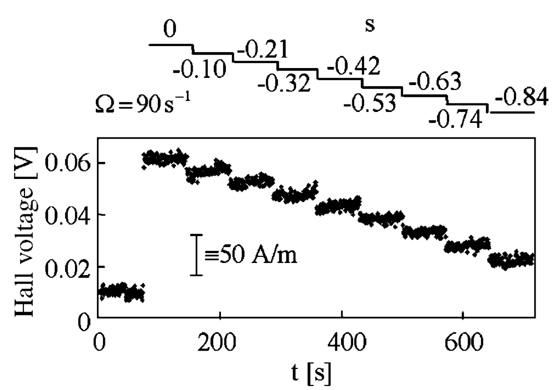

FIG. 3. A typical experiment run: The shear rate was increased by discrete steps in time while keeping the vorticity constant. Simultaneously the voltage signal of the Hall sensor was recorded to detect the x component of the magnetization.

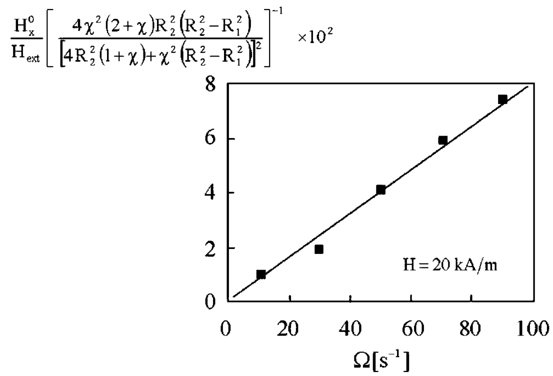

FIG. 4. The off-equilibrium component of the magnetization as a function of the vorticity Ω in the shear-free case ($s = 0$).

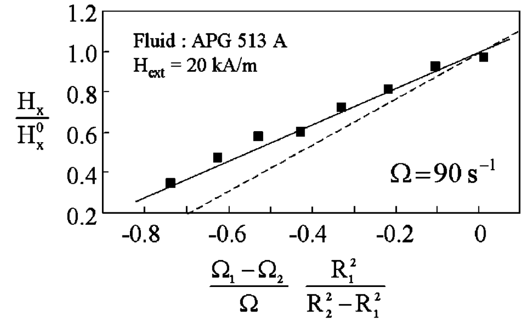

FIG. 5. The dependence of the off-equilibrium magnetization component on the stress control parameter s. Error bars are smaller than the dot size.

strength between 10 and 20 kA/m. The dashed line in Fig. 5 represents the prediction based on the standard magnetization relaxation equation [Eq. (5) with $\lambda_2 = 0$ and a flow-independent relaxation time τ], which can be read off from Eq. (8) by imposing $\lambda_2 = 0$. The measurement gives clear evidence that a finite λ_2 is required for a proper data fit. This concludes the experimental measurement of λ_2.

It is tempting to speculate about the possible microscopic origin for a finite λ_2. One might attribute this phenomenon to a finite asphericity of the colloids: Real ferrofluids are known to exhibit permanent agglomerates or they reversibly build up particle chains, which give rise to an effective particle excentricity. For a rough estimate of how the asphericity enters λ_2, let us consider a dilute suspension of prolate, ellipsoidally shaped, rigid magnetic dipoles (axis ratio $r > 1$), exposed to a pure extensional flow of the form $\mathbf{v} = G(-x/2, -y/2, z)$. The latter corresponds to the extension of a cylindrical thread in the z direction with a shear rate $G > 0$. The particles' preferred orientation in such a flow is parallel to $\mathbf{e}_z$. For zero magnetic field, Brenner [11] provides the orientational distribution of the deflection angle θ in the form $f(\theta) \propto \exp[\frac{3}{4}G\tau_b\kappa\cos^2\theta]$. Here $\tau_b = 6V\eta/(kT)$ is the Brownian relaxation time of an isolated particle of volume V in a carrier liquid of the viscosity η. Furthermore, kT is the thermal energy and κ is a geometry factor

$$\kappa(r) = \frac{2(r^2 - 1)^{5/2}}{3r[(2r^2 - 1)\,\mathrm{arccosh}(r) - r\sqrt{r^2 - 1}\,]}. \qquad (10)$$

Assuming that the magnetic moment m of a colloid is fixed parallel to the longer particle axis, the above extensional flow supports the particle alignment in a magnetic field oriented parallel to the z direction. Accordingly the orientational average $\langle M_z \rangle$ slightly exceeds the no-flow equilibrium value M^{eq}. Multiplying the above orientational distribution with the magnetic field-dependent Boltzman factor gives $f(\theta) \propto \exp[\frac{3}{4}G\tau_b\kappa\cos^2\theta + \alpha\cos\theta]$, where $\alpha = mH/(kT)$ is the Langevin parameter. Evaluating with it the orientational average $\langle M_z \rangle$ yields, for small $G\tau_b$ and small α,

$$1 + \frac{G\tau_b\kappa}{5} = \langle M_z \rangle / M^{\mathrm{eq}} = 1 + G\tau\lambda_2\,. \qquad (11)$$

The second equality is derived from the macroscopic evolution equation (5) if the above elongational flow profile is plugged in. Estimating the magnetic relaxation time τ by the rotary diffusion time τ_b yields, for the dependence of the transport coefficient λ_2 on the particles' axis ratio r, $\lambda_2 \simeq \kappa/5$. For the ferrofluid under consideration with $\lambda_2 \simeq 0.2$, we deduce from Eq. (10) an effective chain length of about $r = 2$ particle diameters.

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