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Hydrodynamic theory of polydisperse chain-forming ferrofluids

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The larger magnetic particles in ferrofluids are known to form chains, causing the fluid to display non-Newtonian behavior. In this paper, a generalization of the familiar ferrofluid dynamics by Shliomis is shown capable of realistically accounting for these fluids. The modification consists of identifying the relaxing magnetization as that of the chain-forming particles, while accounting for the free magnetic particles by dissipative terms in the Maxwell equations.

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I. INTRODUCTION

Ferrofluids are suspensions of magnetic nanoparticles which, created to amend the lack of strongly magnetizable fluids in nature [1], have proved useful in engineering and medical applications [2]. *Ferrofluid dynamics*, derived by Shliomis assuming spherical, noninteracting magnetic particles [3], is the generally employed theory, used, e.g., to account for the field-enhanced viscosity, and how the enhancement diminishes for an oscillatory field. More recently, denser and more strongly magnetizable ferrofluids were found to display non-Newtonian behavior such as shear thinning and normal stress differences [4]. Experiments, microscopic theories [5], and simulations [6] all show this to be the result of magnetic particles forming short chains in the presence of strong fields, making ferrofluids resemble polymer solutions. Facing the need for a macroscopic theory of these ferrofluids, similarly concise and useful as ferrofluid dynamics, the general feeling is that its construction would need input from polymer physics [7], and that the result would be a combination of ferrofluid dynamics and polymer fluid dynamics. A number of useful microscopic results were produced, on chain formation [5], chain flexibility [8], and the influence of particle interaction on the dynamics [9], but such a macroscopic theory has not as yet crystallized.

Studying the thermodynamic framework of ferrofluid dynamics, Müller and Liu found that it is useful to divide the theory into structure and coefficients [10]: The structure, or the form of the differential equations given in terms of the variables and conjugate variables, is determined by general principles and quite generally valid. (The variables are quantities such as density ρ, entropy density s, magnetic field $\boldsymbol{B}$, and magnetization $\boldsymbol{M}$. The conjugate variables are given by the respective derivatives of the energy density w: $\mu \equiv \partial w/\partial\rho$, $T \equiv \partial w/\partial s$, $\boldsymbol{H} \equiv \partial w/\partial \boldsymbol{B}$, and $\boldsymbol{h} \equiv \partial w/\partial \boldsymbol{M}$.) Only the theory's coefficients (especially the relaxation time τ of the magnetization) depend on microscopic details, such as the one mentioned above of spherical, noninteracting magnetic particles. This implies one may retain the structure of ferrofluid dynamics to account for any system sustaining a slowly relaxing magnetization if one ignores the value of the coefficients obtained by simplifying assumptions, taking them instead given by a few defining experiments. Then ferrofluid dynamics is valid irrespective of particle shape and rigidity (be it spherical or elongated, rigid or flexible), independent of the kind of magnetization (or submagnetization), and type of relaxation (be it Néel, Brown, or altogether something else, see the case below). Carrying this thought to its logical end, it is quite cogent to conclude that ferrofluid dynamics is well capable of accounting for chain-forming ferrofluids—although the chains as "constituent particles" are elongated, flexible, and the relaxation rate of the associated magnetization is a complex, composite quantity, determined less by how fast the chains may be oriented, more by how quickly particles can be transported and assembled, to form chains of the appropriate lengths.

It is useful at this point to reflect on the alleged similarity between polymer solutions and chain-forming ferrofluids, which we believe is rather superficial: Polymer strands are entangled without shear, and become aligned along the flow at high shear; magnetic chains are aligned along the field without shear, and fragmented at high shear [4]. Given these differences, it is not surprising that input from polymer dynamics is not appropriate for coming to terms with chain-forming ferrofluids.

This is fortunate, because although empirical constitutive relations for select aspects of non-Newtonian rheology abound, there is no authoritative, universally accepted polymer dynamics, based on irrefutable general principles of macroscopic physics. Ferrofluid dynamics, transparently derived from a sound understanding of the system's physics, is such a theory. But if input from polymer physics, an area that is obviously less well understood, were necessary, trust and unity would both suffer. It is therefore important that ferrofluid dynamics is shown capable of accounting for ferrofluid's non-Newtonian behavior alone. Equally relevant, having a physically cogent and coherent theory for a non-Newtonian system is a useful starting point for coming to terms with non-Newtonian rheology more generally.

Note that magnetorheological fluids are somewhat different: Since the magnetic particles are larger, they form long chains bridging the whole system for a strong field. This is the jamming transition, after which the system is truly elastic [11]. Close to the jamming transition, the system should be "transiently elastic," same as polymer solutions [12].

Assuming linear constitutive relation, which makes analytic solutions possible, the structure of ferrofluid dynamics was extensively probed [13]. The derived expressions, as anticipated by the arguments given above, display a wide range

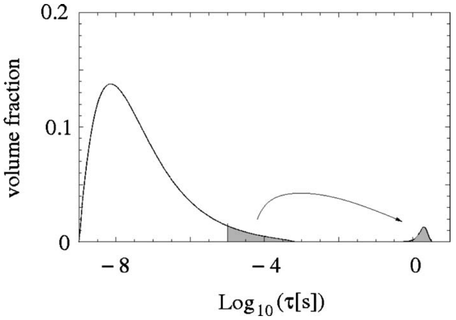

FIG. 1. Particle density versus the logarithms of relaxation time. The large curve shows the distribution at zero field. Particles of the shaded area form chains at finite fields. The associated magnetization relaxes much more slowly, because it is dominated by the transport of particles through the liquid.

of non-Newtonian behavior, both measured and not yet observed, including shear thinning or shear thickening, normal stress differences, viscous-elastic response, and a varying Trouton, or elongational, viscosity. Unfortunately, although this shows our prejudice is right, the agreement between theory and experiment is far from quantitative. In fact, they frequently differ by orders of magnitude. The reason is ferrofluid dynamics such as it stands, with a single relaxation time, describes an idealized fluid in which all particles participate in chain formation—while typically only the largest 1% does. Any realistic hydrodynamic theory for chain-forming ferrofluids must also account for the smaller, free particles.

The theory given here, a generalized ferrofluid dynamics, does this by using the hydrodynamic Maxwell theory [14], which contains irreversible terms to account for dissipation, here to account for the free particles that are not quite in equilibrium. This is possible because there is a separation of two time scales, between the relaxation time τ of the chains, and that of the free particles τ_f, with $\tau_f \ll \tau$.

II. SOME BASIC CONSIDERATIONS

A. Different relaxation times

Converting the measured distribution [4] of particles radii in APG 513A to a distribution of τ_f yields Fig. 1, with $10^{-9} \lesssim \tau_f \lesssim 10^{-3}$ s. At higher fields, the larger particles (say of the shaded area, with $10^{-5} \lesssim \tau_f \lesssim 10^{-3}$ s) participate in chain formation, after which their relaxation time τ are much larger and narrower: The transport of particles through the liquid, usually by far the slowest process, determines the relaxation time. Since the time needed bringing together two particles is comparable to collecting six, the distribution of relaxation times τ for chains with different lengths is much narrower than that of τ_f.

The especially slow relaxation of the submagnetization $\boldsymbol{M}$ from the chain-forming particles is what influence the hydrodynamics most. Focusing on its dynamics, we designate the magnetic relaxation equation for $\boldsymbol{M}$ alone—instead of for the total magnetization, as ferrofluid dynamics does. In addition, we employ the dissipative terms in the Maxwell equations for a more summary account of the rest of the magnetization.

To obtain an estimate for the magnitude of τ, we denote the characteristic distance between two chain-forming particles as $\ell = d\phi^{-1/3}$, where ϕ and d are their volume fraction and diameter, respectively. If τ_{d} is the time to diffuse d, the time needed to bring together two such particles is $\tau_0 = \tau_{\mathrm{d}}(\ell/d)^2 = \tau_{\mathrm{d}}\phi^{-2/3}$. The actual relaxation time is then $\tau \approx \tau_0/\phi = \tau_{\mathrm{d}}\phi^{-5/3}$, because in accordance to standard theories of cluster formation [20], the rate of establishing the equilibrium chain length is proportional to the density of available particles. Taking $\tau_{\mathrm{d}} \approx 10^{-5}$ s, $\phi \approx 10^{-3}$ for APG 513A, we find $\tau \approx 1$ s. As we shall see below, taking $\tau \approx 3$ s produces results that agree with the experimental data on shear thinning. Given this large τ, it is important that the theory below is valid for arbitrary frequencies ω and shear rates $\dot{\gamma}$, including $\omega\tau \gg 1$, $\dot{\gamma}\tau \gg 1$, provided

$$\omega\tau_f \ll 1, \quad \dot{\gamma}\tau_f \ll 1. \tag{1}$$

B. Is the magnetic relaxation time shear dependent?

There are many in this field who believe that transport coefficients depend on the shear rate $\dot{\gamma}$—because strong shear destroys the chains, and the values of the coefficients depend on the chain length, see [15] and the apparently convincing agreement it achieves. In the following, we present our reasons why we believe it is ill advised to include this dependence.

First the more general ones. The Onsager relation is statistically well founded and strictly valid only to its lowest linear order. To this order, none of the Onsager coefficients may depend on thermodynamic forces, only on thermodynamic variables: Pressure P or temperature T are variables, $\nabla_i T$ or $2v_{ij} \equiv \nabla_i v_j + \nabla_j v_i$ are forces. ($2v_{ij}$ reduces to $\dot{\gamma}$ for simple shear.) This implies especially that viscosities do not depend on shear, $\eta_0 \neq \eta_0(\dot{\gamma})$. In non-Newtonian fluids, because of observations such as shear thinning, some people conclude that $\eta_0 = \eta_0(\dot{\gamma})$ is an experimental, hence irrefutable, fact, and one is forced to leave Onsager relation's linear regime. Yet this is too hasty a conclusion.

Complex fluids usually depend on additional, nonhydrodynamic variables that contribute to the stress σ_{ij}. When calculating the effective viscosity, $\sigma_{ij}/\dot{\gamma}$, their contribution typically depend on $\dot{\gamma}$, yielding a natural and transparent explanation for shear thinning (or thickening)—although η_0 is taken as a constant. In contrast, to account for shear thinning via the functional dependence of $\eta_0(\dot{\gamma})$, one typically puts in this dependence by hand, on the evidence of some experimental results—a theoretically far less satisfactory approach. In ferrofluids, this nonhydrodynamic variable is the magnetization $\boldsymbol{M}$ which, as shown in the manuscript, naturally gives rise to shear thinning as measured. It is superfluous and counterproductive to assume an additional shear dependence of the viscosity.

Next, the specific reason why the seductive argument about the dependence on chain length is not cogent. The logical gap lies between a ferrofluid at rest and one subject to strong shear. In a quiescent linear ferrofluid, the magnetization obeys the equation, $\frac{\partial}{\partial t}\boldsymbol{M} = -\delta\boldsymbol{M}/\tau$. The magnetic particles form chains in equilibrium, and the relaxation time τ indeed depends on the *equilibrium chain length*. However, when a shear flow $\dot{\gamma}$ breaks up or shortens the chains, it is a leap of faith to believe that τ assumes the value it would have with the same equilibrium chain length. In fact, for finite $\dot{\gamma}$, $\boldsymbol{M}$ obeys the equation

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla}-\boldsymbol{\Omega}\times\right)\boldsymbol{M}\bigg|_i-\lambda_2 M_j v_{ij}=-\delta M_i/\tau.$$

And two of the three additional terms should be taken as shear-dependent corrections to τ: While τ depends on the equilibrium chain length, the additional terms account for its shear dependence, including the breakup. (More appropriately, we should take these two terms as the shear-dependent corrections of the relaxation process, rather than too narrowly of the relaxation time τ.) This is the specific reason why τ should not be taken as a function of $\dot{\gamma}$, and it concurs with the general ones above. Adopting this view below, we obtain results in quantitative agreement with experiments.

It is worth pointing out that this is a dispute that may be settled by an experiment, in which the relaxation time is actually measured in the presence of a finite shear.

A final point concerns whether the breakup of chains is a process drastic enough to permit considering the fluid as one with an altered structure, which hence possess different Onsager coefficients. We believe this is a red herring. The chain length is a continuous parameter. There is no phase transition, which alone would give an unambiguous boundary at which to switch the coefficients. Moreover, the fact that magnetic particles form chains which are then broken up is, in its significance for the viscous behavior, possibly not as relevant as is generally assumed. Macroscopically, the rather more directly important quantity is the magnetization. Given an external field, it assumes a finite value, which is maximal in a quiescent fluid and approaches zero if the shear is strong enough. Being valid irrespective whether the magnetic particles form chains or not, this is the basic reason for magnetoviscosity and shear thinning, and what our equations describe. That for certain parameters the maximal value is achieved by forming chains, which are then torn apart to have the magnetization vanish, is hence a rather secondary microscopic fact.

C. Ferrofluid dynamics versus nematodynamics

Since many in the field of complex fluids, including some seasoned researchers, believe that ferrofluids, being uniaxial, obey nematodynamics as given by the Leslie-Ericksen theory, or any of its equivalent hydrodynamic variants (for details see [16]), a few words on the crucial difference between nematodynamics and ferrofluid dynamics (i.e., the Shliomis theory and its generalization) appear useful, even necessary, here.

Nematodynamics is appropriate for all uniaxial fluids in which the rotation symmetry, characterized by the director $\boldsymbol{n}$, is spontaneously broken. As a result, $\boldsymbol{n}$ is a hydrodynamic variable, and the associated collective modes are a pair of gapless orbital waves. Nematodynamics is not appropriate for ferrofluids, the symmetry of which is broken by an external field, not spontaneously. The magnetization is nonhydrodynamic, and the associated modes have a gap.

However, circumstances change qualitatively when the paramagnetic ferrofluid undergoes a ferromagnetic transition (something that appears not too far fetched with quantum ferrofluids [17]). Writing the magnetization as $\boldsymbol{M}=M\boldsymbol{m}$, with M the magnitude and $\boldsymbol{m}$ a unit vector, $\boldsymbol{m}$ resembles $\boldsymbol{n}$ greatly in the absence of a field: It will have no preferred direction to align to, and the energy will also be of the structure $K_{ijk\ell}\nabla_i m_j \nabla_k m_\ell$, giving rise to a "molecular field" $\psi_j = K_{ijk\ell}\nabla_i \nabla_k m_\ell$, which is the relevant thermodynamic force. The vector $\boldsymbol{m}$, same as $\boldsymbol{n}$, does not relax, and both obey similar equations of motion. The differences between them are comparatively subtle, one fact being $\boldsymbol{M}$, an axial vector, is different from $-\boldsymbol{M}$, while $\boldsymbol{n}$ is of course equivalent to $-\boldsymbol{n}$.

A different point is the fact that uniaxial symmetry is in general lost for ferrofluids driven away from equilibrium. In the presence of an external flow field, for example, the direction of the magnetic field $\boldsymbol{H}$ does in general not coincide with the direction of the magnetization $\boldsymbol{M}$ [6,18].

D. Symmetry of the stress tensor

Another point of frequent und unnecessary contention concerns the symmetry of the stress tensor Π_{ij}. On one hand, there is little doubt that angular momentum conservation requires a symmetric stress tensor, $\Pi_{ij}=\Pi_{ji}$, while on the other, many antisymmetric terms are known to be quite necessary to account for the behavior of complex fluids, especially those with constituent particles that are either nonspherical, or carry a permanent magnetic moment.

For the Leslie-Ericksen theory, the resolution lies in the fact that stress tensors are not always uniquely determined, and the Leslie-Ericksen stress Π_{ij}^{LE}, containing an antisymmetric part, may be rewritten as a symmetric one Π_{ij}, with $\nabla_j \Pi_{ij}^{LE}=\nabla_j \Pi_{ij}$, for details see [16], or Sec. VI on liquid crystals of [19].

For ferrofluid dynamics, the circumstance is even simpler: While one frequently focuses on the torque $\boldsymbol{M}\times\boldsymbol{H}$, because it gives rise to interesting effects, the total Shliomis stress, including the Maxwell term, H_iB_j, is certainly symmetric,

$$\begin{aligned} H_iB_j+\epsilon_{ijk}(\boldsymbol{M}\times\boldsymbol{H})_k/2 &= H_iB_j+(M_iB_j-M_jB_i)/2 \\ &= (H_iB_j+H_jB_i)/2. \end{aligned} \tag{2}$$

The stress of Eq. (7) may also be shown in a similar fashion to be symmetric.

III. THE EQUATIONS OF MOTION

The equation of motion for $\boldsymbol{M}$, the submagnetization of the chains, has the same structure as that for the total magnetization [3,10]. Including only the demonstrably relevant terms and assuming incompressibility, it reads

$$\left(\frac{\partial}{\partial t}+\boldsymbol{v}\cdot\boldsymbol{\nabla}-\boldsymbol{\Omega}\times\right)\boldsymbol{M}\bigg|_i-\lambda_2 M_j v_{ij}^0=-\chi h_i/\tau, \tag{3}$$

with $\boldsymbol{v}$ the velocity, $\boldsymbol{\Omega}\equiv\frac{1}{2}\boldsymbol{\nabla}\times\boldsymbol{v}$, $v_{ij}^0\equiv\frac{1}{2}(\nabla_i v_j+\nabla_j v_i)-\frac{1}{3}\delta_{ij}\nabla_\ell v_\ell$, χ the initial magnetic susceptibility of $\boldsymbol{M}$, and

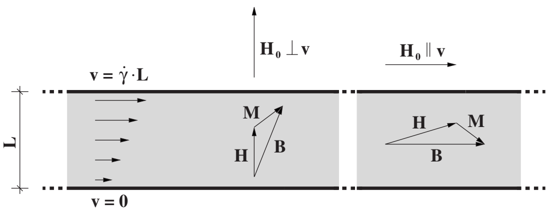

FIG. 2. The two orientations of the external field.

$\boldsymbol{h} \equiv \partial w / \partial \boldsymbol{M} = \boldsymbol{B}^{\mathrm{eq}} - \boldsymbol{B}$, where w is the energy density, and $\boldsymbol{B}^{\mathrm{eq}}(\boldsymbol{M})$ the inverse of $\boldsymbol{M}^{\mathrm{eq}}(\boldsymbol{B})$, the equilibrium value of the submagnetization for given $\boldsymbol{B}$ fields. [In principle, $\boldsymbol{M}^{\mathrm{eq}}(\boldsymbol{B})$ is an input of the theory, which needs to be measured or calculated microscopically. We shall approximate it with the usual Langevin form below.] The transport coefficient λ_2 was measured by Odenbach and Müller, who obtained values between 0 and 0.88 for different ferrofluids [21]. Relating λ_2 to the chain length at zero shear, they found $\lambda_2 \approx 0$ appropriate for chainless ferrofluids, while 0.88 indicates chains of five particles.

Because the magnetic relaxation time of the free particles spans a few orders of magnitude, and the approximation of one relaxation time is obviously bad, an obvious way to account for them is to set up many more equations such as Eq. (3), one each for $\boldsymbol{M}_f^q$, with $q = 1, 2, 3, \ldots$ enumerating the size or time segments. This would result in a highly unwieldy theory containing an excessive number of variables and equations of motion. More economical in this case is the *hydrodynamic Maxwell theory*, which instead of introducing additional variables, uses a dissipative field $\boldsymbol{H}^D$ in the Maxwell equation [14] for a summary account of all magnetizations that are slightly off equilibrium and satisfy Eq. (1),

$$\dot{\boldsymbol{D}} = c\,\boldsymbol{\nabla} \times (\boldsymbol{H} + \boldsymbol{H}^D), \quad \boldsymbol{H} = \boldsymbol{B} - \boldsymbol{M}_f^{eq}(\boldsymbol{B}) - \boldsymbol{M}, \tag{4}$$

$$\boldsymbol{H}^D = \alpha\left(\frac{\partial}{\partial t} + \boldsymbol{v} \cdot \boldsymbol{\nabla} - \boldsymbol{\Omega} \times \right)\boldsymbol{B}, \tag{5}$$

where $\boldsymbol{M}_f^{eq}$ is the equilibrium value of $\Sigma_q \boldsymbol{M}_f^q \equiv \boldsymbol{M}_f = \boldsymbol{M}_f^{eq} - \boldsymbol{H}^D$, the total magnetization of the free particles. Its deviation from equilibrium is accounted for by the dissipative field $\boldsymbol{H}^D$ (which may equivalently be written as $\boldsymbol{H}^D = -\alpha c \boldsymbol{\nabla} \times \boldsymbol{E}_0$, where $\boldsymbol{E}_0$ is the $\boldsymbol{E}$ field in the local rest frame). Assuming linear constitutive relation, the transport coefficient α is given as

$$\alpha = \frac{\sum_q \tau_f^q \chi_f^q}{\left(1 + \sum_q \chi_f^q\right)^2} \rightarrow \frac{\tau_f \chi_f}{(1 + \chi_f)^2}, \tag{6}$$

where τ_f^q, χ_f^q are the relaxation time and susceptibility of $\boldsymbol{M}_f^q$, respectively. The second expression holds in a monodisperse ferrofluid, if there is only one species of magnetization [14]. If $\boldsymbol{H}^D$ is nonzero [say because $\boldsymbol{\Omega} \times \boldsymbol{B}$ is, see Eq. (5)], the field $\boldsymbol{B}$ and the magnetization $\boldsymbol{M}_f$ are off equilibrium.

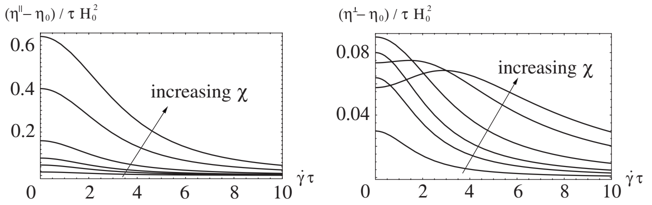

FIG. 3. Shear thinning (and thickening) of a monodisperse ferrofluid obeying linear constitutive relation, for parallel and perpendicular fields. $(\eta^{\|} - \eta_0)/[\tau H_0^2]$ and $(\eta^{\perp} - \eta_0)/[\tau H_0^2]$, calculated using Eqs. (9), with $\chi = 0.1/0.3/0.5/1/2.5/4$ and $\lambda_2 = 0.2$, are plotted against $\xi \equiv \dot{\gamma}\tau$. Note that increasing χ may actually reduce the magnetoviscous effect.

Defining the stress tensor Π_{ij} as the rest frame flux of momentum conservation, $\dot{g}_i + \nabla_j(\Pi_{ij} + \rho v_i v_j) = 0$, we find that, given Eqs. (3)–(5), conservation of energy and momentum force it to assume the form

$$\Pi_{ij} = P\delta_{ij} - (H_i + H_i^D)B_j - \frac{1}{2}[(B_i H_j^D - B_j H_i^D) + (M_i h_j - M_j h_i) - \lambda_2(M_i h_j + M_j h_i)] - 2\eta_0 v_{ij}, \tag{7}$$

where η_0 is the viscosity at vanishing field. Note that without λ_2 and $\boldsymbol{H}^D$, introduced respectively, in [10,14], this is the usual Shliomis expression. (The scalar P contains all diagonal terms [10], not only the pressure. It is not further specified, as it is relevant only for compressional flows such as considered in [22].) Assuming constant temperature and densities, Eqs. (3)–(5) and (7) (in addition to the other three Maxwell equations) are closed and complete, and represent the hydrodynamic theory for polydisperse, chain-forming ferrofluids.

The transport coefficients $\alpha, \eta_0, \lambda_2, \tau$ are material-dependent parameters, and functions of thermodynamic variables, especially the field (but also density and temperature). But they are, as discussed in Sec. II B, emphatically independent from shear.

IV. TWO LIMITS

Before we embark on the study of the theory's ramifications, it is useful to first consider two limits, first the case without any chain formation, then the case of complete chain formation, no free particles. Taking the field $\boldsymbol{B}$ to be time

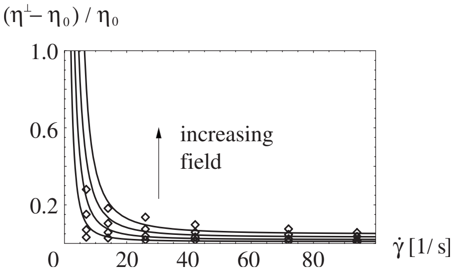

FIG. 4. Shear thinning calculated employing the given theory (lines), and compared to two sets of experimental data [4] from APG 513A (diamonds).

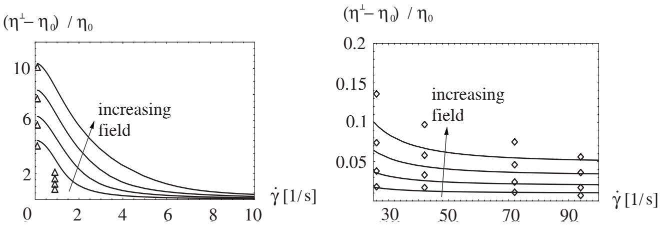

FIG. 5. Same data as Fig. 4, zoomed into two shear regions.

independent and spatially constant, we find, for the first case, $\boldsymbol{M},\boldsymbol{h}\equiv 0$, that the stress, Eq. (7), reduces to

$$-\frac{1}{2}\Pi_{ij}=\eta_0 v_{ij}+\frac{1}{4}\alpha[B_i(\boldsymbol{B}\times\boldsymbol{\Omega})_j-B_j(\boldsymbol{B}\times\boldsymbol{\Omega})_i]. \tag{8}$$

For $\boldsymbol{B}\perp\boldsymbol{\Omega}$ and a plane shear flow, $|\Omega|=\frac{1}{2}\nabla_x v_y$, this expression implies the effective viscosity of $\eta=\eta_0+\frac{1}{4}\alpha B^2$. With α as given in Eq. (6) for a monodisperse fluid, this is the same as the famous Shliomis result, $\eta=\eta_0+\frac{1}{4}\tau_f M_f^{eq}H$, see [1]. Taking the first expression of Eq. (6), the more general α, the viscosity $\eta=\eta_0+\frac{1}{4}\alpha B^2$ gives the result for polydisperse ferrofluids, obtained without introducing the magnetizations as independent variables.

The second limit is given by complete chain formation, no free particles, vanishing $\alpha,\boldsymbol{M}_f,\boldsymbol{H}^D$, and linear constitutive relation ($\boldsymbol{M}^{eq}=\chi\boldsymbol{H}$). The effective viscosity for simple shear may then as mentioned be calculated analytically [13]. We take the external field $\boldsymbol{H}_0$ to assume two orientations, parallel ($\boldsymbol{H}_0\|\boldsymbol{v}$) and perpendicular ($\boldsymbol{H}_0\perp\boldsymbol{v}$, but parallel to the velocity gradient), noting that experiments were performed only in the first [4], see Fig. 2. The respective effective viscosity $\eta^{\perp}$ and $\eta^{\|}$ are obtained as

$$\frac{\eta^{\perp}-\eta_0}{\tau H_0^2}=\frac{(1+\lambda_2)^2[4+(1-\lambda_2)^2\xi^2]}{[4(1+\chi)+(1-\lambda_2^2)\xi^2]^2}\chi, \tag{9}$$

$$\frac{\eta^{\|}-\eta_0}{\tau H_0^2}=\frac{(1-\lambda_2)^2[4(1+\chi)^2+(1+\lambda_2)^2\xi^2]}{[4(1+\chi)+(1-\lambda_2^2)\xi^2]^2}\chi, \tag{10}$$

where $\xi\equiv\dot\gamma\tau=$(the gradient of the velocity)$\times\tau$ is the dimensionless shear rate. Note that the viscosity in the absence of any field, η_0, is also the viscosity for infinite shear, $\xi\to\infty$, as the right side vanishes in both equations. In the limit of small shear, $\xi\to 0$, and assuming $\lambda_2=0$, we have $\eta^{\perp}=\eta_0+\frac{1}{4}\tau H_0^2\chi/(1+\chi)^2$ and $\eta^{\|}=\eta_0+\frac{1}{4}\tau H_0^2\chi$. With $H_0=B$ and $H_0=H$, respectively, both imply $\eta^{\perp}=\eta^{\|}=\eta_0+\frac{1}{4}\tau M^{eq}H$, as discussed below Eq. (8). Note however that $\eta^{\|}$ is much larger than $\eta^{\perp}$ for given external field H_0. For finite shear, Eqs. (9) show shear thinning (and thickening), see Fig. 3.

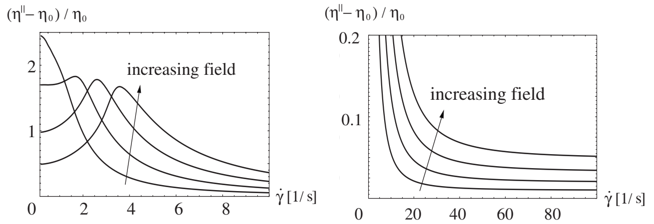

FIG. 6. Shear thinning for the parallel field orientation, $(\eta^{\|}-\eta_0)/\eta_0$ versus $\dot\gamma[1/s]$, using the same parameters as in Fig. 3.

V. SHEAR THINNING

Finally, we consider the realistic case of polydisperse, partially chain-forming ferrofluids, again with parallel and perpendicular field orientation, resorting to numerical evaluation of the hydrodynamic theory, Eqs. (3)–(5) and (7), for the geometry of simple shear. Experimental data only exist for the perpendicular case in APG 513A [4], for which the saturation magnetization is $M_s=32\times 10^3$ A/m, the initial susceptibility $\chi+\chi_f=1.57$, and $\eta_0=0.128$ Pa s. Our results agree satisfactorily well with these data, see Fig. 4, if we take the fraction of chain-forming population to be $\phi=0.3\%$, and its initial susceptibility as $\chi=0.01$ (implying a total susceptibility of $\chi/\phi=3.3$ if the fraction were 1). For the free particles, we consequently have $\chi_f=1.56$, and assume in addition $\alpha=2.6\times 10^{-5}$ s (taken for simplicity independent of the field). Also, we take $\tau=3.3/2.8/2.5/2.3$ s and $\lambda_2=0.05/0.23/0.42/0.6$ at $H=4850/6850/8800/10750$ A/m (or $H_0=12\,500/17\,500/22\,500/27\,500$ A/m), respectively. The field $\boldsymbol{h}=\boldsymbol{B}^{\mathrm{eq}}-\boldsymbol{B}$ is given by taking B^{eq} as the inverse of the Langevin function $M^{\mathrm{eq}}(B)=M_s\{\coth[3\chi B/(1+\chi)M_s]-M_s(1+\chi)/(3\chi B)\}$, with $M_s=100$ A/m denoting the saturation magnetization of the chain-forming particles.

For intermediate values of the shear rate, the agreement is less satisfactory, as can be seen in Fig. 5, a blownup version of Fig. 4. There are a few obvious reasons for this discrepancy: (1) We are attempting to fit two different experiments, $0.1\frac{1}{s}\leqslant\dot\gamma\leqslant 0.9\frac{1}{s}$ and $4\frac{1}{s}\leqslant\dot\gamma\leqslant 94\frac{1}{s}$, performed some time apart [4], using only one set of parameters. (2) The Langevin function is not probably a fair approximation of the equilibrium magnetization of the chains, because in addition to stronger alignment at higher fields, the chains are also becoming longer. (3) Including more than one relaxation time for the chains should further improve the agreement.

In Fig. 6, the parallel case is calculated using the same parameters. As mentioned, no experiments have as yet been performed in this geometry.

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