

The rheology of field-responsive suspensions

J M Rubí† and J M G Vilar‡

† Departament de Física Fonamental, Universitat de Barcelona, Diagonal 647,
E-08028 Barcelona, Spain

‡ Departments of Physics and Molecular Biology, Princeton University, Princeton, NJ 08544,
USA

Received 10 September 1999

Abstract. We present some aspects of the rheology of field-responsive suspensions, a class of field-responsive liquid-matter systems possessing the ability to undergo significant changes in their strength upon application of an external field. Both the single-particle and the many-particle domains are discussed. In the former, consideration of the full non-linear dynamics of the particles leads to an anomalous behaviour of the viscosity whereas in the latter the most salient feature is the formation of chains and fractal structures. We indicate how to deal with the rheology at moderate concentrations, leaving open the problem at higher concentrations for which the complexity of the emergent structures strongly limits the knowledge of their dynamics.

1. Introduction

The term ‘field-responsive liquid matter’ embraces a class of soft-condensed-matter systems which exhibit peculiar behaviour upon application of an external field. Of particular interest is the family of two-phase systems in which one of the phases is responsive whereas the other is practically unresponsive to the effect of the field. The active phase consists of single dipolar particles which at low concentrations remain randomly dispersed in the liquid phase but at larger concentrations have a tendency to aggregate forming chains or more complex branched structures. These structures are embedded in the liquid phase which may be a simple liquid, a polymer, or a liquid crystal, to name just a few possibilities.

As occurs in dispersions of neutral colloidal particles or polymer solutions, the objects of the suspended phase interact with their fluid surroundings, thus modifying the flow of this fluid. Unlike the case for those systems, the interactions of the particles with the fluid are assisted by the external field; moreover, for a given concentration, structures which for neutral particles would be stable may evolve over time giving rise to interesting collective phenomena. The consequence of these features is that some static and dynamic properties of the system such as the overall magnetization or the viscosity may vary substantially as a consequence of the external field or the dipolar interactions among particles. This fact constitutes one of the most important characteristics of these systems, which has been used in many technological applications. Electro- and magneto-rheological fluids [1] and ferrofluids [1–5] belong to that class of systems whose static and dynamic properties have been subjects of great interest in recent years.

Our purpose in this paper is to present several relevant aspects of the rheology of field-responsive suspensions. We will discuss the single-particle and the many-particle regimes. For dilute suspensions, the case of constant field has been extensively studied and shows

a monotonic increase of the viscosity when the field increases. For time-dependent fields this behaviour breaks down and even in the linear domain the viscosity may decrease upon increasing the field. This phenomenon leading to a diminution of the total viscosity of the suspension has been found recently and has been referred to as the negative-viscosity effect [6–8]. Interesting non-linear effects may arise from the coupling of the dynamics of the magnetic moment, described by the Landau–Gilbert equation, to that for the orientation of the particle. The dynamics in this regime exhibits a rich phenomenology whose main macroscopic implication is the breaking of the monotonic behaviour of the viscosity [9]. The main feature in the moderately concentrated regime is the formation of chains and branched structures. Chains appear at low temperatures, for which Brownian effects are irrelevant, or for strong dipolar interaction, which occurs when the particles are induced dipoles (electro- and magneto-rheological fluids). They are also formed in one-dimensional adsorption processes in the presence of dipolar interactions [10]. In the opposite limit, including the case of nanosized ferromagnetic particles or ferrofluids, more compact aggregates may be found.

Kinetic models have been proposed to analyse the dynamics of chains of induced dipoles and its implications for the rheological behaviour. The structures emerging at high temperatures are sometimes hierarchical. The rheology in this regime is more complex and the modelling of the dynamics needs to be developed.

The paper has been organized as follows. In section 2 we analyse the macroscopic implications of the rotational dynamics of the particles by establishing a relationship between the viscosity associated with the rotation of the particle, or rotational viscosity, and its dynamics. This formula is applied to several cases already addressed in the literature, which in this framework can be treated in a very simple and systematic way. Section 3 is devoted to presenting some well-known examples belonging to the single-particle domain. In section 4 we analyse the non-linear domain and discuss very briefly the appearance of a dynamical transition breaking the monotonic nature of the rotational viscosity as a function of the field. In section 5 we deal with the rheology of the moderately concentrated phase. Finally, in the discussion section we summarize the main results obtained in the regimes addressed previously and point out some methodological aspects useful in the treatment of these systems.

2. From mesoscopic to macroscopic

To illustrate the implications of the mesoscopic dynamics of the suspended particles for the macroscopic behaviour of the system, we consider first the case in which the field-responsive fluid consists of a dilute suspension of spherical dipolar particles in a simple liquid under the influence of an external magnetic field which may be constant or time dependent. The dipole moments remain rigidly attached to the particles, being parallel to their orientations. The dynamics of both the magnetic moment and orientation of the particle are given by

$$\frac{d\hat{R}}{dt} = \vec{\Omega} \times \hat{R} \quad (1)$$

where \hat{R} is the unit vector along the dipole moment and $\vec{\Omega}$ is the angular velocity of the particle. A very common situation arises when inertial effects can be neglected. In this case, the angular velocity of the particle is completely determined by the balance of magnetic, hydrodynamic, and Brownian torques. It is given by

$$\vec{\Omega} = \vec{\omega}_0 + \frac{1}{\xi_r} \vec{m} \times \vec{H} + \frac{1}{\xi_r} \hat{R} \times \vec{F}_B(t). \quad (2)$$

Here $\vec{m} = m_0 \hat{R}$ is the dipole moment, and \vec{H} is the applied field. The hydrodynamic torque arises from the angular velocity difference between the particle and the fluid with vorticity

$2\omega_0$; its strength also depends on the rotational friction coefficient, ξ_r . Brownian effects are taken into account through a random force, $\vec{F}_B(t)$, with zero mean and correlation function

$$\langle \vec{F}_B(t) \vec{F}_B(t') \rangle = 2\xi_r k_B T \vec{1} \delta(t - t')$$

where k_B , T , and $\vec{1}$ are the Boltzmann constant, the absolute temperature, and the unit tensor, respectively.

Previously given equations describe the rotational dynamics of the particle inside the fluid, but do not give information about the effects of this mesoscopic motion in the macroscopic flow. In particular, the presence of colloidal particles in a liquid modifies the macroscopic properties of the fluid by changing the transport coefficients. Several methods have been developed to compute the dependence of the transport coefficients upon the presence of these particles. Here, however, we follow an alternative approach which directly relates the mesoscopic dynamics of the particle to its macroscopic effects. To this end we consider the power dissipated in the fluid by the motion of the particle. Since the rotational motion is assisted by the external field, its angular velocity does not necessarily have to be adapted to the local angular velocity of the fluid, i.e. to the local vorticity. This gives rise to additional dissipation in the system resulting from the torque exerted by the particle on the fluid. Therefore, the power dissipated per unit of volume due to the presence of the particles is

$$\sigma_{mes} = n\xi_r (\vec{\omega}_0 - \langle \vec{\Omega} \rangle) \cdot \vec{\omega}_0 \quad (3)$$

where $n = N/V$ is the concentration of colloidal particles and $\langle \cdot \cdot \cdot \rangle$ stands for the average over thermal noise. The rotational viscosity, η_r , accounts for the change in the total viscosity of the system due to the rotational degrees of freedom of the particles. From a macroscopic point of view, the power dissipated by this change in the viscosity [11] is given by

$$\sigma_{mac} = \eta_r (2\omega_0)^2. \quad (4)$$

The relationship between mesoscopic and macroscopic properties follows straightforwardly since the previous equations are merely two different expressions for the same quantity, i.e., $\sigma_{mac} = \sigma_{mes}$. In this way, we obtain

$$\eta_r = \frac{1}{4} n\xi_r (1 - \langle \Omega \rangle / \omega_0) \quad (5)$$

which leads to the same result as in reference [8] when the rotational friction coefficient is replaced by its explicit expression for a sphere, $\xi_r = 8\pi\eta_0 a^3$, with η_0 and a being the viscosity of the carrier fluid and the radius of the particle, respectively. Notice, however, that our expression is not restricted to just spheres, like those of reference [6]; it can also be applied to any other type of particle just by considering the appropriate expression for the rotational friction coefficient. From this expression the rotational viscosity follows from the knowledge of the dynamics of the particle in the host medium. It may take positive or negative values depending on the ratio between the mean angular velocity of the particle and the local vorticity.

The methodology introduced previously, far from being specific, can be applied to a wide variety of situations, including different types of particle and flow. Let us outline here its applicability to a rod-like colloid in an elongational flow defined through the velocity field $\vec{v}_s = \vec{\kappa} \cdot \vec{r}$, with

$$\vec{\kappa} = \beta(3\hat{e}_x \hat{e}_x - \vec{1})$$

and β representing the velocity gradient and the elongation rate, respectively. The dynamics of the particle follows in a similar way to in the previous situation, but now with the hydrodynamic torque given by

$$\vec{T}^H = -\xi_r [\vec{\Omega} - \hat{R} \times (\vec{\kappa} \cdot \hat{R})]. \quad (6)$$

The power dissipated can be expressed as both

$$\sigma_{mes} = n \left\langle \vec{\xi} : (\vec{\kappa} \cdot \hat{R} - \vec{\Omega} \times \hat{R})(\vec{\kappa} \cdot \hat{R}) \right\rangle \quad (7)$$

and

$$\sigma_{mac} = 2\eta_e \vec{\kappa} : \vec{\kappa} = 12\eta_e \beta^2 \quad (8)$$

where

$$\vec{\xi} = \xi_{\parallel} \hat{R} \hat{R} + \xi_{\perp} (\mathbb{1} - \hat{R} \hat{R})$$

is the friction tensor [12, 13]. Therefore, the elongational viscosity is given by

$$\eta_e = \frac{\sigma_{mes}}{12\beta^2}. \quad (9)$$

Notice that, in contrast with the previous situation, the elongational viscosity depends on correlations of $\vec{\Omega}$ and \hat{R} . Vorticity effects can also be considered in this case. Their contribution to the rotational viscosity is obtained in a completely analogous way to previously.

3. Some representative examples in the single-particle domain

Our purpose in this section is to present some illustrative examples which have already been discussed in the literature. Here, however, we follow the method proposed in the previous section from which much of the essential information obtained from more complicated procedures can be recovered.

The simplest case addressed is the one in which the suspended dipoles are rigid and relax in a noiseless environment in the presence of a constant magnetic field. The dynamics of the magnetic moment is given by equations (1) and (2) where now the random force, $\vec{F}_B(t)$, has to be omitted. To better illustrate the essentials of the phenomenon, the explicit situation that we consider consists in an applied magnetic field along the x -direction, $\vec{H} = H_0 \hat{e}_x$, and a vorticity perpendicular to it along the y -direction, $\vec{\omega}_0 = \omega_0 \hat{e}_y$.

The equilibrium orientation of the particle for the previous situation is given by

$$\hat{R}_s = \begin{cases} \sqrt{1 - (1/\alpha)^2} \hat{x} - (1/\alpha) \hat{z} & \text{if } \alpha \geq 1 \\ \pm \sqrt{1 - \alpha^2} \hat{y} - \alpha \hat{z} & \text{if } \alpha < 1 \end{cases} \quad (10)$$

where $\alpha = m_0 H / \xi_r \omega_0$ is the ratio between the magnetic and hydrodynamic torques. The expression for the rotational viscosity readily follows after substituting the value for the orientation of the particle in the expression for the angular velocity, resulting in

$$\eta_r = \begin{cases} \frac{1}{4} n \xi_r & \text{if } \alpha \geq 1 \\ \frac{1}{4} n \xi_r \alpha^2 & \text{if } \alpha < 1. \end{cases} \quad (11)$$

Notice that the rotational viscosity increases quadratically with the intensity of the applied field until it reaches a saturation value at fields which are strong enough to prevent particle motion.

Let us now look at just the opposite situation, in which Brownian effects dominate the dynamics. Taking averages in equation (2), for the component of the angular velocity parallel to the vorticity, we obtain

$$\langle \Omega_y \rangle = \omega_0 + \frac{1}{\xi_r} m_0 H_0 \langle R_z \rangle \quad (12)$$

whereas from equation (1),

$$\frac{d}{dt} \langle R_z \rangle = \omega_0 \langle R_x \rangle - \frac{m_0 H_0}{\xi_r} \langle R_z R_x^2 \rangle - \frac{k_B T}{\xi_r} \langle R_z \rangle \quad (13)$$

$$\frac{d}{dt} \langle R_x \rangle = -\omega_0 \langle R_z \rangle + \frac{m_0 H_0}{\xi_r} \langle 1 - R_x^2 \rangle - \frac{k_B T}{\xi_r} \langle R_x \rangle. \quad (14)$$

From the previous equations we can easily obtain the viscosity for some representative cases in the stationary state ($d\langle \vec{R} \rangle / dt = 0$). For instance, in the high-field limit we have $R_x \sim 1$. Therefore,

$$\langle R_z \rangle = \frac{\xi_r \omega_0}{m_0 H_0 + k_B T} \quad \text{and} \quad \eta_r = \frac{n \xi_r}{4 + 4k_B T / m_0 H_0}. \quad (15)$$

In contrast, for high noise or low field we have $m_0 H_0 \ll k_B T$, which leads to

$$\langle R_x \rangle = \frac{k_B T}{\xi_r \omega_0} \langle R_z \rangle.$$

Moreover, since the distribution of orientations is almost uniform, i.e. $\langle R_x^2 \rangle \sim 1/3$,

$$\langle R_z \rangle = \frac{2m_0 H_0 / \xi_r \omega_0}{3 + 3(k_B T / \xi_r \omega_0)^2} \quad (16)$$

and

$$\eta_r = \frac{1}{24} n \xi_r \left[\frac{(m_0 H_0)^2}{(\xi_r \omega_0)^2 + (k_B T)^2} \right]. \quad (17)$$

As a common feature, in all these examples in which the magnetic field is constant, the rotational viscosity is a monotonic function of the field, reaching a saturation limit at high values of the field. This behaviour has been observed experimentally [17].

Let us now consider the situation in which the field is oscillating in time, $\vec{H} = H_0 e^{i\omega t} \hat{e}_x$. For the sake of simplicity we assume, as previously, that the amplitude of the field is sufficiently small. In this case the mean angular velocity is given by

$$\langle \Omega_y \rangle = \omega_0 + \frac{1}{\xi_r} m_0 \overline{\Re(H_0 e^{i\omega t}) \Re(\langle R_z \rangle_\omega)} \quad (18)$$

where $\langle \vec{R} \rangle = \langle \vec{R} \rangle_\omega e^{i\omega t}$ and the overline stands for time average and \Re for the real part of its argument. The solution of the previous equations follows straightforwardly by just realizing that since $d\langle \vec{R} \rangle / dt = i\omega \langle \vec{R} \rangle$ the resulting equations are then formally identical to equations (13) and (14) if one replaces $k_B T$ by $k_B T + i\xi_r \omega$. Taking the real part of the viscosity obtained in that way leads to

$$\eta_r = n \frac{m_0^2 H_0^2}{24 \xi_r} \left\{ \frac{\omega_0^2 - \omega^2 + (k_B T / \xi_r)^2}{[(\omega_0^2 - \omega^2 + (k_B T / \xi_r)^2)^2 + 2(k_B T / \xi_r)^2 \omega^2]} \right\} \quad (19)$$

which corresponds to the increase of the viscosity due to the presence of the oscillating field. It is worth pointing out the remarkable feature that this correction to the viscosity can take negative as well as positive values. Negative values of this quantity mean that the mean angular velocity of the particle is higher than that of the fluid. Therefore, the energy of the oscillating field is transformed into kinetic energy that contributes to diminishing the effective viscosity of the fluid. Notice that for this situation to happen, $\langle \vec{R}_z \rangle$ and H_x must be anticorrelated, which can never happen when $d\langle \vec{R}_z \rangle / dt = 0$.

Particles of different shape can also be included in this framework. For instance, in the case of a suspension of rod-like particles, the elongational viscosity follows from the dissipated

power (equation (7)). This quantity can be decomposed into its elastic, σ^E , and viscous, σ^V , contributions, i.e., $\sigma_{mes} = \sigma^E + \sigma^V$:

$$\sigma^E = n\xi_{\perp} \left\langle \left[\hat{R} \times (\vec{k} \cdot \hat{R}) - \vec{\Omega} \right] \cdot \hat{R} \times (\vec{k} \cdot \hat{R}) \right\rangle \quad (20)$$

$$\sigma^V = n\xi_{\parallel} \left\langle (\hat{R} \cdot (\vec{k} \cdot \hat{R}))^2 \right\rangle. \quad (21)$$

Therefore, for an elongational flow and a magnetic field applied along the x -direction we obtain

$$\sigma^E = 3n\beta \left[k_B T \langle (3R_x^2 - 1) \rangle - m_0 H_0 \langle R_x (1 - R_x^2) \rangle \right] \quad (22)$$

$$\sigma^V = n\beta^2 \xi_{\parallel} \langle (3R_x^2 - 1)^2 \rangle \quad (23)$$

where the averages involved can be computed from the probability distribution of R_x [12, 13]:

$$P(R_x) \propto \exp \left(\frac{m_0 H_0}{K_B T} R_x + \frac{\beta \xi_r}{K_B T} (3R_x^2 - 1) \right). \quad (24)$$

From previous equations then, we can easily obtain the elongational viscosity. This and other types of viscosity have been computed in reference [13] following a different approach. They have been found to depend also on the magnetic field and the aspect ratio of the particles. Notice that here the dependence on the form of the particles enters through the explicit values of ξ_{\perp} and ξ_{\parallel} .

4. Rheology in the non-linear regime

When the magnetic moment of the particle is not necessarily rigidly attached, it is oriented along an intermediate direction between those of the magnetic field and the easy axis of magnetization. The two relaxation mechanisms can be identified through the energy of the particles, which for uniaxial crystals reads

$$U = -\vec{m} \cdot \vec{H} - K_a V_p (\hat{n} \cdot \hat{R})^2 \quad (25)$$

where K_a is an effective constant incorporating contributions from crystalline and shape anisotropies, V_p is the volume of one of these spheres, and \hat{n} is the unit vector along the direction of the easy axis of magnetization. The expression for the energy includes the case of the rigid dipole, in which the vectors \hat{R} and \hat{n} are parallel, and the case of soft dipoles in sufficiently high magnetic fields, in which the magnetic moment orients itself in the direction of the field very quickly, then the particle rotates towards the stationary orientation where \hat{R} and \hat{n} are parallel. In this case the energy of the particle reduces to the energy of the anisotropy.

The dynamics of the magnetic moment is governed by the Landau–Gilbert equation. When the ferromagnetic particle is rotating with angular velocity $\vec{\Omega}$, it is expressed as

$$\frac{d\hat{R}}{dt} = -h\hat{R} \times \frac{\partial U}{\partial \hat{R}} \times \hat{R} + (\vec{\omega}_L + \vec{\Omega}) \times \hat{R}. \quad (26)$$

Here, $\vec{\omega}_L = -g\partial U/\partial \hat{R}$ is the Larmor frequency and h and g are constants. Additionally, the orientation of the easy axis of magnetization, \hat{n} , evolves according to the rigid-rotor equation (equation (1)) whereas the angular velocity follows from the balance of torques (equation (2)).

The dynamics of the particle has been solved analytically for the case of low vorticity and magnetic field [14], belonging to the validity domain of linear response theory. In this sense the rotational viscosity can be computed through a Green–Kubo formula [15] and, as in the case of the rigid dipole, exhibits a monotonic behaviour when represented as a function of the field. Additionally, from that formalism one can compute the time for relaxation of the

magnetic moment towards the field for different substances [15] arriving at good agreement with birefringence experiments [16].

The non-linear dynamics described by equations (25), (26), and the non-rigid dipole counterpart of equations (1) and (2) reveals the existence of a rich phenomenology. As discussed previously, in the linear regime deviations from the monotonic behaviour of the rotational viscosity have only been found for time-dependent magnetic fields. In the case of constant magnetic field the viscosity always increases with the field, reaching a saturation limit [17, 18]. In the non-linear domain the orientation of the particle may explore states which otherwise would not be accessible, opening the possibility for the appearance of dynamical transitions among different states. Upon increase of the vorticity the system passes from a state in which the particle behaves essentially as a rigid dipole to another in which the orientation of the particle relaxes towards the magnetic moment which in turns undergoes an oscillatory motion around the imposed field. The macroscopic implications of this dynamics is important and manifests itself in the rotational viscosity. Anomalous behaviour of this coefficient has been found even at constant magnetic field [9]. In the first state the viscosity increases with the field as usual, but in the second it decreases. During this dynamical transition the system can exhibit hysteresis.

5. Rheology in the moderately concentrated phase

When the concentration of particles increases, dipolar interactions become important and an aggregation process takes place. To avoid this process the magnetic particles are coated with a surfactant which introduces a steric repulsion. In the regime of low concentrations the interactions balance each other out and the suspension is stable. Beyond that regime, particles aggregate; the system then loses its original nature, evolving towards more stable configurations. This process is in the most general situation a dynamical process in which the structures may change over time by growth or fragmentation of some parts and may in general be controlled by noise, the presence of an external field (constant or time dependent), and the action of an imposed velocity field. When the individual particles assemble into chains, the length has been found to depend on time through a scaling law whose predicted dynamic exponent agrees with experimental results. In the absence of field, dipolar particles self-organize hierarchically and fractal structures are formed. Their shapes depend on the competition of dipolar forces and thermal agitation and can be characterized by means of the fractal dimension of the aggregates. The probabilities of growth, P_g , and splitting, P_s , of the structure are related through [19]

$$\frac{P_g}{P_s} \sim e^{1/T_r} \quad (27)$$

where T_r is a reduced temperature comparing thermal and dipolar energies. This expression may intuitively account for the appearance of different structures. In the limit $T_r \rightarrow 0$, since $P_s \sim 0$, chains are the most likely structure. In the opposite limit, $P_s \sim P_g$, spherical aggregates are formed. The fractal dimension of the aggregates ranges from 1.1, at low temperatures, to 1.7 which corresponds to the limit of pure diffusion-limited aggregation, occurring at high temperatures. Consequently, the condition of clusters being mutually opaque: $D_1 + D_2 > 2$, where D_1 and D_2 are the fractal dimensions of two interacting clusters, holds and they may behave in solution as spheres with an effective radius. The appearance of fractal structures predicted in two dimensions [19] has been corroborated by experiments on aggregation of magnetic particles in Langmuir monolayers [20].

The analysis of the rheological properties at higher concentrations constitutes an open problem which needs the implementation of new theoretical approaches. In the regime in which particles self-organize forming chains, kinetic models have been proposed in which the length of the chains may vary over time due to growth and fragmentation processes. The dynamics of the orientation of the chain is in essence that of a non-linear oscillator. As an example, for a chain of induced dipoles rotating under the influence of both field and shear flow, the angle of the chain with the direction of the field evolves according to [21]

$$\dot{\theta} + \omega_0 \sin(2\theta) = \dot{\gamma} \cos^2 \theta \quad (28)$$

where ω_0 is a characteristic frequency and $\dot{\gamma}$ the shear rate. The dynamics of other elongated structures can be formulated in a similar way [22]. These models have predicted the behaviour of the viscosity as a function of the shear rate in particular situations when the field is constant. The rheology is very sensitive to the form of the underlying structure which tacitly implies that its characterization must be very precise. The case of a time-dependent field is more complex, and new non-linear rheological behaviours have been observed [23]. Modelling at higher concentration, for which chains interact and branched structures are formed, constitutes a challenge for future developments.

The methods proposed based upon Fokker–Planck dynamics, dealing essentially with single particles, could in principle be generalized by considering the presence of dipolar interactions among particles as a new ingredient. There are only a few results in this context. Extension of the Fokker–Planck dynamics, developed for the case of single particles, to the case of dipolar interactions has been carried out to analyse the dynamics of a moderately concentrated suspension of ferromagnetic particles [24]. Fokker–Planck dynamics has also been treated perturbatively to calculate the viscosity of a suspension of chains of ferromagnetic particles in an elongational flow [25]. As we have seen previously, rheological properties depend on the dynamics of the emergent structures and therefore the knowledge of those properties is highly limited when the dynamics of the different entities integrating into the solid phase is unknown.

6. Discussion

Throughout this paper, we have discussed rheological properties of field-responsive fluids. The main characteristics of these systems, as regards the dynamics, are that it is assisted by the external field and it is influenced by dipolar interactions, which are the dominant ones. The single-particle regime is much more complex than in the case of neutral colloids and therefore its study has intrinsic interest. The dynamics of a single particle is in general non-linear and its description requires the knowledge of the evolution of two vectors: the magnetic moment and the orientation of the particle, whose dynamics are coupled. The linear domain is well known and can be analysed using continuum theories or linear response theory; the classical results for the viscosity as a function of the field have been obtained in this situation. The non-linear dynamics has not been explored in depth and deserves more attention. The analysis of some particular situations belonging to that domain makes evident the presence of new phenomenology, sometimes counterintuitive. The many-particle domain has as a main feature the formation of structures—mainly chains or branched structures—which may in general evolve over time. Information about rheological properties at moderate concentrations when chains are the emergent structures can be obtained from kinetic models. In the more concentrated regime in which the very notion of a chain breaks down, new approaches have to be implemented.

The methodology used to analyse the dynamics of these systems is quite similar to that

used in the study of other soft-condensed-matter systems. At the phenomenological level, continuum theories may provide information on the dilute regime. Scaling laws can be proposed for example to analyse the length of chains or the form of fractal aggregates. Fokker–Planck dynamics always provides a useful framework for analysing dynamical properties, for example the viscosity. This method has limitations when the system is complex, which is the case that we are concerned with. Even in the linear regime one obtains hierarchies of equations for the moments, which may provide information after decouplings. When dipolar interactions are considered, the Fokker–Planck dynamics can only be solved perturbatively for particular situations. Contrasting with the case for this methodology, in the formalism that we have proposed the viscosity is given in terms of the angular velocity of the particle, which in turn may easily be computed via simulations. This procedure may provide a useful framework within which rheological properties of these systems could be analysed. Numerical simulations on mesoscopic and macroscopic scales [26,27] constitute an increasingly valuable adjunct to theoretical and experimental studies.

In this paper we have dealt mainly with ferrofluids, a class of field-responsive systems in which the particles are single-domain magnetic particles with permanent dipole moments. The methods that we have proposed and the problems that we have outlined also hold or have a counterpart in the case in which the particle bears induced dipoles, as occurs in electro- and magneto-rheological fluids or even in suspensions of latex particles in a ferrofluid—the so-called magnetic holes whose non-linear dynamics has been analysed for assemblies of dimers [28].

Acknowledgments

We wish to acknowledge R Pastor-Satorras, M C Miguel, and A Pérez-Madrid for useful discussions. This work was supported by the DGES of the Spanish Government under grant PB95-0881 and by the INCO-COPERNICUS programme of the European Commission under contract IC15-CT96-0719. JMGV acknowledges financial support from the Ministerio de Educación y Cultura (Spain).

References

- [1] Phule P P and Ginder J M 1998 *MRS Bull.* **23** 19
- [2] Rosenweig R E 1985 *Ferrohydrodynamics* (Cambridge: Cambridge University Press)
- [3] Gast A P and Zukoski C F 1989 *Adv. Colloid Interface Sci.* **30** 153
- [4] Odenbach S 1993 *Adv. Colloid Interface Sci.* **46** 263
- [5] Blums E, Cebers A and Maiorov M 1997 *Magnetic Fluids* (Berlin: de Gruyter)
- [6] Gazeau F, Baravian C, Bacri J C, Perzynsky R and Shliomis M I 1997 *Phys. Rev. E* **56** 614
- [7] Rosenweig R E 1996 *Science* **271** 614
- [8] Pérez-Madrid A, Alarcon T, Vilar J M G and Rubí J M 2000 *Physica A* at press
- [9] Saiz L, Vilar J M G and Rubí J M 1999 *Preprint*
- [10] Pastor-Satorras R and Rubí J M 1998 *Phys. Rev. Lett.* **80** 5373
- [11] de Groot S R and Mazur P 1984 *Non-Equilibrium Thermodynamics* (New York: Dover)
- [12] Doi M and Edwards S F 1988 *The Theory of Polymer Dynamics* (New York: Oxford University Press)
- [13] Salueña C, Pérez-Madrid A and Rubí J M 1994 *J. Colloid Interface Sci.* **164** 269
- [14] Shliomis M I and Stepanov V I 1993 *J. Magn. Magn. Mater.* **122** 196
- [15] Miguel M C and Rubí J M 1995 *Phys. Rev. E* **51** 2190
- [16] Bacri J C, Djerfi K, Neveon S and Perzynsky R 1993 *J. Magn. Magn. Mater* **123** 67
- [17] MacTague J P 1969 *J. Chem. Phys.* **51** 133
- [18] Shliomis M I 1972 *Sov. Phys.—JETP* **34** 1291
- [19] Pastor-Satorras R and Rubí J M 1995 *Phys. Rev. E* **51** 5994
- [20] Lefebure S *et al* 1998 *J. Phys. Chem. B* **102** 2733

- [21] Martin J E and Odinek J 1995 *Phys. Rev. Lett.* **75** 2827
- [22] Halsey T C, Martin J E and Adolf D 1992 *Phys. Rev. Lett.* **68** 1519
- [23] Negita K and Ohsawa Y 1995 *Phys. Rev. E* **52** 1934
- [24] Zubarev A Yu 1998 *Sov. Phys.-JETP* **87** 484
- [25] Miguel M C and Rubí J M 1999 *J. Chem. Phys.* **110** 6007
- [26] Bossis G, Grasselli Y, Lemaire E, Meunier A, Brady J F and Phung T 1993 *Phys. Scr. T* **49** 89
- [27] Hess S, Aust C, Bennett L, Kröger M, Pereira Borgmeyer C and Weider T 1997 *Physica A* **240** 126
- [28] Helgensen G, Pieranski P and Skjeltorp A T 1990 *Phys. Rev. Lett.* **64** 1425