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Anisotropy of field-controlled shear viscosity of dipolar fluids

To cite this article: Christopher D Fjeldstad *et al* *J. Stat. Mech.* (2023) 123204

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Anisotropy of field-controlled shear viscosity of dipolar fluids

Christopher D Fjeldstad^{1,*}, Faezeh Pousaneh¹,
Roberto E Troncoso^{1,*} and Astrid S de Wijn^{1,2,*}

¹ Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

² PoreLab, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

E-mail: christopher.fjeldstad@ntnu.no, r.troncoso@ntnu.no and astrid.dewijn@ntnu.no

Received 14 July 2023

Accepted for publication 10 October 2023

Published 11 December 2023



Online at stacks.iop.org/JSTAT/2023/123204
<https://doi.org/10.1088/1742-5468/ad06a4>

Abstract. We numerically study the anisotropic viscous response of dipolar hard spheres in the presence of an electric field. We find that the shear viscosity is sensitive to both the strength and orientation of the field relative to the shearing direction. The effect on the viscosity is strongest when the field is oriented in the shear gradient direction. We investigate the structure of the fluid in detail to explain the mechanism for the changes in viscosity, and show that the reorientation of chain-like clusters plays a crucial role. We show that the anisotropy arises from the polarization of the fluid induced by the field, leading to the orientation of chain-like clusters along the direction of the field.

Keywords: molecular dynamics, transport properties, cluster aggregation

*Authors to whom any correspondence should be addressed.



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Contents

1. Introduction	2
2. Physical model	3
3. Analytical foundation	4
4. Simulation setup	5
5. Results and discussion	7
5.1. Thermodynamic equilibrium and Newtonian regime	7
5.2. Field-controlled viscosity	8
5.3. Fluid structure	11
6. Discussion	17
7. Conclusion	18
Acknowledgments	19
References	19

1. Introduction

Viscosity, a fundamental transport property of fluids, has captured the attention for centuries [1] in science and engineering. It plays a crucial role in the flow of water and air, as well as in biological systems such as blood and synovial fluids. It is also the most important parameter in many engineering applications involving fluids, such as pipe flow and lubrication [2]. Despite long efforts [3], current understanding of viscosity, especially in dense (i.e. liquids) and highly-interacting fluids, is far from complete.

Polar fluids are gaining popularity as lubricants, for instance in water-based environmentally friendly lubricants. Yet, the viscosity of polar fluids is even more challenging to understand. The long range electrostatic interactions are qualitatively different from short-range interactions that are often approximated as (nearly) hard spheres (HS). Nevertheless, analytical results have been obtained for viscosity of such fluids [4, 5]. Despite the theoretical challenges, polar fluids have a lot of potential applications due to their rich chemistry. Geometry and interactions can be tuned to engineer specific desired behaviour. This also provides an interesting tool for gaining basic understanding, allowing us to probe specific mechanisms.

A particularly intriguing tunable aspect of polar fluids is the possibility of manipulating them externally with an electric (or magnetic) field. External fields break rotational symmetry, leading to a potentially anisotropic response, and can also have a significant impact on the magnitude of the response. This electro-viscous effect allows us to probe the electrostatic interactions and their effect on viscosity. The impact of an external field

on viscosity has been investigated experimentally for a variety of systems, and a wide variety of mechanisms have been identified. Some early work [6] for example showed quite strong effects for some compounds, like acetonitrile, which were subsequently [7, 8] linked to injection of charges into the system that are surrounded by large clusters of bound-together polar molecules. It has also been shown that external fields can induce flow directly in some liquids that contain charged particles [7, 8]. Nevertheless, even without charges in the system, the viscosity of a polar fluid can be affected by an external field. Simulations of water [9], for example, have shown that field-induced restructuring of hydrogen bond can have an impact on the viscosity of water.

The electroviscous effect, and its magnetic equivalent, the magnetoviscous effect, are particularly often studied in suspensions. In such systems, due to the additional complexity, many more mechanisms come into play [10], such as fibrillation and field-induced alignment of particles [11]. Simulations of ferro fluids, magnetic colloidal systems, in external magnetic fields show that the field can not only affect the orientation of clusters, but also lead to the creation of larger clusters [12–16].

In this work, we study the effect of an external electric field on the viscosity of dipolar HS (DHS) using molecular dynamics (MD) simulations. These relatively simple interactions are computationally less expensive than more realistic systems, while also allowing us to isolate some of the geometry-related mechanisms at play in real systems. In sections 3 and 4 we describe the theoretical foundation for this work and the simulation setup and parameter choices. The shear viscosity results are presented in section 5.2 and an in depth study of the fluid structure is presented in section 5.3. Further discussion of the mechanisms and conclusions are presented in sections 6 and 7.

2. Physical model

We consider a system of N identical HS particles with diameter σ , each carrying an electric dipole moment of magnitude μ . They are at temperature T and confined to a volume V with volume fraction $\xi = \frac{\pi}{6} \frac{N}{V} \sigma^3$, with number density $\rho = \frac{N}{V}$. In addition, a constant external electric field $\vec{E}$ of magnitude E is applied. The total potential energy U_{pot} can be separated into the particle–particle contribution U_{DHS} and particle–field contribution U_{E} , i.e. $U_{\text{pot}} = U_{\text{DHS}} + U_{\text{E}}$. The particle–particle term can then be separated into HS and dipole contribution,

$$U_{\text{DHS}} = \sum_{i>j}^N (u_{ij}^{\text{HS}} + u_{ij}^{\text{D}}) , \quad (1)$$

with U_{ij}^{HS} the HS contribution from particles i and j and U_{ij}^{D} the dipole–dipole contribution. We denote the distance between two particles i and j by r_{ij} . The HS and dipole–dipole interactions are then given by

$$u_{ij}^{\text{HS}} = \begin{cases} \infty, & r_{ij} < \sigma \\ 0, & r_{ij} > \sigma \end{cases} , \quad (2)$$

and

$$u_{ij}^D = \left[\frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r_{ij}^3} - \frac{3(\vec{\mu}_i \cdot \vec{r}_{ij})(\vec{\mu}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right], \quad (3)$$

respectively, where $\vec{\mu}_i$ is the dipole moment of particle i . The dipole-field interaction is given by

$$u_i^E = -\vec{\mu}_i \cdot \vec{E}, \quad (4)$$

so that

$$U_E = \sum_{i=1}^N -\vec{\mu}_i \cdot \vec{E}. \quad (5)$$

We define the dimensionless coupling constant λ and field parameter α based on the dipole strength, μ , and field strength, E , as

$$\lambda = \frac{\mu^2}{k_B T 4\pi\epsilon_0 \sigma^3}, \quad (6)$$

and

$$\alpha = \frac{\mu E}{k_B T}. \quad (7)$$

3. Analytical foundation

As a starting point, we now briefly introduce the theoretical background of viscosity of HS and HS with point dipoles without external fields.

Theoretical descriptions for the viscosity of complex fluids begin with Enskog's theory for simple dense fluids. Enskog derived expressions for transport coefficients of dense fluids of HS, including one for the viscosity,

$$\eta_{\text{Enskog}} = \eta_0 \left[g(\sigma)^{-1} + 0.8V_{\text{excl}}\rho + 0.776V_{\text{excl}}^2\rho^2 g(\sigma) \right], \quad (8)$$

where $V_{\text{excl}} = (2/3)\pi\sigma^3$ is the excluded volume around a particle. The zero density limit η_0 is given as

$$\eta_0 = \frac{5}{16\sigma^2\Omega^{*(2,2)}} \sqrt{\frac{mk_B T}{\pi}}, \quad (9)$$

where $\Omega^{*(2,2)}$ is the collision integral and k_B the Boltzmann constant. For HS, $\Omega^{*(2,2)} = 1$. For other interaction potentials, $\Omega^{*(2,2)}$ generally deviates from unity. The radial distribution function (RDF) at contact, $g(\sigma)$, is reflective of the collision rate between individual particles in the fluid. For HS, $g(\sigma)$ is often estimated using the expression derived from the Carnahan–Starling (CS) equation of state,

$$g_{\text{HS}}(\sigma) = \frac{1 - 0.5\xi}{(1 - \xi)^3}. \quad (10)$$

At higher densities, the CS expression underestimates $g(\sigma)$ for HS systems.

For DHS systems Pousaneh and de Wijn [5] proposed a method to predict the viscosity by starting from the HS approximation of equation (8), and then estimating $g(\sigma)$ for DHS from the free energy using the logarithmic free energy (LFE) theory of Elfimova *et al* [17] by making use of the relation

$$\frac{pV}{Nk_B T} = 1 + \frac{\langle U_{\text{pot}} \rangle}{Nk_B T} + \frac{2\pi\rho\sigma^3}{3}g(\sigma), \quad (11)$$

with p the pressure. In LFE-theory, the Helmholtz free energy, F , is expressed as

$$F = F^{\text{HS}} + F^{\text{D}}, \quad (12)$$

with

$$\frac{\beta F^{\text{D}}}{N} = -\log \left[1 + \sum_{n=1}^{\infty} n^{-1} I_n \xi^n \right], \quad (13)$$

and the coefficients I_n are derived from the virial coefficients for the DHS fluid using a Maclaurin Series. The compressibility can then be written as

$$\begin{aligned} Z = \frac{pV}{Nk_B T} &= Z^{\text{HS}} - \frac{\sum_{n=1}^{\infty} I_n \xi^n}{1 + \sum_{n=1}^{\infty} n^{-1} I_n \xi^n} \\ &= Z^{\text{HS}} - \frac{I_1 \xi + I_2 \xi^2 + I_3 \xi^3 + I_4 \xi^4}{1 + I_1 \xi + \frac{1}{2} I_2 \xi^2 + \frac{1}{3} I_3 \xi^3 + \frac{1}{4} I_4 \xi^4} \end{aligned} \quad (14)$$

and the potential energy as

$$\begin{aligned} U_{\text{pot}} &= -\frac{\sum_{n=1}^{\infty} J_n \xi^n}{1 + \sum_{n=1}^{\infty} n^{-1} J_n \xi^n} \\ &= -\frac{J_1 \xi + J_2 \xi^2 + J_3 \xi^3 + J_4 \xi^4}{1 + J_1 \xi + \frac{1}{2} J_2 \xi^2 + \frac{1}{3} J_3 \xi^3 + \frac{1}{4} J_4 \xi^4}, \end{aligned} \quad (15)$$

where $J_n = (\lambda/n)(\partial I_n / \partial \lambda)$ [5]. The RDF at contact for DHS from the equations above compares well to results of numerical simulations [5]. In addition, it can be used in combination with equation (8) to obtain a better prediction for the viscosity than a purely HS model [5].

4. Simulation setup

We simulate the system with MD performed in LAMMPS [19]. We express all quantities in dimensionless LJ-units. Because LAMMPS, as other large MD codes, is made for continuous interactions, we approximate the HS-potential using a steep cut-and-shifted Mie potential introduced by Jover *et al* [20],

$$u_{ij}^{\text{PHS}} = \begin{cases} 50 \left(\frac{50}{49} \right)^{49} \epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{50} - \left(\frac{\sigma}{r_{ij}} \right)^{49} \right] + \epsilon, & r > \frac{50}{49} \sigma, \\ 0, & r \leq \frac{50}{49} \sigma \end{cases}, \quad (16)$$

where the parameters ϵ and σ reflect the interaction energy and particle size respectively. At a reduced temperature $T^* = k_B T / \epsilon = 1.5$ in MD simulations this pseudo HS potential reproduces the theoretically predicted shear viscosity of HS fluids [21]. It has also been shown that it describes the HS component of DHS fluids [5] in simulations of viscosity.

The long range dipole–dipole interaction potential is used as given in equation (3). In order to efficiently calculate these interactions, we used the Ewald summation [22] as implemented in the KSPACE style package of LAMMPS for a particle–particle particle mesh dipole solver (pppm/dipole) [23]. The dipole cutoff is 2.6σ and the Ewald accuracy used to determine mesh size is 10^{-3} .

In what follows, we use reduced Lennard–Jones units to express physical quantities. The fundamental quantities mass, (m), σ and ϵ in addition to k_B are all set equal to 1. Reduced units are denoted as follow: mass, $M^* = M/m$, distance, $r^* = r/\sigma$, time, $\tau^* = \tau(\epsilon/m\sigma^2)^{1/2}$, number density, $\rho^* = \rho\sigma^3$, volume fraction $\xi^* = \pi\rho^*/6$, dipole moment, $\mu^* = \mu/(4\pi\epsilon_0\sigma^3\epsilon)^{1/2}$ and viscosity, $\eta^* = \eta\sigma^3/(\epsilon\tau)$.

The viscosity was obtained using non-equilibrium simulations with the method developed by Müller–Plathe [18]. This method relies on creating a shear rate without inserting energy by the non-physical transfer of momentum using particle swapping. This induces a velocity gradient, $\partial v_x / \partial z$, through the fluid as shown in figure 1 and causes a flux of momentum, j_z , along the swapping direction. This momentum flux is related to the shear viscosity of the system through $j_z = -\eta \partial v_x / \partial z$.

The simulation box was divided into 100 chunks. The swaps were made every 500 time steps or a swap rate of 0.002 swaps per time step. The simulation box is rectangular and oriented so that x and y span the box base and z spans the height, as shown in figure 1. It has periodic boundary conditions in all direction. Particles are exchanged along z and carry momentum in the x direction. The external electric field is applied along one of the three main axes, x , y , or z . Since the applied field breaks the rotational symmetry, it leads to an anisotropic viscosity tensor. The three most relevant components of the viscosity tensor are investigated by considering the three different directions of the field compared to the velocity gradient tensor.

A shear rate is induced by the momentum flux, which is controlled by the momentum swapping rate. However, because we control the momentum flux and not the shear rate, it is sensitive to the viscosity, and therefore to the choice of interaction parameters, density, and field orientation. We therefore do not have a constant shear rate across all data points. Instead, we have picked a swapping rate that produces a reasonably Newtonian response across a wide set of parameter choices while balancing between convergence and computing time. However, because of limitations in computing time, a small degree of non-Newtonian behaviour is unavoidable. Any potential non-Newtonian effects are investigated in section 5.2.

The system was simulated in the canonical ensemble (NVT) and with a time step $\delta\tau^* = 0.0011$. This time step was chosen in order to match the simulations of DHS systems in [5]. The system was equilibrated using the Nose/Hoover thermostat with a dimensionless relaxation time $T_{\text{damp}}^* = 100\delta\tau^* = 0.11$. Because this thermostat does not work well with the Müller–Plathe method, the thermostat is switched to canonically sampled velocity re-scaling [24] with a relaxation time $T_{\text{damp}}^* = 10000\delta\tau^* = 11$. This thermostat has a minimal impact on the dynamics, as it does not change the direction

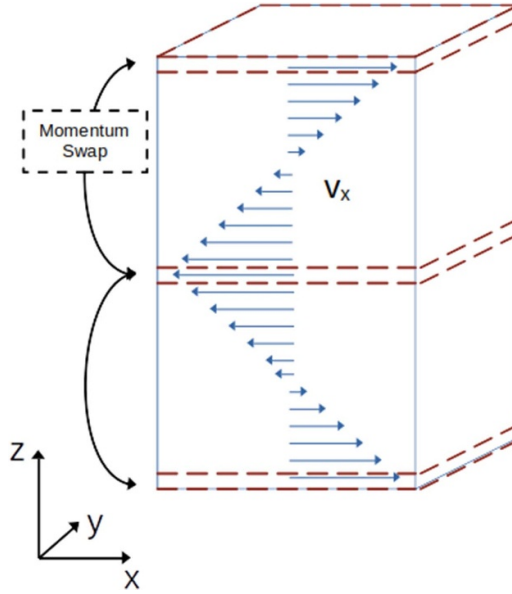


Figure 1. The geometry of the simulation box, along with a diagram of the setup for calculating the fluid viscosity using the method proposed by Müller-Plathe [18]. The simulation box is 3 times larger in the z -direction, which is the direction of the gradient, than in the other two directions. The box is divided into chunks, and particles are swapped between the outer and middle chunks. The swapping results in a transfer of momentum which leads to a velocity gradient. The viscosity is determined using $j_z = -\eta \partial v_x / \partial z$.

of the ballistic motion, and its effects are small as long as the total kinetic energy does not fluctuate much. We have also confirmed that it does not impact the Müller-Plathe algorithm for PHS by comparing to Enskog's expression for HS. Other thermostats, such as Langevin, affect the dynamics more drastically, and lead to systematic errors.

Other important simulation parameters include particle count $N = 1000$. Finally, the system was equilibrated for $t^* = 4000$. After equilibration, the Müller-Plathe swapping is initiated and is run for $t^* = 4000$. The steady state is reached quickly and the resulting velocity profile is used to determine the viscosity of the system. We investigated volume fractions in the range $\xi \in \{0.1 - 0.4\}$.

5. Results and discussion

5.1. Thermodynamic equilibrium and Newtonian regime

We start out by ensuring that our system is properly equilibrated, and that we are in the Newtonian regime. We begin by studying the compressibility and compare it to the predictions of LFE theory. Figure 2 shows the compressibility, $Z = pV/Nk_B T$, as a function of density ξ . The figure shows that both an increase in the dipole interactions and an increase in the field strength have an impact on the fluid compressibility. In general, stronger interactions cause the system to deviate from HS-behaviour, as expected. LFE

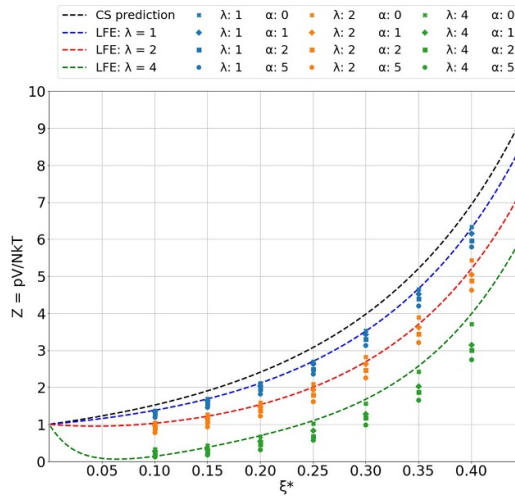


Figure 2. The compressibility, $Z = pV/Nk_B T$. Both the dipole interaction strength and the field strength cause the system to deviate from HS behaviour. The reasonable correspondence between the simulations and LFE theory suggests that the system is well equilibrated and behaving as intended.

theory works out describing the general behaviour of the equilibrated system. However, for the strongest interactions, $\lambda = 4$, the numerical results start deviating from theory. This is in accordance with expectations based on the expansion used to derive LFE theory [5]. We also see that an increase in field strength causes the system to deviate from LFE theory. This is expected because the field causes slight changes in the system structure. The impact of the field on the structure is discussed in section 5.3. In general, the correspondence between the simulations and LFE theory in figure 2 suggests that the system is well equilibrated and behaving as intended.

Once the system is equilibrated, momentum swapping is initiated as described in section 4. In order to investigate the choice of swapping rate and resulting shear rates, the viscosity as a function of shear rate is shown in figure 3 for some extreme cases. For clarity, the relevant points corresponding to our choice of swapping rate have been emphasized. The figure does not include simulation points with weaker interactions and low fields, because these systems tend to be more well behaved and Newtonian. We see from figure 3 that the emphasized points correspond to regions where the viscosity as a function of shear rate is reasonably constant, indicating Newtonian behaviour. However, there are a few important exceptions. For systems with the field aligned in the z -direction, the fluid behaves in a non-Newtonian manner. In addition, from figure 3(c), we see that as the density increases, the system in general becomes more non-Newtonian.

5.2. Field-controlled viscosity

We now investigate the impact of the field on the viscosity. Figures 4–6 show the viscosity as a function of the volume fraction. In panels 4(b), 5(b) and 6(b) the viscosity is normalized by the Enskog prediction for HS systems. The blue line represents the LFE theory prediction for DHS in zero external field. The theory uses two fitting parameters:

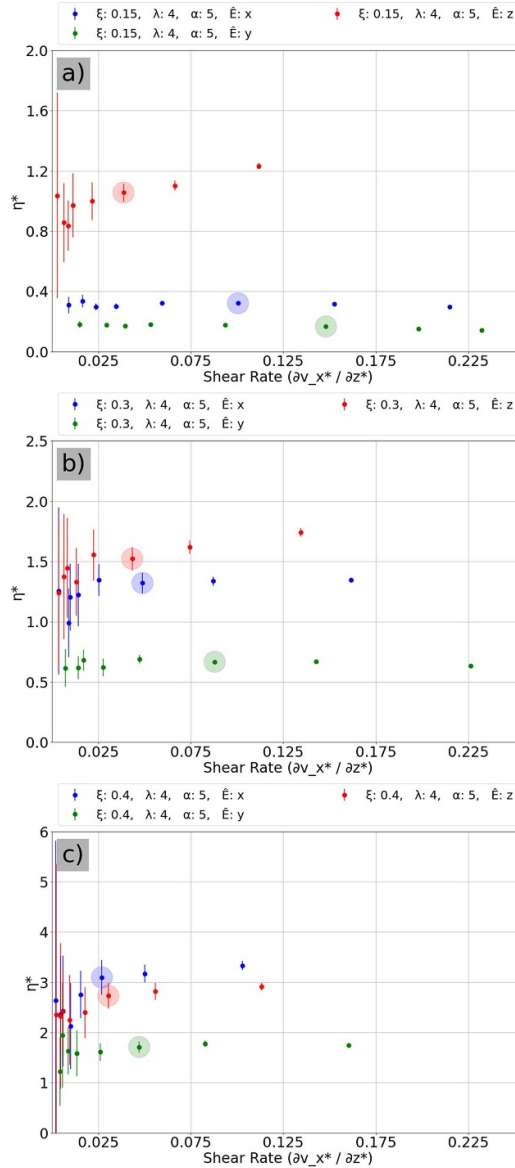


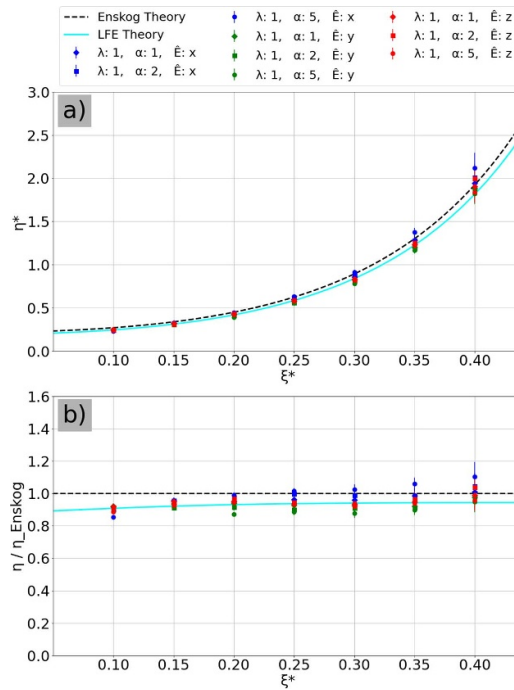
Figure 3. The reduced shear viscosity as a function of reduced shear rate. Panels (a)–(c) show the viscosity of strongly interacting dipoles for three different densities, 0.15, 0.3 and 0.4 respectively. The data points corresponding to the swapping rate chosen for the rest of our simulations have been highlighted.

λ and $\Omega^{*(2,2)}$. The theory is fit to DHS system with no field and $\xi^* \in \{0.1 - 0.3\}$. The values of the fit parameters can be found in table 1. The theory is fitted to the data and both are shown together in figure 7. The fit parameters deviate slightly from [5], which is likely because of finite size effects in our simulations as well as using a different fitting range for the density.

For small dipole coupling constant $\lambda = 1$, shown in figure 4, the interactions are on the order of the thermal energy in the system. Although the dipole–dipole interactions have some impact on the system, the field has little impact. There is little evidence

Table 1. The fitting parameters λ and $\Omega^{*(2,2)}$ for DHS in zero field using LFE theory. The theory was fit to the density range $\xi^* \in \{0.1 - 0.25\}$.

	λ_{eff}	$\Omega_{\text{eff}}^{*(2,2)}$
$\lambda = 1$	0.36	1.08
$\lambda = 2$	0.88	1.14
$\lambda = 4$	2.18	1.24

**Figure 4.** The case of relatively weak dipoles. (a) Reduced shear viscosity as a function of density and (b) the same normalized by the Enskog prediction for HS. The field does not have a large impact on the viscosity of the system.

of anisotropy in the system, at both high and low densities. Because the electric field in general has little impact, LFE theory describes the viscous behaviour for low to intermediate densities even when the field is strong. For $\lambda = 2$, the results are displayed in figure 5. In this case, the field is having an impact on the viscosity and the LFE theory no longer captures the full behaviour. In addition, the system has now started behaving anisotropically across the full density range. Although it is not a very strong effect this is more clear in panel (b).

The strong interacting regime, set by $\lambda = 4$, is shown in figure 6. The system is strongly dependent on both field strength and orientation and the viscosity is also very anisotropic, especially at lower densities. It is worth to note the qualitative difference in the behaviour for a field aligned in the z direction and in the x or y direction. When the field is aligned along the z direction, perpendicular to the shearing plane, the field strength has a considerable effect on the viscosity. However, when the field is aligned in

Anisotropy of field-controlled shear viscosity of dipolar fluids

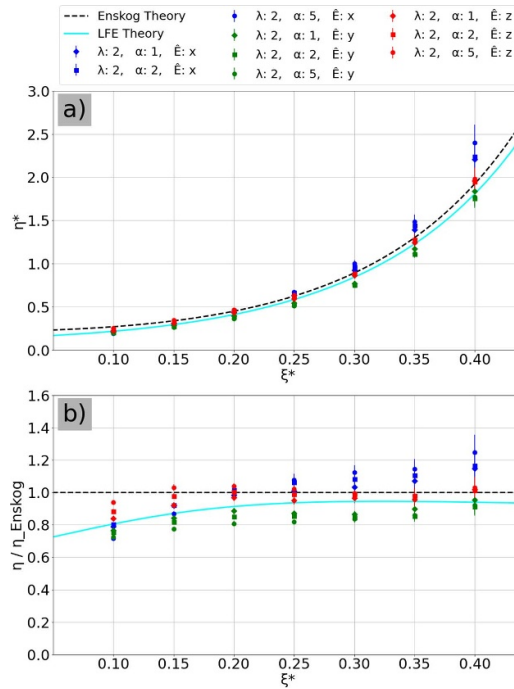


Figure 5. The case of intermediate-strength dipoles. (a) Reduced shear viscosity as a function of density and (b) the same normalized by the Enskog prediction for HS. The field causes the system to be weakly anisotropic across the entire density range.

either the x or y direction, the impact of the field is less relevant, although still present. For these fields, however, the viscosity still shows qualitatively very similar behaviour, even when compared to the case without a field. We discuss the mechanism of these differences between the different field directions in more detail in section 6. We also note that the field only has a significant impact when the dipoles are strong enough. This is obvious when comparing figures 4–6. The effect of a weak field with strong dipole-dipole interactions ($\lambda = 4$) is displayed in figure 8, where the anisotropy disappears as the field gets weaker and the system approaches the behaviour of a DHS system with zero external field.

5.3. Fluid structure

Clustering behaviour has been previously observed in a variety of dipolar fluids, including simulated DHS systems and colloidal fluids [5, 25–29] and in experiments on colloidal ferrofluids [12, 13, 30, 31]. If a strong enough field can impact the size, geometry, and orientation of the clusters in the fluid, this will impact the rate and geometry of collisions and therefore the rate of momentum transfer and the viscosity. In order to fully explain our results we will need to investigate these structures and how the field impacts them.

To investigate the fluid structure we begin by studying the RDF. The RDF is defined as the average distribution of particles, $g(r^*)$ around any given particle. As such, it

Anisotropy of field-controlled shear viscosity of dipolar fluids

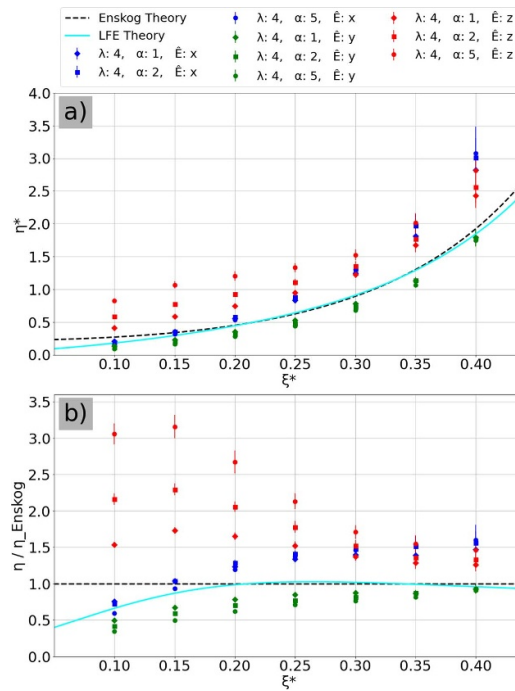


Figure 6. The case of strong dipoles. (a) Reduced shear viscosity as a function of density and (b) the same normalized by the Enskog prediction for HS. The field leads to a high degree of anisotropy at low densities, increasing the viscosity especially in the z direction. At higher densities this anisotropy is reduced.

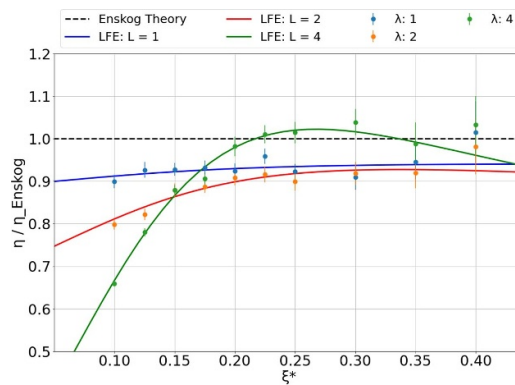


Figure 7. Normalized shear viscosity of DHS in zero field as a function of density. The shear viscosity is normalized by the Enskog prediction for HS. The coloured lines represent LFE prediction using the fitting parameters in table 1.

provides information about both the short range coordination as well as any larger structures that might be present. Figures 9(a)–(c) show $g(r^*)$ for systems with densities $\xi = 0.15, 0.3$ and 0.4 respectively and for a number of different combinations of interactions (λ) and fields (α).

The initial peak, as stated in section 3, is reflective of the collision rate between HS particles. $g(\sigma)$ is estimated as the maximum value of the RDF. For HS and other

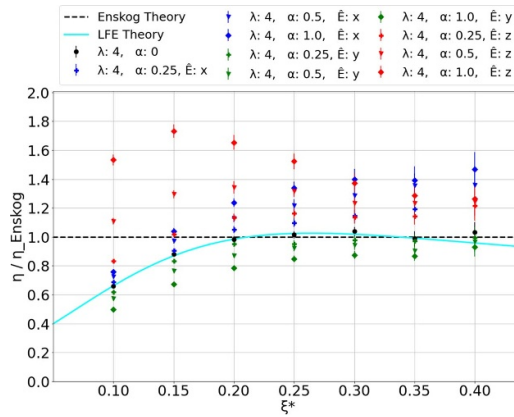


Figure 8. The case of strong dipoles in a weak field. (a) Reduced shear viscosity as a function of density and (b) the same normalized by the Enskog prediction for HS. As the field gets weaker, the anisotropy goes away and the behaviour approaches that of DHS in zero external field.

particles that do not cluster, $g(\sigma)$ approaches unity as the density decreases. If $g(\sigma)$ does not approach unity in the low-density limit, it means that particles are clustering. Figure 10 shows $g(\sigma)$ as a function of density. In addition we plot the LFE prediction according to equation (11).

From figure 10, we see that $g(\sigma)$ increases when the fluid interactions get stronger. Even for the weakest dipoles, $g(\sigma)$ does not approach unity as the density decreases. This is because the dipoles cause particles to cluster. This effect is exaggerated as the dipoles get stronger and is in accordance with LFE theory. The deviation between simulations and theory is similar to that found in [5].

The external field also affects $g(\sigma)$, which is due to the polarization of the fluid. Figure 11 shows the polarization of the system as a function of the density, determined as the average of the dipoles component along the field divided by the absolute strength of the dipole. As expected, the dipoles align in the field.

In figure 9(a) we clearly see that the system with the strongest dipoles, represented by the green line, has an RDF that distinctly deviates from unity for distances as large as $r^* = 3\sigma$. Fluids with weaker dipole–dipole interactions lack this long-range coordination. A similar trend is visible at intermediate densities in figure 9(b). Although some packing related coordination is now present, the strongest dipoles still produce an RDF that is distinctly different from the RDF for HS. The long-range coordination suggests that some of the clusters are larger in size. The small peak at 3σ in figures 9(a) and (b) indicates that clusters consisting of up to 4 particles are not uncommon. The lack of longer-range coordination in systems with weaker interactions indicates that any clustering happening in these systems is more limited.

Both figures 9 and 10 suggest that the structure of strongly interacting fluids is highly density dependent. There is a distinct difference in behaviour between low density systems and high density systems. At low density, the fluid structure is dominated by the clustering of particles. $g(\sigma)$ increases as the fluid becomes less dense. As the fluid gets denser, $g(\sigma)$ starts decreasing until it reaches a minimum at roughly $\xi = 0.3$. Above this

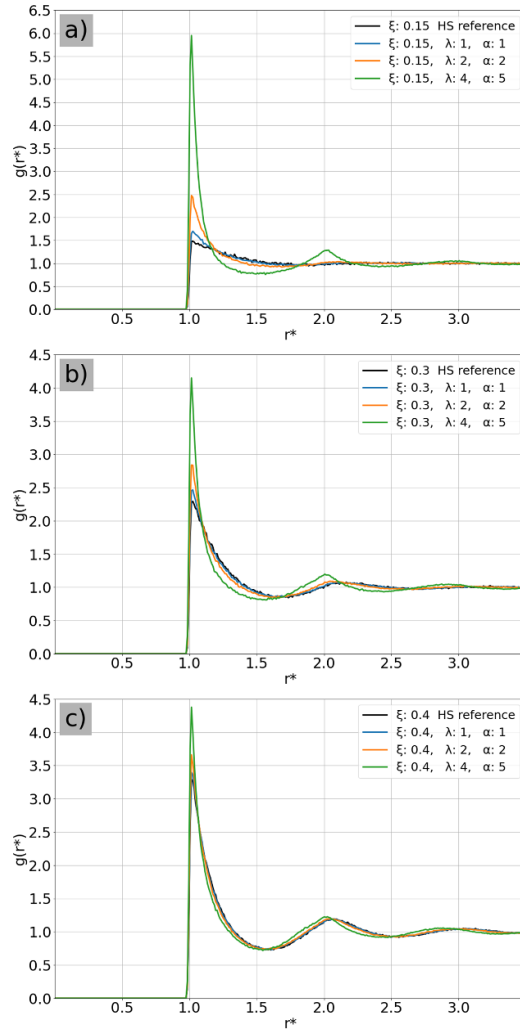


Figure 9. The RDF, $g(r^*)$ at three different densities. For strongly interacting fluids, $\lambda = 4$, $g(r^*)$ deviates significantly from that of HS, indicating larger clusters in the fluids. When the dipoles are weaker, the long range coordination is reduced and the fluids behave similarly to an HS fluid.

density, the fluid structure is no longer dominated by the clustering of dipoles. Instead, the coordination of particles arises from dense packing. This is why, in figures 9(b) and especially (c), we see the RDF for highly interacting fluids approach that of an HS fluid. A similar density dependence was noted by [5]. For more weakly interacting systems, the clusters are never prominent enough to dominate the fluid structure. For these fluids, packing considerations will be the main factor of density dependent coordination.

The size and geometry of clusters will have a substantial impact on the viscosity of the fluid. In order to investigate this impact further, we need a way to visualize them and quantify their size. We therefore need to define when two particles can be considered part of the same cluster. Essentially, this is the case when their dipole–dipole interaction has to be stronger than what would be expected from random interactions. We define

Anisotropy of field-controlled shear viscosity of dipolar fluids

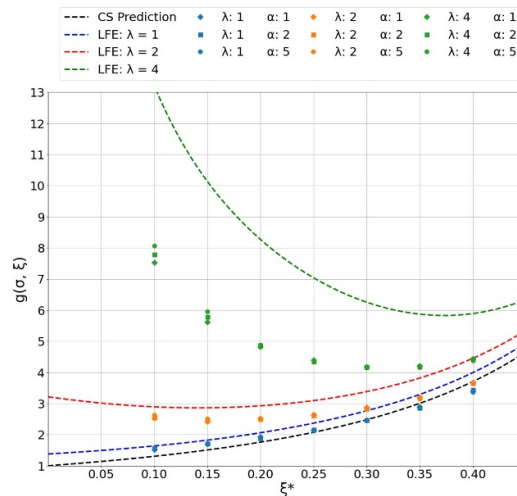


Figure 10. The RDF at contact, $g(\sigma)$. The dipole–dipole interactions have a large impact on $g(\sigma)$. In all cases, $g(\sigma)$ does not approach unity in the low density limit. This indicates clustering behaviour. For the largest dipoles, the clusters seem to dominate the fluid at low density. At higher density, $\xi > 0.3$, coordination is primarily related to packing considerations.

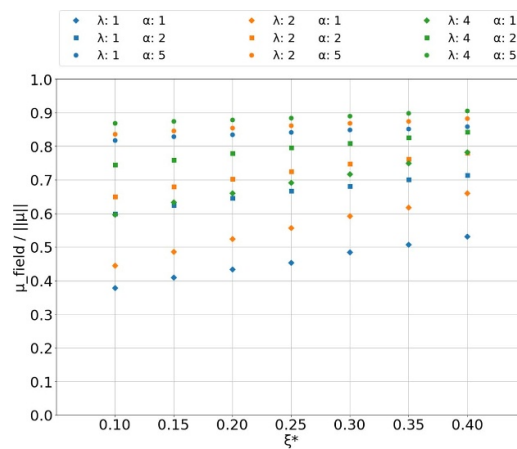


Figure 11. Polarization, $\mu_{\text{field}}/\|\vec{\mu}\|$. The polarization is strongly dependent on the field strength across all sets of interaction parameters. In addition the polarization is somewhat dependent on density.

two particles as having a cluster-like geometry if their interaction energy is more than the typical interaction energy μ^{*2} . In addition we eliminate the statistical background by comparing to a system without dipole interactions. To obtain this background, we use a system of pseudo HS in equilibrium, and assign randomly oriented dipoles to the particles. This eliminates the statistical bias at high densities, where the particles are always close together. Other possible choices of threshold, such as $k_B T$, produce similar results. However, comparing to μ^{*2} is more robust, as this ensures detection of clustering even at low interaction strengths, where at the closest approach the interaction energy

Anisotropy of field-controlled shear viscosity of dipolar fluids

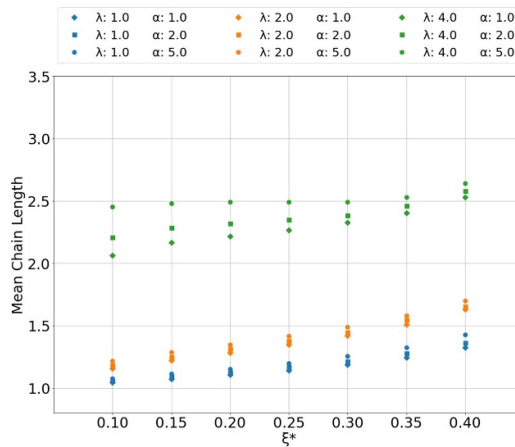


Figure 12. The mean cluster size depends on the dipole interaction strength, the field strength and the fluid density. At low to intermediate densities, the mean cluster size of the strongly interacting fluids is between 2 and 2.5. For weaker interactions, the clusters are much smaller.

is still low. We have also checked that adding prefactors in front of μ^{*2} does not qualitatively affect the results, as long as the energy of closest approach is still considered cluster-like.

In figure 12 the mean cluster size is plotted as a function of density, with the statistical background subtracted. Consistent with the RDF-data, we conclude that strong dipoles and fields lead to larger clusters. For the strongest interactions, these clusters have an average size between 2 and 2.5 particles. For weaker interactions, the clusters are much smaller. In the context of the RDFs plotted in figure 9(a) we understand this to mean that large clusters are rare. Instead, particles mostly exist either separately or in pairs. For all sets of interaction parameters, we see that the average cluster size increases as a function of density. We know from figure 11 that denser systems are more strongly polarized. As the dipoles get closer together, they tend to align with each other, thereby amplifying the effect of the field. This increased polarization means that particles are more likely to have a favourable cluster-like interaction.

Figure 13 shows a snapshot of the simulation box with the chains visualized in different colours, for $\xi = 0.15$, $\lambda = 4$ and $\alpha = 5$. The field is aligned in the z -direction, corresponding to the longest edge of the box. The region has periodic boundary conditions, so some of the clusters can be observed to cross these boundaries. In figures 13(c)–(e) we see only particles that are part of clusters of size 2, 3 and 4 respectively. We see the clusters are chain-like, i.e. they are stretched. In addition we observe that the chains are oriented along the direction of the field. This is consistent with the results shown in figure 11, i.e. that strong fields do in fact polarize the system. The dipoles of particles that have sufficient interaction energy to be considered clustered must be at least somewhat aligned. This means that any existing clusters generally orient in such a way that the particles mostly align with the field. This alignment gets stronger when the field is stronger. This alignment provides a mechanism by which the symmetry breaking imposed by the field causes an anisotropic viscous response. This anisotropy can only

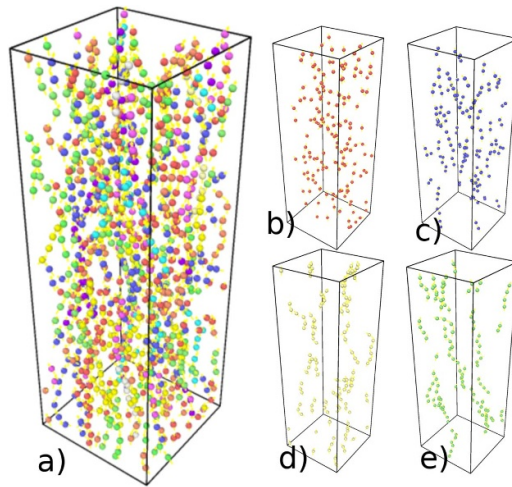


Figure 13. Visualizing the clusters in a low density, $\xi = 0.15$ fluid. Panel (a) shows all the particles in the system. Panels (b)–(e) only show particles belonging to clusters of size 1, 2, 3 and 4 respectively. The field is aligned in the vertical direction (z). Notice that the clusters seem to be aligning in the field.

arise when two requirements are fulfilled: (1) the dipole–dipole interactions are strong enough to produce larger chain-like clusters, and (2) the field is strong enough to align those clusters along the field direction.

6. Discussion

Having established that oriented chain-like clusters form in the DHS fluids in an external field, we now interpret the results from section 5.2 in light of this. We know from the results described in figure 6 in section 5.2 that the viscous behaviour depends strongly on the orientation of the chain-like clusters. Figure 14 is a cartoon showing the alignment of chains relative to the shearing direction and the field. Especially the case where the field, and thus the chains, point in the direction of the gradient (z), the viscosity exhibits substantially different behaviour than if the field (and therefore the chains) is in the plane perpendicular to the direction of the gradient. We therefore propose two different underlying mechanisms for the anisotropy. The viscous behaviour will depend on the dominating mechanism.

We first discuss the case of the field in the z direction. A collision at one end of a chain will transmit momentum through the chain to the other end. When the chains orient along the z -axis, momentum is thus transferred more efficiently along the gradient compared to randomly oriented chains. The viscosity is sensitive to the field strength because the momentum transfer is sensitive to the orientation of the chains.

The effect is the strongest at intermediate densities. At high densities, around $\xi > 0.3$, the system becomes less sensitive to the field strength. We suspect that this is related to the fact that particles are colliding more frequently. Above a certain density, momentum will take longer to transfer through the chains than the average inter particle collision

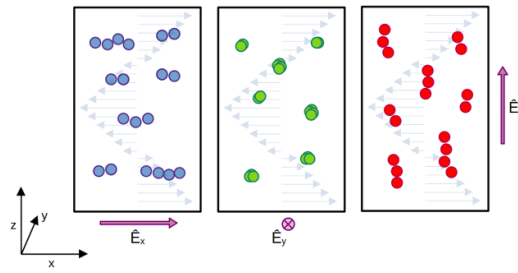


Figure 14. Cartoon illustrating how the chains are orienting in the fluid depending on field alignment.

time. In this regime, the chains do not act as a large effective particles that transmits momentum. The viscosity then becomes similar to that of dipoles without a field. At very low densities, the mean free path becomes longer than the chain length, and thus becomes the more dominant contribution to the distance over which momentum is moved, and the viscosity. This is also indicated in our simulations, where we see that the rescaled viscosity has a maximum around density 0.2.

When the chains align along the x - or y -axis, the collision integral and dynamics are still changed, but not as dramatically. However, there is no extra mechanism for efficient transfer of momentum along the gradient direction. We therefore observe a much more subtle, but consistent impact of the field strength on the anisotropy.

7. Conclusion

In this paper, we have investigated the viscous behaviour of DHS in an external electric field. We show that, depending on the dipole interaction strength, complex, anisotropic viscous behaviour, arises in even the simplest possible polar fluids, a HS with an embedded point dipole. We find that the shear viscosity is sensitive to both the strength and orientation of the field relative to the shearing direction. The effect on the viscosity is strongest when the field is oriented in the shear gradient direction.

We have investigated the mechanism by which the field affects the viscosity in detail. The field induced polarization of the fluid causes existing chain-like clusters to orient along the field direction. When the dipole–dipole interactions are weak, there is limited clustering of particles and consequently little anisotropy. For stronger dipoles, the clusters are larger and more chain-like. The chains orient in the direction of the field, triggering a strong anisotropic dependence of the shear viscosity on the field alignment. This effect is most extreme when the field is aligned along the gradient.

Similar structure-based mechanisms have been observed to mediate the effect of an external field on the viscosity in complex fluids. The authors of [9] performed simulations of water, finding a small change in the viscosity in an electric field, and found that the field is imposing a structural change to the hydrogen bonds. In colloidal systems dispersed magnetic particles form structures in an external magnetic field that affect the

viscosity [13–16]. Similar effects have been observed with an external electric field [11] in crude oil, which is a naturally occurring suspension of particles like asphalt, paraffin, sulphur, in a weakly polar base liquid (a mixture of gasoline, kerosene, diesel, etc). While the structure is similar, the dynamics of these systems, which is of crucial importance for transport properties like the viscosity, is quite different.

Our investigations demonstrate one mechanism out of many that can affect the viscosity of fluids in external fields. The simplicity of our HS molecule eliminates some effects, such as charge injection, and simplifies the geometry compared to real polar fluids such as water and acetonitrile. Crucially, by studying such a simple model we have been able to look more closely at the formation and reorientation of structures, and their effects on the anisotropy of the viscosity. This can serve as a basis for understanding such changes in more complex systems, including for example non-Newtonian behaviour due to shear-induced changes in the structure.

Acknowledgments

This work has been supported by the Research Council of Norway through its Centres of Excellence funding scheme, Project No. 262644, and FRIPRO Project No. 275507, as well as the National Infrastructure for Computational Science in Norway (UNINETT Sigma2), Project No. NN9573K.

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