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BOUNDARY CONDITIONS AND EXTENDED CONSTITUTIVE RELATIONS FOR SPIN-FLOW COUPLING IN DIPOLAR FLUIDS

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ABSTRACT. Boundary conditions are formulated, within the framework of irreversible thermodynamics, for the velocity, the angular velocity and the dipole vector parallel to the average electric dipole moment of a streaming dipolar fluid. The local conservation and balance equations for linear and angular momenta and for the dipole vector are complemented by extended constitutive relations for the symmetric and antisymmetric parts of the friction pressure tensor as well as for the flux tensors of the spin, *i.e.*, the internal angular momentum, and of the dipole. Following the original idea of Ludwig Waldmann (Z. Naturforsch, 22a, 1967, p. 1269), the surface entropy production is inferred from the entropy flux. The desired boundary conditions are the linear constitutive relations set up such that the standard requirement of non-negative entropy production holds true, also at the surface. Thus "diagonal" surface phenomenological coefficients, like various slip length coefficients, need not be negative. Furthermore, coupling coefficients obey Onsager-Casimir symmetry relations. Some applications are presented for the plane Couette-flow geometry.

1. Introduction

The partial differential equations of Thermo-Hydrodynamics and their extended versions (De Groot and Mazur 1962; Hess 1975a,b; Jou *et al.* 1988; Restuccia and Kluitenberg 1988, 1990; Blenk *et al.* 1994; Maugin and Muschik 1994; Ehrentraut and Hess 1995; Francaviglia *et al.* 2004; Hess *et al.* 2008; Hess 2015; Ciancio and Restuccia 2016) have to be supplemented by *boundary conditions*. Temperature-jump and slip-flow conditions have been measured in rarefied gases (Kundt and Warburg 1875; Smoluchowski von Smolan 1898) and treated theoretically (Maxwell 1879) over a century ago. Ludwig Waldmann (1967) laid a proper theoretical foundation for the formulation of boundary conditions within Non-Equilibrium Thermodynamics which can also be applied to dense fluids studied in micro- and nano-fluidics. The basic idea is: consider the entropy flux density occurring in the entropy balance equation, the pertaining volume integral yields an expression for the entropy production in a surface or boundary layer which involves surface "force-flux" pairs. Linear constitutive relations, subject to the relevant constraints, then lead to the appropriate

This paper is dedicated to Prof. Wolfgang Muschik on the occasion of his 80th birthday.

boundary conditions. An extension of this method, including singular densities on the surface which allows to treat also surface tension, was proposed in Bedeaux *et al.* (1976). The Waldmann scheme has been applied to transport and relaxation phenomena involving molecular orientations in rarefied polyatomic gases (Vestner 1973) as well as in dense fluids of non-spherical particles and in liquid crystals (Hess and Koo 1989; Heidenreich *et al.* 2007). Motivated by theoretical studies on the spin-flow coupling in water (Bonhuis *et al.* 2009; Hansen *et al.* 2010), more general boundary conditions are presented here for the velocity, the angular velocity and for the dipole vector proportional to the average electric dipole moment. First, however, the constitutive relations in the bulk are formulated for the symmetric and the antisymmetric parts of the friction pressure tensor, for the dipolar relaxation as well as for the spin-flux and dipole-flux tensors. Cross coupling terms possible for non-chiral fluids in an isothermal state, are taken into consideration in the bulk and at the surface.

This article proceeds as follows. The macroscopic variables and the basic equations are presented in Section **2**. In particular, the time change of the entropy associated with the macroscopic variables are stated and the constitutive relations needed for the bulk are formulated. The resulting dynamic equations for the flow velocity, the angular velocity or spin, and for the dipole vector are presented in Section **2.7**. The Section **3** is devoted to the surface entropy production, as inferred from the entropy flux, and the pertaining boundary conditions. Slip lengths associated with the velocity, the spin and the dipole vector, as well as some simple models for surface phenomena are discussed. The applications, restricted to a planar geometry and in particular a plane Couette flow, are considered in Section **4**. The roles of the various material coefficients are discussed. Flow profiles and profiles for the angular velocity are displayed for different parameters needed to specify the behavior in the bulk and at the walls. The dependence of an apparent slip length and an effective viscosity on the model parameters, in particular on the angular velocity at the walls, is analyzed. Bulk and surface phenomena associated with an electric dipole in a Couette flow are presented in Section **4.3**.

2. Variables and basic equations

2.1. Macroscopic variables. The variables describing the fluid are the mass density $\rho = mn$, where m is the mass of a molecule and n is the number density, the flow velocity $\mathbf{v}$, the average internal angular momentum $\mathbf{J} = <\mathbf{j}> = \Theta\mathbf{w}$, where $\mathbf{j}$ is internal angular momentum ("spin") of a molecule, Θ is an effective moment of inertia and $\mathbf{w}$ is the average angular velocity. The bracket $< \dots >$ indicates an average. Furthermore, the polar vector $\mathbf{d} = <\mathbf{e}>$ is included in the set of macroscopic variables. Here $\mathbf{e}$ is a unit vector parallel to the electric dipole moment $\mathbf{p}^{el}$ of a molecule, *viz.*: $\mathbf{p}^{el} = \mu^{el}\,\mathbf{e}$, where μ^{el} is the magnitude of the electric dipole moment.

2.2. Linear and angular velocities. The conservation laws for the linear and the angular momenta imply, in the absence of external forces and torques,

$$\rho\,\frac{dv_\mu}{dt} + \nabla_\mu P + \nabla_\nu p_{\nu\mu} = 0\,, \tag{1}$$

$$(\rho/m)\left(\frac{dJ_\mu}{dt} + \nabla_\nu J_{\nu\mu}\right) = -\,p_\mu\,. \tag{2}$$

The symbol $\frac{d}{dt} = \frac{\partial}{\partial t} + v_\lambda \nabla_\lambda$ denotes the substantial time derivative, The summation convention is used for the Greek subscripts of cartesian vectors and tensors. Here $p_{\nu\mu} = P_{\nu\mu} - P\,\delta_{\nu\mu}$ is the non-equilibrium part of the pressure tensor $P_{\nu\mu}$ and P, which can depend on the position vector $\mathbf{r}$, is the local hydrostatic equilibrium pressure. The tensor $p_{\nu\mu}$, sometimes referred to as *friction pressure tensor*, characterizes the part of the momentum transport, which is not of convective type. The gradient $\nabla_\nu p_{\nu\mu}$ is an internal force density. The pressure tensor can be decomposed into its isotropic, its symmetric traceless and its antisymmetric parts (Hess 2015). Thus

$$p_{\nu\mu} = \tilde{p}\,\delta_{\mu\nu} + \overline{p_{\nu\mu}} + \frac{1}{2}\varepsilon_{\nu\mu\lambda}\,p_\lambda\,. \tag{3}$$

In thermal equilibrium, the part $\tilde{p} = (1/3)p_{\lambda\lambda}$ of the scalar pressure is zero, just as

$$\overline{p_{\nu\mu}} = (1/2)(p_{\nu\mu} + p_{\mu\nu}) - (1/3)p_{\lambda\lambda}\,\delta_{\nu\mu} \tag{4}$$

and the axial vector

$$p_\lambda = \varepsilon_{\lambda\alpha\beta}\,p_{\alpha\beta}$$

which is associated with the antisymmetric part of the pressure tensor and which occurs in the balance equation (2) for the rotational angular momentum. The quantity

$$J_{\nu\mu} = < c_\nu j_\mu >$$

is the flux of internal angular momentum. As any second rank tensor, it can be decomposed into isotropic, symmetric traceless and antisymmetric parts, in analogy to (3).

2.3. Electric dipole moment. In the absence of an external electric field, the polar vector $\mathbf{d}$ obeys the balance equation

$$\frac{d}{dt}d_\mu - \varepsilon_{\mu\nu\lambda}w_\nu d_\lambda + \nabla_\nu d_{\nu\mu} = (\frac{\delta d_\mu}{\delta t})^{irrev}\,. \tag{5}$$

The term involving $\mathbf{w}$ describes the temporal change of $\mathbf{d}$ caused by the average angular velocity. The quantity

$$d_{\nu\mu} = < c_\nu e_\mu >$$

is the dipole-flux tensor. The change of the dipolar vector caused by irreversible processes is denoted by $(\frac{\delta d_\mu}{\delta t})^{irrev}$.

Constitutive relations are needed for this quantity, just as for the symmetric traceless and the antisymmetric parts of the friction pressure tensor, as well as for the angular momentum and dipole flux tensors.

2.4. Time change of the entropy. The various contributions to the entropy production and to the entropy flux are presented separately. The time change of the specific entropy associated with the pressure tensor and with the internal angular momentum is determined by

$$\rho\,T(\frac{ds}{dt})^{pJ} = -[\overline{p_{\nu\mu}}\;\overline{\nabla_\nu v_\mu} + p_\mu(\omega_\mu - w_\mu) + (\rho/m)\,J_{\nu\mu}\nabla_\nu w_\mu] + (\rho/m)\,\nabla_\nu\,(J_{\nu\mu}w_\mu). \tag{6}$$

The first three terms on the right hand side give rise to the entropy production caused by the viscous flow and by the flow of the angular momentum, the last term contributes to the entropy flux. It is assumed that the flow is incompressible, otherwise, an additional term $-\tilde{p}\nabla_\lambda v_\lambda$ occurs in (9).

Let $k_B T\,\Phi^d = k_B T\,\Phi^d(\mathbf{d})$ be the free energy per particle associated with the dipolar orientation. Following Grandner *et al.* (2007), an ansatz is used which guarantees that the magnitude of **d** is bounded by 1, more specifically:

$$\Phi^d = \frac{1}{2}A_d\,\mathbf{d}\cdot\mathbf{d} - \frac{1}{4}B\ln[1-(\mathbf{d}\cdot\mathbf{d})^2]\,. \tag{7}$$

Here A_d and B are positive coefficients. Comparison with the Langevin function, valid for non-interacting dipole moments, yields $A_d = 3$ and $B \approx 3$. In general, A_d depends on the temperature and on the density. In a system where a spontaneous transition to a ferro-electric state can occur, the coefficient A_d changes sign at the transition. This case is not studied here, *i.e.*, $A_d > 0$ is assumed throughout.

The derivative of the dimensionless potential function with respect to d_μ is

$$\partial\Phi^d/\partial d_\mu = \Phi^d_\mu = A_d\,d_\mu + B\,d_\mu\,(\mathbf{d}\cdot\mathbf{d})/[1-(\mathbf{d}\cdot\mathbf{d})^2]\,. \tag{8}$$

When the magnitude of **d** small, the linear approximation $\Phi^d_\mu = A_d\,d_\mu$ is appropriate.

In the presence of an orienting electric field E_μ, the quantity Φ^d_μ contains an additional term proportional to the E- field. At the same time, a torque caused by the field has to be taken into account in the angular momentum balance.

In the spirit of the considerations presented by Hess and Pardowitz (1981), the time change of the specific entropy s associated with the dipolar orientation vector is determined by

$$\rho(\frac{ds}{dt})^d = -(\rho/m)\,k_B[\Phi^d_\mu\,(\frac{\delta d_\mu}{\delta t})^{irrev} + d_{\nu\mu}\nabla_\nu\Phi^d_\mu] + (\rho/m)\,k_B\,\nabla_\nu\,(d_{\nu\mu}\Phi^d_\mu). \tag{9}$$

The first two terms on the right hand side are due to the entropy production caused by the dipolar relaxation and diffusion, the last term contributes to the entropy flux.

2.5. Bulk constitutive relations. The flux tensors $J_{\nu\mu}$ and $d_{\nu\mu}$ occurring in (2) and (5) can be decomposed into isotropic, antisymmetric and symmetric traceless parts, in analogy to the pressure tensor, cf. (3). These tensors have negative and positive parity, respectively. Thus the vectors associated with their antisymmetric parts can be coupled with other polar and with axial vectors. Furthermore, notice that the parity of the thermodynamic fluxes $\overline{p_{\nu\mu}}$, p_λ , $d_{\nu\mu}$ as well as of the thermodynamic forces $\overline{\nabla_\mu v_\nu}$, $\omega_\lambda - w_\lambda$, $\nabla_\nu\Phi^d_\mu$ is positive. The fluxes $(\frac{\delta d_\mu}{\delta t})^{irrev}$, $J_{\nu\mu}$ as well as the forces Φ^d_μ , $\nabla_\nu w_\mu$ have negative parity. The time-reversal behavior is positive for $\overline{p_{\nu\mu}}$, p_λ , Φ^d_μ , $\nabla_\nu\Phi^d_\mu$,$J_{\nu\mu}$ and it is negative for $\overline{\nabla_\mu v_\nu}$, $\omega_\lambda - w_\lambda$, $(\frac{\delta d_\mu}{\delta t})^{irrev}$, $\nabla_\nu w_\mu$. Observing parity conservation, as it is required for non-chiral media, and when no orienting external electric field is present, cross-couplings are possible only between the symmetric traceless fluxes $\overline{p_{\nu\mu}}$, $\overline{d_\nu v_\mu}$ and forces $\overline{\nabla_\nu v_\mu}$, $\overline{\nabla_\nu\Phi^d_\mu}$ as well as between the axial vector fluxes p_λ , $\varepsilon_{\lambda\nu\mu}\,d_{\nu\mu}$ and forces $\omega_\lambda - w_\lambda$, $\varepsilon_{\lambda\nu\mu}\nabla_\nu\Phi^d_\mu$. The ensuing constitutive relations are

$$\overline{p_{\mu\nu}} = -2\,\eta\,\overline{\nabla_\mu v_\nu} - p_0\,L^{2d}\,\overline{\nabla_\nu\Phi^d_\mu} \tag{10}$$

$$\overline{d_{\mu\nu}} = -L^{d2}\,\overline{\nabla_\mu v_\nu} - D^d_2\,\overline{\nabla_\nu\Phi^d_\mu} \tag{11}$$

where the ideal gas expression $p_0 = (\rho/m)\,k_B\,T$ is used as a reference value for the pressure. Due to the different time reversal behavior of the two fluxes and the two forces occurring here, the coupling coefficients, which have the dimension of a length, obey the Onsager-Casimir relation (Onsager 1931; De Groot and Mazur 1962; Hess 2015),

$$L^{2d} = -L^{d2}\,. \tag{12}$$

The corresponding extended ansatz for the axial vectors associated with the antisymmetric parts of the tensors is

$$p_\lambda = -2\,\eta_{rot}\,(\omega_\lambda - w_\lambda) - p_0\,L^{1d}\,\varepsilon_{\lambda\nu\mu}\nabla_\nu\Phi^d_\mu \tag{13}$$

$$\varepsilon_{\lambda\nu\mu}\,d_{\nu\mu} = -2L^{d1}\,(\omega_\lambda - w_\lambda) - D^d_1\,\varepsilon_{\lambda\nu\mu}\,\nabla_\nu\Phi^d_\mu\,. \tag{14}$$

Again, the coupling coefficients obey a Casimir relation:

$$L^{1d} = -L^{d1}\,. \tag{15}$$

For completeness, note that the scalar part of the friction pressure tensor $\tilde{p}$, in principle, is also coupled with $\nabla_\lambda\Phi^d_\lambda$. in particular, these relations are

$$\tilde{p} = -\eta_V\,\nabla_\lambda v_\lambda - p_0\,\tfrac{1}{3}\,L^{0d}\,\nabla_\lambda\Phi^d_\lambda \tag{16}$$

and

$$d_{\lambda\lambda} = -L^{d0}\,\nabla_\lambda v_\lambda - D^d_0\,\nabla_\lambda\Phi^d_\lambda\,. \tag{17}$$

Here, η_V is the volume viscosity coefficient and the coupling lengths coefficients obey the symmetry relation $L^{0d} = -L^{d0}$.

In the standard constitutive laws for the symmetric traceless and for the antisymmetric parts of the pressure tensor, the coupling terms are neglected, then one has (De Groot and Mazur 1962; Hess 2015)

$$\overline{p_{\nu\mu}} = -2\,\eta\,\overline{\nabla_\nu v_\mu} \tag{18}$$

$$p_\mu = -2\eta^{rot}\,(\omega_\mu - w_\mu)\,, \tag{19}$$

with the *shear viscosity* $\eta > 0$ and the *rotational viscosity* coefficient $\eta^{rot} > 0$. The relation (18) is linked with *Newton*. The corresponding law (19) for the axial vector associated with the antisymmetric part of the pressure tensor was first formulated by Born (1920) (Hess and Waldmann 1966; Brunn 1975; Evans and Streett 1978; Condiff and Dahler 2004). The viscosity coefficient η_r used by De Groot and Mazur (1962) and others is related to η^{rot} by $\eta^{rot} = 2\,\eta_r$. Use of (19) in (2) yields a relaxation equation for the average angular velocity $\mathbf{w}$ which will be discussed later. The rotational viscosity plays an important role for the influence of a magnetic field on the viscous behavior of ferro-fluids (McTague 1969; Shliomis 1972; Levi *et al.* 1973; Odenbach 2002; Ilg and Hess 2003; Ilg *et al.* 2003).

The standard ansatz for the scalar $\tilde{p}$ associated with the isotropic part of the friction pressure tensor is $\tilde{p} = -\eta_V\,\nabla_\lambda v_\lambda$, where η_V is the *volume viscosity*, also referred to as *bulk viscosity*.

When the positive dipole diffusion coefficients D^d_ℓ, $\ell = 0,1,2$ for the different ranks of the flux tensor $d_{\nu\mu}$ are approximately equal and when coupling terms are ignored, the simpler "isotropic" approximations

$$d_{\nu\mu} = -D^d\, \nabla_\nu \Phi^d_\mu \tag{20}$$

can be used with the single dipole diffusion coefficient $D^d \geq 0$. Assuming that the derivative of the potential function can be approximated by its linear term, this constitutive relation reduces to

$$d_{\nu\mu} = -\tilde{D}^d\, \nabla_\nu d_\mu\,, \;\; \tilde{D}^d = A_d\, D^d\,. \tag{21}$$

The constitutive laws for the spin flux tensor $J_{\nu\mu}$ and the dipole relaxation term are formulated next. For the symmetric parts of the tensor one has

$$J_{\lambda\lambda} = -\Theta D^J_0\, \nabla_\lambda w_\lambda\,, \;\; \overline{J_{\nu\mu}} - \Theta D^J_2\, \overline{\nabla_\nu w_\mu}\,, \tag{22}$$

with the spin diffusion coefficients $D^J_0 \geq 0\,,\; D^J_2 \geq 0$. In general, the antisymmetric part can be coupled with the dipole relaxation. With the abbreviations $v_0 = (k_B T/m)^{1/2}$ and $w_0 = (k_B T/\Theta)^{1/2}$, the appropriate relations are

$$\varepsilon_{\lambda\nu\mu} J_{\nu\mu} \;=\; -\Theta D^J_1\; \varepsilon_{\lambda\nu\mu} \nabla_\nu w_\mu - 2\Theta\, \alpha^{Jd}\, \Phi^d_\lambda \tag{23}$$

$$\left(\frac{\delta d_\lambda}{\delta t}\right)^{irrev} \;=\; -w_0^{-2}\, \alpha^{dJ}\; \varepsilon_{\lambda\nu\mu} \nabla_\nu w_\mu - \nu^d\, \Phi^d_\lambda\,, \tag{24}$$

Here $D^J_1 \geq 0$ is spin diffusion coefficient. Due to Φ^d_μ as given by (8), the dipolar relaxation time τ^d is related to the dipole relaxation frequency $\nu^d > 0$ by

$$\tau^d = (A_d\, \nu^d)^{-1}\,. \tag{25}$$

The coupling coefficients $\alpha^{\cdot\cdot}$ which have the dimension of an acceleration, obey the Casimir relation

$$\alpha^{Jd} = -\alpha^{dJ}\,. \tag{26}$$

When the spin diffusion coefficients for the different ranks of the relevant flux tensor are approximately equal, *viz.*:

$$D^J_0 \approx D^J_1 \approx D^J_2 = D^J,$$

the simpler "isotropic" approximations

$$J_{\nu\mu} = -\Theta D^J\, \nabla_\nu w_\mu\,, \tag{27}$$

can be used, provided that the coupling terms can be ignored. This implies $\nabla_\nu J_{\nu\mu} = -\Theta D^J \Delta w_\mu$ The "spin-viscosity" coefficients $\zeta_{..}$ as used in the literature are just spin diffusion coefficient multiplied with the number density ρ/m times the moment of inertia Θ, *i.e.*, $\zeta_\ell = (\rho/m)\Theta D^J_\ell$, with $\ell 0,1,2$ and $\zeta = (\rho/m)\Theta D^J$, $\delta\zeta = (\rho/m)\Theta\, \delta D^J$. Notice that the dimension of a spin-viscosity is $kg\, m\, s^{-1}$, in SI-units, whereas that of an ordinary viscosity is $Pascal\, s = kg\, m^{-1} s^{-1}$.

Spin diffusion was first considered by Torrey (1956) in connection with nuclear magnetic resonance and spin echo experiments, see also Robertson (1966). The kinetic theory for spin relaxation and spin diffusion in gases was treated by Hess (1967, 1968b), Hess and Waldmann (1968), and Hess (1969). For classically rotating colloidal particles, these phenomena were studied theoretically by Hess (1968a).

For sake of completeness it is mentioned that the set of the vectorial constitutive relations (24) is to be enlarged by an equation for the heat flux and for the diffusion flow in systems with temperature and concentration gradients. In this case additional coupling terms have to be included which, *e.g.*, lead to thermo-electric (Waldmann and Hess 1969) and diffusio-electric effects (Hess 1974). Possible interactions of vector fluxes and forces in mixtures is also discussed in Restuccia and Kluitenberg (1987). The coupling between the heat flux and the vector associated with the antisymmetric part of the spin flux tensor plays a role for the influence of a magnetic field on the heat conductivity of an electrically neutral gas: Senftleben-Beenakker effect (McCourt *et al.* 1990).

2.6. Flow terms. The flow terms in the conservation and balance equations for the linear and angular momenta and for the dipolar vector involve the gradients of the flux tensors. The first to be considered is the force density

$$K_\mu = \nabla_\nu p_{\nu\mu} = K^v_\mu + K^{vd}_\mu \,. \tag{28}$$

For spatially constant transport and coupling coefficients, the constitutive relations for the various parts of the friction pressure tensor, the part of the force density due to second spatial derivatives of the velocity and first derivatives of the angular velocity is

$$\begin{aligned} K^v_\mu &= -\eta\,\Delta v_\mu - (\eta_V + \tfrac{1}{3}\eta)\,\nabla_\mu\nabla_\nu v_\nu - \eta^{rot}\,\varepsilon_{\nu\mu\lambda}\nabla_\nu(\omega_\lambda - w_\lambda) \\ &- (\eta + \tfrac{1}{2}\eta^{rot})\,\Delta v_\mu - (\eta_V + \tfrac{1}{3}\eta - \tfrac{1}{2}\eta^{rot}))\,\nabla_\mu\nabla_\nu v_\nu + \eta^{rot}\,\varepsilon_{\nu\mu\lambda}\nabla_\nu w_\lambda \,, \end{aligned} \tag{29}$$

The contribution caused by the coupling with the dipole vector is

$$K^{vd}_\mu = -p_0(L^{pd}\,\Delta\Phi^d_\mu + \delta L^{pd}\,\nabla_\mu\nabla_\nu\Phi^d_\nu)\,. \tag{30}$$

The coupling parameters used here are linked with those introduced in the constitutive relations formulated above by

$$L^{pd} = \tfrac{1}{2}(L^{2d} + L^{1d})\,,\; \delta L^{pd} = \tfrac{1}{6}L^{2d} - \tfrac{1}{2}L^{1d} + \tfrac{1}{3}L^{0d}\,. \tag{31}$$

Similarly, the constitutive laws for the flux of the internal angular momentum lead to

$$\nabla_\nu J_{\nu\mu} = -\Theta(D^J\,\Delta w_\mu + \delta D^J\nabla_\mu\nabla_\nu w_\nu) - \Theta\,\alpha^{Jd}\,\varepsilon_{\mu\nu\lambda}\nabla_\nu\,\Phi^d_\lambda\,, \tag{32}$$

The spin diffusion coefficients used here are related to those introduced above by

$$D^J = \tfrac{1}{2}(D^J_2 + D^J_1)\,,\;\; \delta D^J = \tfrac{1}{6}D^J_2 - \tfrac{1}{2}D^J_1 + \tfrac{1}{3}D^J_0\,. \tag{33}$$

The coefficient δD^J vanishes for the isotropic case where $D^J_0 = D^J_1 = D^J_2 = D^J$. Likewise, the constitutive relations for the flux of the dipolar vector imply

$$\nabla_\nu d_{\nu\mu} = -(D^d\,\Delta\Phi^d_\mu + \delta D^d\nabla_\mu\nabla_\nu\Phi^d_\nu) - (L^{dv}\,\Delta v_\mu + \delta L^{dv}\nabla_\mu\nabla_\nu v_\nu) + L^{d1}\,\varepsilon_{\nu\mu\lambda}\,\nabla_\nu w_\lambda \tag{34}$$

In analogy to (33) and (31), the diffusion coefficients and the length parameters are linked with those introduced above by

$$D^d = \tfrac{1}{2}(D^d_2 + D^d_1)\,,\;\; \delta D^d = \tfrac{1}{6}D^d_2 - \tfrac{1}{2}D^d_1 + \tfrac{1}{3}D^d_0\,, \tag{35}$$

and

$$L^{dv} = \tfrac{1}{2}(L^{d2} + L^{d1})\,,\;\; \delta L^{dv} = \tfrac{1}{6}L^{d2} - \tfrac{1}{2}L^{d1} + \tfrac{1}{3}L^{d0}\,. \tag{36}$$

The coefficients δD^d and $\delta L^{dv} = -\delta L^{vd}$ vanish in the isotropic case where the coefficients pertaining to the different tensorial ranks are equal.

2.7. Dynamic equations. Insertion of the expressions stated above for the force density into the local momentum conservation equation (1) yields, for an incompressible flow, the generalized *Navier-Stokes* equation

$$\rho\,\frac{dv_\mu}{dt}+\nabla_\mu P-(\eta+\tfrac{1}{2}\eta^{rot})\,\Delta v_\mu-\eta^{rot}\varepsilon_{\mu\nu\lambda}\nabla_\nu w_\lambda=p_0\,(L^{pd}\,\Delta\Phi^d_\mu+\delta L^{pd}\,\nabla_\mu\nabla_\nu\Phi^d_\nu)\,. \tag{37}$$

The resulting relaxation equation for the angular velocity, then reads

$$\frac{dw_\mu}{dt}-D^J\Delta w_\mu-\delta D^J\nabla_\mu\nabla_\nu w_\nu+\nu^{rot}\,(w_\mu-\tfrac{1}{2}\,\varepsilon_{\mu\nu\lambda}\nabla_\nu v_\lambda)=\alpha^{wd}\,\varepsilon_{\mu\nu\lambda}\nabla_\nu\Phi^d_\lambda\,. \tag{38}$$

The angular velocity relaxation frequency $\nu^{rot}=(\tau^{rot})^{-1}$, where τ^{rot} is the pertaining relaxation time, is linked with the rotational viscosity by

$$\nu^{rot}=2\,(m/\rho)\Theta^{-1}\eta^{rot}\,. \tag{39}$$

Likewise, the coupling coefficient α^{wd} which has the dimension of an acceleration, is proportional to the coupling length L^{1d} and the α-coefficient of (32), more specifically

$$\alpha^{wd}=w_0^2L^{1d}+\alpha^{Jd}\,. \tag{40}$$

The resulting equation for the dynamics of the dipole vector is,

$$\frac{d}{dt}d_\mu-\varepsilon_{\mu\nu\lambda}w_\nu d_\lambda-D^d\Delta\Phi^d_\mu-\delta D^d\,\nabla_\mu\nabla_\nu\Phi^d_\nu+\nu^d\,\Phi_\mu=L^{dv}\,\Delta v_\mu+L^{d1}\,\varepsilon_{\mu\nu\lambda}\,\nabla_\nu w_\lambda\,. \tag{41}$$

Notice that $\Phi^d_\mu=A_d\,d_\mu$ with $A_d>0$, when the magnitude of the dipole vector is small, cf. (8).

The expressions on the right hand side of the equations above stem from the coupling terms in the constitutive relations. Some simple consequences of these terms are indicated next.

2.8. Bulk coupling effects. The terms on the right hand side of (37) act like an extra force. In a stationary state and even when no flow is allowed and when $\mathbf{w}=0$, a second spatial derivative of the dipole vector d_μ and thus of Φ^d_μ gives rise to a pressure gradient $\nabla_\mu P=p_0\,(L^{pd}\,\Delta\Phi^d_\mu+\delta L^{pd}\,\nabla_\mu\nabla_\nu\Phi^d_\nu)$. Under the same conditions, the term on the right hand side of (38) acts like a torque $T_\mu=\Theta\,\alpha^{wd}\,\varepsilon_{\mu\nu\lambda}\nabla_\nu\Phi^d_\lambda$.

The terms on the right hand side of (41) give rise to shear-flow induced dipole vector $\mathbf{d}$ which implies an electric polarization proportional to $\Delta\mathbf{v}$. The effects of the coupling terms are expected to be small, such that the standard solutions of hydrodynamics can applied, then one has $\omega_\lambda=(1/2)\varepsilon_{\lambda\nu\mu}\nabla_\nu v_\mu$. For simplicity, consider a plane stationary Poiseuille flow where $\Delta v_\mu=const.$ in regions far away from boundary layers. Disregarding the non-linear term $\varepsilon_{\mu\nu\lambda}w_\nu d_\lambda$ and using $\Phi^d_\mu=A_d d_\mu$, valid for small values of $\mathbf{d}$, the *flow-induced dipole vector* is

$$d_\mu=\frac{1}{2}\tau^d\,L^{d2}\,\Delta v_\mu\,.$$

3. Surface entropy production and boundary conditions

3.1. Entropy production at an interface. A fluid in contact with an impenetrable solid wall is considered which moves with the velocity $\mathbf{v}^{wall}$. The outer normal unit vector of the fluid is denoted by $\mathbf{n}$. The local conservation and balance equations in the bulk of the fluid contain flow terms. A volume integration and application of the Gauss theorem yields surface integrals. From the entropy balance follows the surface entropy production

$$\frac{dS^{wall}}{dt} = \int df\, T^{-1} \left[k_\mu^{tan} (v_\mu - v_\mu^{wall})^{tan} + (\rho/m)\, n_\nu\, J_{\nu\mu} w_\mu + p_0\, n_\nu\, d_{\nu\mu} \Phi_\mu^d \right] . \tag{42}$$

Here df denotes the surface element. The superscript tan indicates the component tangential to the surface, *i.e.*, normal to $\mathbf{n}$, *e.g.*, $v_\mu^{tan} = v_\mu - (n_\nu v_\nu) n_\mu$. As before, $p_0 = (\rho/m) k_B T$ is a reference pressure. The surface force density

$$k_\mu = n_\nu\, p_{\nu\mu} = k_\mu^v + k_\mu^{vd}$$

caused by the friction pressure tensor is inferred from (28) and (29), (30) with ∇_ν replaced by n_ν, in particular,

$$\begin{aligned} k_\mu^v &= -\eta\, n_\nu \nabla_\nu\, v_\mu - (\eta_V + \tfrac{1}{3}\eta)\, n_\nu \nabla_\mu v_\nu - \eta^{rot} \varepsilon_{\nu\mu\lambda} n_\nu (\omega_\lambda - w_\lambda) \\ &- (\eta + \tfrac{1}{2}\eta^{rot})\, n_\nu \nabla_\nu\, v_\mu - (\eta_V + \tfrac{1}{3}\eta - \tfrac{1}{2}\eta^{rot}))\, n_\nu \nabla_\mu v_\nu + \eta^{rot} \varepsilon_{\nu\mu\lambda} n_\nu w_\lambda\, , \end{aligned} \tag{43}$$

$$k_\mu^{vd} = -p_0 (L^{pd}\, n_\nu \nabla_\nu\, \Phi_\mu^d + \delta L^{pd}\, \nabla_\mu n_\nu \Phi_\nu^d)\, . \tag{44}$$

The first term on the right hand side of (42) was already used by Waldmann (1967), as well as by Vestner (1973), Hess and Koo (1989), and Heidenreich *et al.* (2007) where, however, $p_{\nu\mu}$ was symmetric. The last term of (42) involving the vector $\mathbf{d}$ is analogous to expressions used by Vestner (1973) and Heidenreich *et al.* (2007) for second rank tensors. The quantities k_μ , v_μ , $n_\nu\, d_{\nu\mu}$, Φ_μ^d occurring above are polar vectors, *i.e.*, they have negative parity, whereas $n_\nu\, J_{\nu\mu}$, w_μ are axial vectors with positive parity. On the other hand, the cross product of the normal vector $\mathbf{n}$ with one of these vectors generates a vector with the other parity. This allows the coupling of thermodynamic fluxes at the surface which have different parities.

3.2. Boundary conditions. The expression (42) can be rewritten as

$$\frac{dS^{wall}}{dt} = \int df\, \tfrac{\rho}{m} k_B\, v_0 \left[F_\mu^v\, v_0^{-1} (v_\mu - v_\mu^{wall})^{tan} + F_\mu^w\, w_0^{-1} (w_\mu - w_\mu^{wall}) + F_\mu^d\, \Phi_\mu^d \right] , \tag{45}$$

with the dimensionless thermodynamic fluxes

$$F_\mu^v = p_0^{-1}\, k_\mu^{tan}\, , \; F_\mu^w = v_0^{-1}\, w_0^{-1}\, \Theta^{-1}\, n_\nu\, J_{\nu\mu}\, , \; F_\mu^d = v_0^{-1}\, n_\nu\, d_{\nu\mu}\, . \tag{46}$$

It is understood that the force density k_μ at the surface is given by $k_\mu = n_\nu p_{\nu\mu}$. The quantity w_μ^{wall} is the angular velocity which can possibly be prescribed at the wall, Furthermore, at the surface, an internal field may cause a non-zero value d_μ^{wall}. Then $\Phi_\mu^d = A_d\, (d_\mu - d_\mu^{wall}) + \ldots$ is to be used in (45), with terms nonlinear in $\mathbf{d}$ indicated by the dots. In the following, these non-linear terms are disregarded at the surface.

The constitutive laws governing the boundary conditions at the surface are:

$$
\begin{aligned}
v_0^{-1}\,(v_\mu - v_\mu^{wall})^{tan} &= C_v\,F_\mu^v + C_{vd}\,(F_\mu^d)^{tan} + C_{vw}\,\varepsilon_{\mu\nu\lambda}\,n_\nu\,F_\lambda^w\,,\\
A_d\,(d_\mu - d_\mu^{wall}) &= C_{dv}\,F_\mu^v + C_d\,F_\mu^d \;+\; C_{dw}\,\varepsilon_{\mu\nu\lambda}\,n_\nu\,F_\lambda^w\,,\\
w_0^{-1}\,(w_\mu - w_\mu^{wall}) &= C_{wv}\,\varepsilon_{\mu\nu\lambda}\,n_\nu F_\lambda^v + C_{wd}\,\varepsilon_{\mu\nu\lambda}\,n_\nu F_\lambda^d + C_w\,F_\mu^w\,.
\end{aligned}
\tag{47}
$$

The diagonal coefficients have to be non-negative to ensure a non-negative entropy production at the surface, *viz.*:

$$
C_v \geq 0\,,\; C_d \geq 0\,,\; C_w \geq 0\,. \tag{48}
$$

The non-diagonal coefficients obey the Onsager-Casimir symmetry relations:

$$
C_{vd} = -C_{dv}\,,\; C_{vw} = C_{wv}\,,\; C_{dw} = C_{wd}\,. \tag{49}
$$

All cross terms do not contribute to the entropy production, so they may have either sign and their magnitude is not bounded. However, according to general experience, such coupling coefficients are expected to be small.

The role of a thermodynamic flux and of a thermodynamic force is flexible, to some extent. So one can also choose the pair of terms $J_{\nu\mu}$ and $n_\nu w_\mu$ which possess an antisymmetric parts associated with polar vectors.

3.3. Slip lengths. Disregarding couplings in the bulk and ignoring non-diagonal terms at the surface, the first equation of (48) the slip velocity $\delta v_\mu = -(v_\mu - v_\mu^w)^{tan}$ is determined by

$$
\delta v_\mu = \ell_v\,\left(n_\nu \nabla_\nu v_\mu^{tan} + (\eta^{rot}/\eta)\,\varepsilon_{\nu\mu\lambda} n_\nu(\omega_\lambda - w_\lambda)\right)\,,\;\; \ell_v = C_v\,\eta\,v_0 p_0^{-1} \geq 0\,, \tag{50}
$$

where ℓ_v is the velocity slip length. When $\omega_\lambda = w_\lambda$ holds true, the standard expression for the velocity slip is recovered.

Corresponding relations involving the slip lengths ℓ_w and ℓ_d for the angular velocity $\mathbf{w}$ and the dipolar vector $\mathbf{d}$ are obtained from (48) with non-diagonal terms disregarded and subject to the isotropic approximations (27):

$$
\begin{aligned}
w_\mu - w_\mu^{wall} &= -\ell_w\,n_\nu \nabla_\nu w_\mu\,,\;\; \ell_w = C_w\,D^J\,v_0^{-1} \geq 0\,,\\
d_\mu - d_\mu^{wall} &= -\ell_d\,n_\nu \nabla_\nu d_\mu\,,\;\; \ell_d = C_d\,D^d\,v_0^{-1} \geq 0\,.
\end{aligned}
\tag{51}
$$

In the last boundary condition, the linear approximation $\Phi_\mu^d \sim d_\mu$ was used.

The velocity slip length ℓ_v has been calculated in Non-Equilibrium Molecular Dynamics (NEMD) computer simulations for a simple liquid composed of spherical particles (Hess and Loose 1989). In fluids of particles with internal degrees of freedom, coupling phenomena may lead to velocity profiles and flow behavior which can be characterized by an apparent velocity slip length (see, *e.g.*, Heidenreich *et al.* (2007)) where the internal variable is the second rank alignment tensor. The apparent slip flow for the coupling with the spin and dipole vectors, as treated here, is discussed below.

Typically, a boundary affects the solutions of the dynamic equations just in a surface layer with thickness of the order of a few slip lengths. Some applications are presented next.

3.4. Some surface phenomena. Qualitative features of an angular velocity and an electric dipole induced by moving walls are discussed next, cf. Fig.1 with a schematic drawing of phenomena plausible for a plane Couette flow. When particles roll in the vicinity of a moving wall, as expected for larger, colloidal particles, the magnitude of their angular velocity w^{wall} may even be larger than in the interior of the fluid. This is in contradistinction to the frequently made assumption $w^{wall} = 0$. A possible mechanism for a surface induced dipole d^{wall} is indicated on the right hand side of Fig.1. Consider flexible molecules with an embedded electric dipole grafted at the walls. When the walls move, the molecules are bent and a dipole d^{wall} can be induced, with a component parallel or antiparallel to the flow direction.

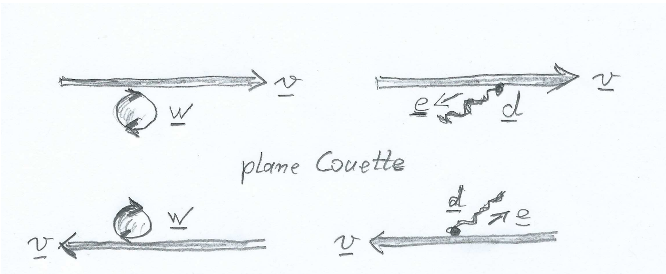

FIGURE 1. Cartoon of possible mechanisms inducing an angular velocity and an electric dipole at the walls of a plane Couette flow arrangement.

3.5. Consequences of surface coupling. The non-diagonal terms in the boundary conditions (48) for the dipole vector and the angular velocity can effectively be taken into account in the slip boundary conditions (51) by the modifications

$$d_\mu^{wall} \to d_\mu^{wall} + d_\mu^{walleff}\,,\;\; w_\mu^{wall} \to w_\mu^{wall} + w_\mu^{walleff} \tag{52}$$

with the effective wall contributions

$$d_\mu^{walleff} = A_d^{-1}\left(C_{dv}\,F_\mu^v + C_{dw}\,\varepsilon_{\mu\nu\lambda}\,n_\nu\,F_\lambda^w\right), \tag{53}$$

$$w_\mu^{walleff} = w_0\left(C_{wv}\,\varepsilon_{\mu\nu\lambda}\,n_\nu F_\lambda^v + C_{wd}\,\varepsilon_{\mu\nu\lambda}\,n_\nu F_\lambda^d\right). \tag{54}$$

For F_μ^v, F_μ^w and F_μ^d see (46). In the following, the surface force density is approximated by the expression (44), *i.e.*, a contribution proportional to the bulk coupling coefficient L^{pd} is ignored. Furthermore, the isotropic approximations are used for the spin- and dipole-fluxes, cf. (20) and (27). This implies

$$F_\mu^v = -p_0^{-1}\left((\eta + \tfrac{1}{2}\eta^{rot})\,n_\nu\nabla_\nu\,v_\mu + \eta^{rot}\varepsilon_{\nu\mu\lambda}n_\nu w_\lambda\right), \tag{55}$$

and

$$F_\mu^d = -v_0^{-1}A_d\,D^d\,n_\nu\,\nabla_\nu d_\mu\,,\;\; F_\mu^w = -v_0^{-1}\,w_0^{-1}\,D^J\,n_\nu\,\nabla_\nu w_\mu\,. \tag{56}$$

Similarly, the non-diagonal terms in the boundary conditions for the velocity appear as if the relevant wall velocity differs from the externally imposed velocity of the wall. In the applications below, this certainly small effect is not taken into account.

4. Applications

4.1. Planar geometry. Consider a geometry where the flow is in x-direction and bounded by two planes normal to the y-direction. Thus one has $v_\mu = v e^x_\mu$ and $\gamma = \partial v/\partial y$ is the shear rate which, in general depends on y. Unit vectors parallel to the coordinate axes are denoted by $\mathbf{e}^i$, $i = x,y,z$. For this geometry, the vorticity is $\frac{1}{2}\varepsilon_{\mu\nu\lambda}\nabla_\nu v_\lambda = -\frac{1}{2}\gamma e^z_\mu$. The ansatz $w^z_\mu = w e^z_\mu$ is made with $w = w(y)$. The derivative with respect to y is indicated by a prime. Then the dynamic equations for the velocity and the angular velocity reduce to

$$\rho\,\frac{dv}{dt} + \frac{\partial P}{\partial x} - (\eta + \tfrac{1}{2}\eta^{rot})\,\gamma' - \eta^{rot} w' = p_0 L^{pd}\,\phi''\,, \tag{57}$$

$$\frac{dw}{dt} - D^J w'' + \nu^{rot}\,(w + \tfrac{1}{2}\,\gamma) = \alpha^{wd}\,\phi'\,. \tag{58}$$

Notice that $\nu^{rot} \sim \eta^{rot}$, cf. (39).

For the time being, the dipole vector is assumed to be of the form $d_\mu = d\, e^x_\mu$, this means that the rotation of the dipole caused by the angular velocity is disregarded as a non-linear effect. Furthermore, $\Phi^d_\mu = \phi\, e^x_\mu$ with $d = d(y)$ and $\phi = \phi(y)$, then

$$\frac{d}{dt}d + \ldots - D^d\phi'' + \nu^d\,\phi = L^{dv}\,\gamma' + L^{d1}\,w'\,. \tag{59}$$

Notice that $\phi = A_d\, d + B d^3/(1-d^4)$, cf. (8). In most applications it suffices to use the linear approximation $\phi = A_d\, d$.

For this geometry, the slip boundary conditions (50),(51) where the surface coupling terms are disregarded, reduce to

$$v - v^{wall} = -\ell_v\,\left(\gamma + (\eta^{rot}/\eta)\,(\tfrac{1}{2}\gamma + w)\right)\,,\;\; w - w^{wall} = -\ell_w\, w'\,, \tag{60}$$

and, within the approximation $\phi = A_d\, d$,

$$d - d^{wall} = -\ell_d\, d'\,. \tag{61}$$

The dots $\ldots$ in (59) stand for terms which couple the x-component of the dipole vector with its y-component due to the rotation induced by the angular velocity. This non-linear effect which breaks the planar symmetry will be discussed later.

4.2. Plane Couette flow. Consider a stationary Couette flow between two flat plates located at $y = \pm b$ moving in x-direction with the opposite velocities $\pm v^{wall}$. Assuming that both plates are identical, the velocity function $v = v(y)$ is antisymmetric with respect to $y = 0$. Thus the ansatz

$$v = \gamma_1\, y + \gamma_2\,\kappa^{-1}\, sinh(\kappa y)\,, \tag{62}$$

is made, with the shear rate parameters γ_1, γ_2 and the reciprocal length κ. The resulting shear rate γ is symmetric, *viz.*,

$$\gamma = \gamma_1 + \gamma_2\, cosh(\kappa y)\,. \tag{63}$$

The angular velocity $w = w(y)$ is also symmetric, thus the ansatz

$$w = w_1 + w_2\, cosh(\kappa y)\,, \tag{64}$$

is made. The parameters w_1, w_2, as well as γ_1, γ_2 and κ have to be determined by the differential equations and the boundary conditions.

Next, the equations for the velocity and the angular velocity are solved by ignoring any influence of the dipole vector, *i.e.*, $L^{pd} = 0$ and $\alpha^{wd} = 0$ is used in (57) and (58).

For $\rho \, \frac{dv}{dt} = 0$ and $\frac{\partial P}{\partial x} = 0$, one has

$$\kappa \, (\eta + \tfrac{1}{2} \eta^{rot}) \gamma_2 + \kappa \, \eta^{rot} w_2 = 0 \, , \tag{65}$$

and for $\frac{dw}{dt} = 0$,

$$- \kappa^2 D^J w_2 + \nu^{rot} \, (w_2 + \tfrac{1}{2} \gamma_2) = 0 \, , \;\; \nu^{rot} \, (w_1 + \tfrac{1}{2} \gamma_1) = 0 \, . \tag{66}$$

For $\kappa \neq 0$, these equations imply

$$\kappa^2 D^J = \nu^{rot} \, (1 - q/(1+q)) = 2 \, (m/\rho) \Theta^{-1} \eta^{rot}/(1+q) \, , \;\; q = \tfrac{1}{2} \eta^{rot}/\eta \, , \tag{67}$$

where q is a measure for the relative importance of the rotational viscosity compared with the shear viscosity. The quantity q is referred to as "spin coupling parameter". The "diffusion length" parameter $\ell = \kappa^{-1}$ is given by

$$\kappa^{-1} = \ell = \left((D^J/\nu^{rot})(1+q) \right)^{1/2} = \left(\tfrac{1}{2} \, (\rho/m) \, (\Theta D^J/\eta^{rot})(1+q) \right)^{1/2} . \tag{68}$$

Notice that, for $\kappa \neq 0$, equation (65) is equivalent to $(1+q) \, \gamma_2 + 2 \, q \, w_2 = 0$.

The symmetry used for v and w applies to the case where upper and lower plates are such that it suffices to consider the boundary conditions on one of them, *e.g.*, for $y = b$. The slip boundary conditions (60) lead to

$$\gamma_1 \, b + \gamma_2 \, \kappa^{-1} sh - v^{wall} = -\ell_v \, ((1+q) \, (\gamma_1 + \gamma_2 \, ch) + 2 \, q \, (w_1 + w_2 \, ch)) = -\ell_v \, \gamma_1 \, , \tag{69}$$

and

$$w_1 + w_2 \, ch = -\ell_w \;\kappa \, w_2 \, sh + w^{wall} \, , \tag{70}$$

with the abbreviations $sh = sinh(\kappa b)$ and $ch = cosh(\kappa b)$. The last equation is equivalent to

$$w_2 = -(w_1 - w^{wall}) \, R = (\tfrac{1}{2} \gamma_1 + w^{wall}) \, R \, , \;\; R = (ch + (\ell_w/\ell) \, sh)^{-1} \, . \tag{71}$$

From (65) and (70) follows

$$\gamma_2 = -\frac{2q}{1+q} \, w_2 = -\frac{q}{1+q} \, (\gamma_1 + 2 \, w^{wall}) \, R \, . \tag{72}$$

Thus w_1, w_2 and γ_2 are related to γ_1. The boundary condition for the velocity finally links γ_1 with the "external shear rate" $\gamma^{ext} = v^{wall}/b$, *viz.*,

$$\gamma_1 = \left(\gamma^{ext} + 2 \, Q \, w^{wall} \right) \, \left[1 + \frac{\ell_v}{b} - Q \right]^{-1} \, , \tag{73}$$

where the function Q is the abbreviation

$$Q = \frac{q}{1+q} \, \frac{\ell}{b} \, sh R = \frac{q}{1+q} \, \frac{1}{\kappa b} \, \frac{sinh(\kappa b)}{cosh(\kappa b) + (\ell_w \, \kappa) sinh(\kappa b)} \, . \tag{74}$$

Notice that $\ell = \kappa^{-1}$.

The case $q = 0$ and $\kappa = 0$, where $\ell \to \infty$, but $\ell q \to 0$, corresponds to an ordinary fluid without the spin-flow coupling. Then one has $Q = 0$, $\gamma_2 = 0$ and the standard slip relation

$$\gamma_1 = \gamma^{ext} \, \left[1 + \frac{\ell_v}{b} \right]^{-1}$$

is recovered. On the other hand, the same result is obtained, even for $q \neq 0$ and $\kappa \neq 0$, when the surface angular velocity $w^{wall} = -\frac{1}{2}\gamma^{ext}$ is imposed.

Notice that w^{wall} may as well be an effective angular velocity caused at the wall by $C_{wv} \neq 0$, cf. (54), (55). For the present geometry one has

$$w^{walleff} = -w_0\, p_0^{-1}\, \eta\, C_{wv}\, \gamma_1\,.$$

With $w^{wall} \approx w^{walleff}$ and $\gamma_1 \approx \gamma^{ext}$, the order of magnitude of the coefficient C_{wv} can be estimated from

$$w_0\, p_0^{-1}\, \eta\, C_{wv} \approx -w^{wall}/\gamma^{ext}\,.$$

Consequently one finds

$$C_{wv} \approx p_0/(2w_0\,\eta)\,,$$

when $w^{wall} \approx -\gamma^{ext}/2$ holds true.

4.2.1. *Flow profiles.* Flow profiles are displayed in Fig.2 for the case of vanishing surface angular velocity, *viz.*, $w^{wall} = 0$. T The y-coordinate is expressed in units of b, the velocity

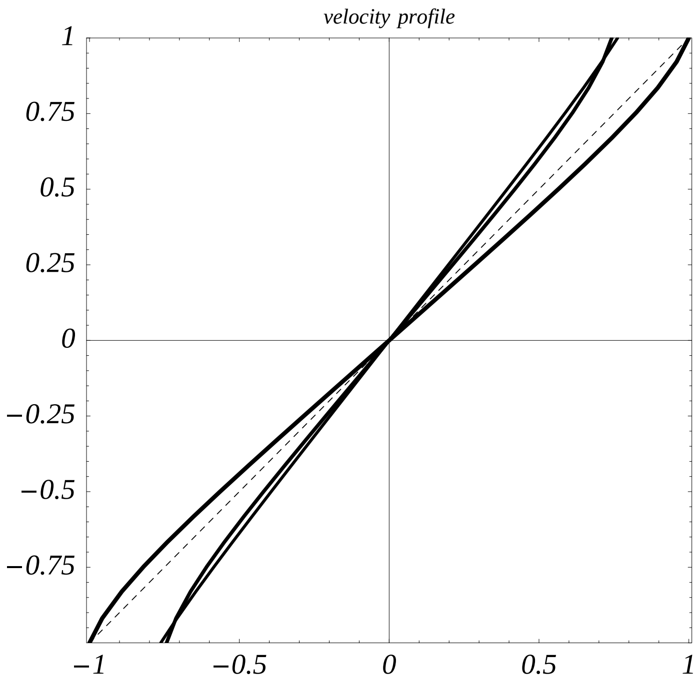

FIGURE 2. The velocity profile, in units of v^{wall} for $w^{wall} = 0$. The values of the other parameters $\{q, \ell, \ell_v, \ell_w\}$ are $\{2, 0.2, 0, 0\}$, $\{2, 0.2, 0.3, 0\}$, $\{2, 0.2, 0.3, 0.5\}$, see the text, and $\{0, 0.2, 0, 0\}$, for the dashed line.

is in units of $v^{wall} = \gamma^{ext}\, b$. The diffusion length is ℓ 0.2 b, in all cases. The straight dashed line and the curve starting and ending at the corners pertain to a no-velocity-slip situation, *i.e.*, to $\ell_v = 0$. The ratio $q = \eta^{rot}/(2\,\eta)$ between the rotational and the shear viscosities is 0 and 2, respectively, and $\ell_w = 0$ applies for the later case. Due to the spin-flow coupling, the velocity is bent forward. This implies a negative apparent slip length. The curves which start and end off the corners are for the finite velocity slip length $\ell_v = 0.3b$ and $q = 2$. The curve which is slightly stronger bent is for the angular velocity slip length $\ell_w = 0$ and $\ell_w = 0.5\,b$ was chosen for the other one.

The frequently made assumption of a vanishing surface angular velocity (Brunn 1975; Condiff and Dahler 2004; Bonhuis *et al.* 2009), seems plausible. Nevertheless, it is of interest to study the case $w^{wall} \neq 0$, in particular for macro-fluids. Colloidal particles may pick up a finite angular velocity by a moving wall. When the upper plate of a plane Couette set up is moving towards the right, the angular velocity w^{wall} is negative, its magnitude is bounded by $w^{wall}/a = (b/a)\,\gamma^{ext}$ where a is the radius of the rotating particle. Here w^{wall} may as well stand for an effective angular velocity caused at the wall by $C_{wv} \neq 0$, cf. (54), (55).

The velocity profiles displayed in Figs.3,4 show the influence of $w^{wall} \neq 0$.

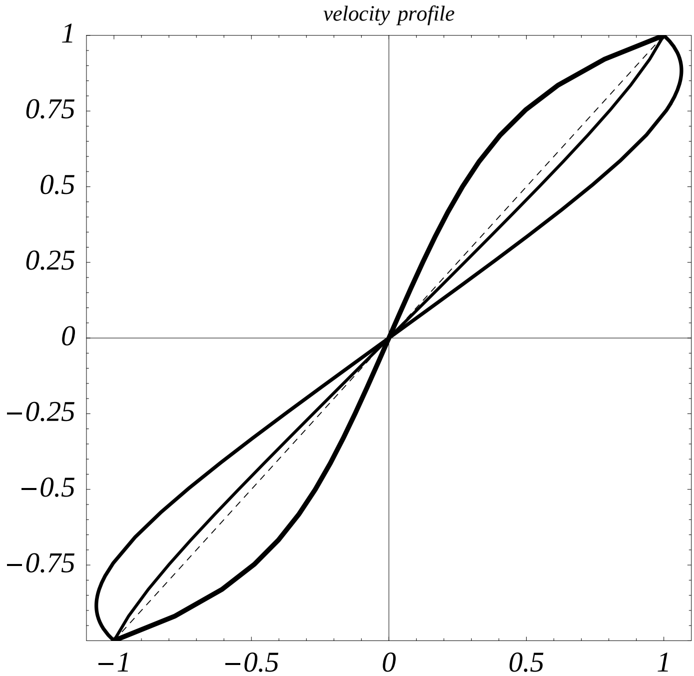

FIGURE 3. The velocity profile, in units of v^{wall} for $w^{wall} = -3, -0.5, 0.0, 2$, see the text. For all curves the values of the other parameters $\{q, \ell, \ell_v, \ell_w\}$ are $\{1, 0.2, 0, 0\}$.

In all cases $q = 1$, $\ell = 0.2\,b$ and $\ell_v = \ell_w = 0$ were chosen. The curve bending towards the left is for $w^{wall} = -3$, the dashed straight line corresponds to $w^{wall} = -1/2$, in units of γ^{ext}. The other two curves, bending slightly and more strongly towards the right pertain to $w^{wall} = 0$ and 2, respectively. Notice, an apparent slip length inferred from these velocity profiles is positive for $w^{wall} < -1/2$ and negative for $w^{wall} > -1/2$. Angular velocity profiles for $w^{wall} = -1.5, -0.5, 0.0$ and 0.5 are shown in Fig.4. As in the previous figure, $q = 1$, $\ell = 0.2b$ and $\ell_v = \ell_w = 0$ were chosen. The dashed vertical line pertaining to $w^{wall} = -1/2$ corresponds to the situation where the antisymmetric part of the pressure tensor is zero, as realized in the absence of external torques and when the influence of the surface does not matter.

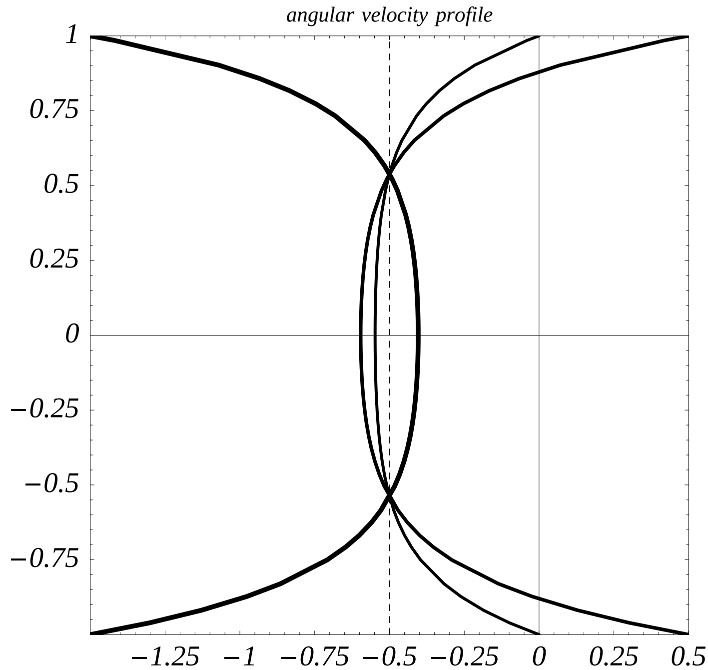

FIGURE 4. The angular velocity profile, in units of the imposed shear rate γ^{ext} for $w^{wall} = -1.5, -0.5, 0.0, 0.5$, see the text. For all curves the values of the other parameters $\{q, \ell, \ell_v, \ell_w\}$ are $\{1, 0.2, 0, 0\}$.

4.2.2. *Apparent slip length.* In general, an *apparent slip length* ℓ^{app} can be defined by comparing the linear extrapolation of the velocity in the center., at $y = 0$, *i.e.*, $\gamma(0)b$ with the wall velocity and equating this with ℓ^{app} times the apparent shear rate $\gamma^{ext} = v^{wall}/b$. This prescription corresponds to

$$\ell^{app} = b\,(1 - \gamma(0)/\gamma^{ext}) = b\,(1 - (\gamma_1 + \gamma_2)/\gamma^{ext})\,. \tag{75}$$

The dependence of the apparent slip length on the surface angular velocity is shown in Fig.5. Notice that he apparent slip length can be determined experimentally (Joseph and Tabeling 2005).

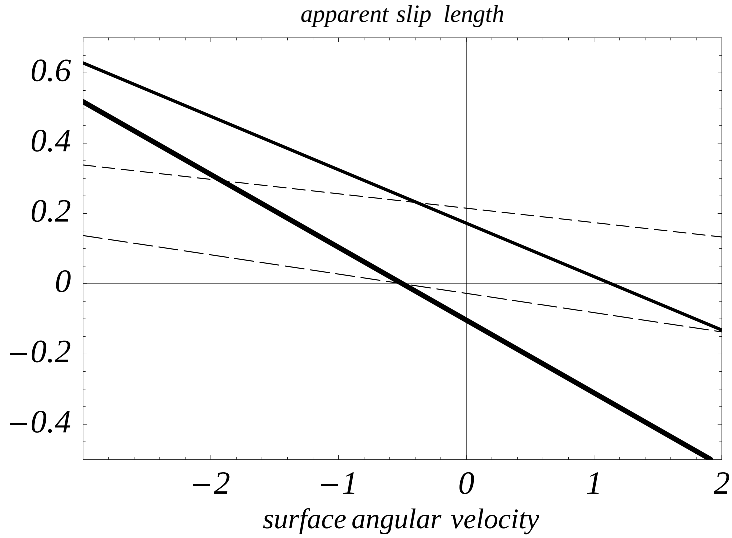

FIGURE 5. The apparent slip length, in units of b as function of surface angular velocity w^{wall}, in units of the imposed shear rate γ^{ext}. For all curves, the parameters q and ℓ are equal to 1 and 0.2, respectively. The velocity slip length is equal to 0 for the two curves which cross the horizontal line at -0.5 and it is 0.3 for the two other ones. The other slip length ℓ_w is equal to 0 for the full curves and 0.5 for the dashed ones.

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4.2.3. *Effective viscosity.* An effective viscosity coefficient η^{eff} is defined as the ratio of the tangential shear stress at the upper plate divided by the external shear rate. This implies

$$\eta^{eff} = (\gamma_1/\gamma^{ext})\, \eta\,. \tag{76}$$

In Fig.6, the effective viscosity, in units of the shear viscosity, is displayed as function of the spin coupling parameter q. For all curves, the spin diffusion length ℓ, in units of b, is 0.2. The curves staring at 1 and at $1.3 \approx 0.77$ are for $\ell_v = 0$ and $\ell_v = 0.3$, respectively. The thick curves, increasing with increasing q pertain to $w^{wall} = 0$, the decreasing curves are for $w^{wall} = -1$. The parameters for the dashed increasing curves are those of the thick curves above but with $\ell_w = 0.3$ rather than $\ell_w = 0$. The exactly and the approximately horizontal dashed lines are for $w^{wall} = -0.5$.

For vanishing angular velocity at the wall, the relative effective viscosity increases with increasing spin coupling, *i.e.*, with an increasing ratio of the rotational viscosity to the shear viscosity. This viscosity increase, caused by a hindered rotational motion, is similar to the magnetic field induced increase of the viscosity of a ferro-fluid, as described in McTague (1969) and Levi *et al.* (1973). Here, the influence of the boundary is diminished by the spin slip, *i.e.*, by $\ell_w > 0$. On the other hand, a surface induced rotation of the particles leads to a decrease of the effective viscosity.

In experiments, the linear dimension, *i.e.*, the distance $2b$ between the plane walls can be varied. So it is of interest to show, in Fig.7 the effective viscosity as function of the

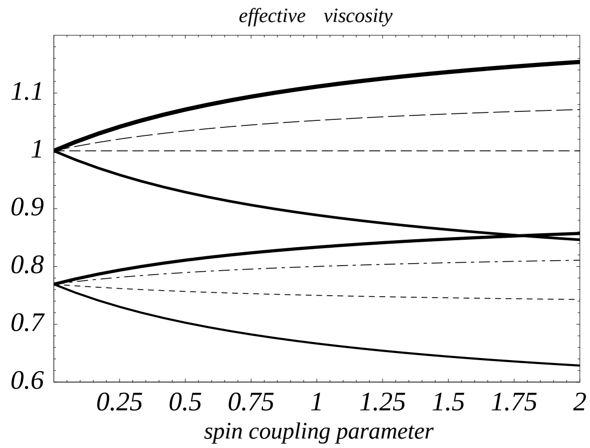

FIGURE 6. The effective viscosity, in units of the shear viscosity, as function of the spin coupling parameter q. The parameters $\{\ell, \ell_v, \ell_w, w^{wall}\}$, from top to bottom, are $\{0.2, 0, 0, 0\}$, $\{0.2, 0, 0.2, 0\}$, $\{0.2, 0, 0, -0.5\}$, $\{0.2, 0, 0, -1\}$, $\{0.2, 0.3, 0, 0\}$, $\{0.2, 0.3, 0.2, 0\}$, $\{0.2, 0.3, 0, -0.5\}$, and $\{0.2, 0.3, 0, -1\}$,.

.

ratio b/ℓ, where ℓ is recalled as the spin-diffusion length. A logarithmic scale is used for b/ℓ. Notice: the value $\ell = 0.2$ in Fig.6 actually means $\ell/b = 0.2$ which corresponds to $b/\ell = 5$ in Fig.7. For large values of b/ℓ all curves approach the horizontal line $\eta^{eff}/\eta = 1$. For comparison: in simple fluid without spin-coupling, *i.e.*, for $q = 0$, but with a non-zero velocity slip length ℓ_v, the effective viscosity is equal to $\eta^{eff}/\eta = (b/\ell_v)/(1 + b/\ell_v)$. In that case, the pertaining curve approaches the asymptotic value 1 from below.

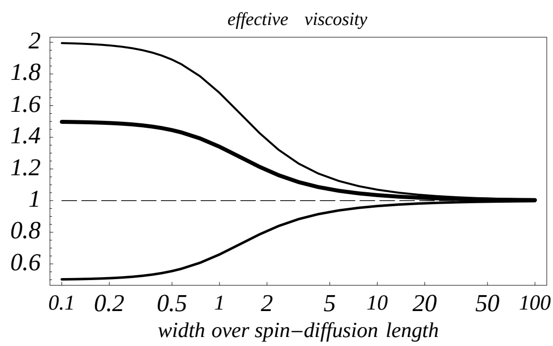

FIGURE 7. The effective viscosity, in units of the shear viscosity, as function of b/ℓ. The spin coupling parameter is $q = 0.5$, the slip lengths ℓ, ℓ_v, ℓ_w are zero, for all curves. The angular velocity at the wall, w^{wall}, from top to bottom, is 0.5, 0 (thick curve), -0.5 (dashed line), and -1.

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4.2.4. *Rotation driven flow.* Consider a situation, where the walls are at rest but a rotation of the particles is imposed close to the walls, in opposite direction, such that plane Couette geometry applies. Torques due electromagnetic fields of evanescent waves provide a feasible mechanism for the generation of such a spin-rotation at the walls. An example for the resulting profiles of the velocity and of the angular velocity is shown in Fig. 8, There $w^{wall} = -1$, $q = 1$, $\ell = 0.2b$ and $\ell_v = \ell_w = 0$ were chosen. Units are as in the previous figures, except that the velocity has been multiplied by a factor 10 in order to show the S-shape of the curve more clearly.

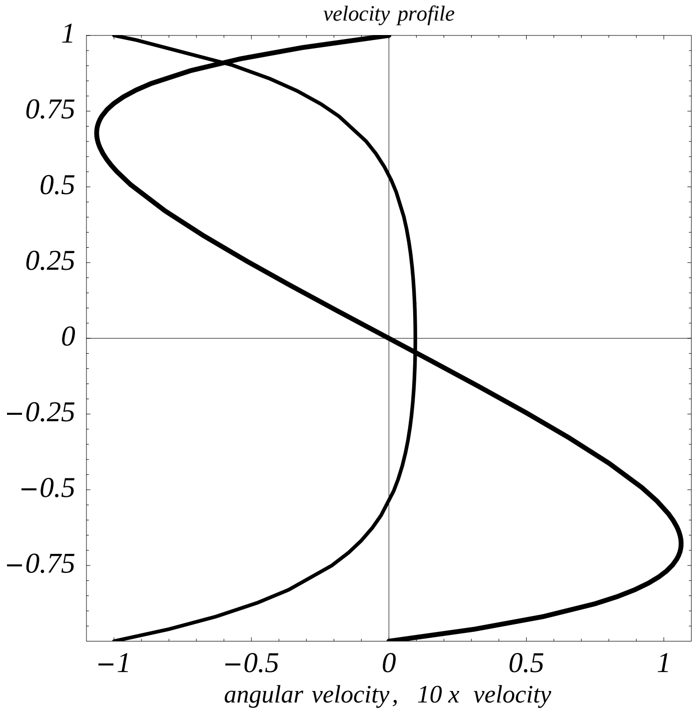

FIGURE 8. The velocity (S-shaped curve) and angular velocity profiles for $v^{wall} = 0$ and $w^{wall} = -1$. The values of the other parameters $\{q, \ell, \ell_v, \ell_w\}$ are $\{1, 0.2, 0, 0\}$.

4.3. Dipole subjected to a Couette flow.

4.3.1. *Wall-induced dipole.* First, the spatial dependence of the dipole vector caused by $d^{wall}_\mu \neq 0$ is considered for the plane Couette symmetry. For simplicity, it is assumed that the angular velocity w_μ is spatially constant and equal to $w\, e^y_\mu$ with $w = -0.5\gamma^{ext}$. Furthermore, the bulk coupling terms between flow and dipole are ignored. Then, with $\Phi^d_\mu \approx A_d\, d_\mu$ and for an isotopic dipole diffusion tensor, the stationary version of the relaxation equation (41) reduces to

$$-D^d A_d\, \Delta d_\mu - \varepsilon_{\mu\nu\lambda} w_\nu\, d_\lambda + \nu^d A_d\, d_\mu = 0\,.$$

This equation is equivalent to

$$-\,\kappa_0^{-2}\,\Delta d_\mu - \varphi\, \varepsilon_{\mu\nu\lambda} h_\nu\, d_\lambda + d_\mu = 0\,,\;\; \kappa_0^2 = D^d/\nu^d\,,\;\; \varphi = w\,\tau^d\,, \qquad (77)$$

where $\tau^d = (A_d\, \nu^d)^{-1}$ is recalled as the dipole relaxation time and $h_\nu = e^z_\nu$ is used for ease of notation. With the help of the projection tensors (Hess 2015),

$$P^{(0)}_{\mu\nu} = h_\mu h_\nu\,,\;\; P^{(\pm)}_{\mu\nu} = \tfrac{1}{2}(\delta_{\mu\nu} - h_\mu h_\nu \mp i\,\varepsilon_{\mu\lambda\nu} h_\lambda)\,,$$

which have the property

$$P^{(m)}_{\mu\sigma}\,\varepsilon_{\sigma\lambda\nu}\,h_\lambda = i\,m P^{(m)}_{\mu\nu}\,,\;\; m = 0, \pm 1\,,$$

the pseudo-spherical components $d^{(m)}_\mu = P^{(m)}_{\mu\sigma} d_\sigma$ of the dipole vector are seen to obey

$$-\,\kappa_0^{-2}\,\Delta d^{(m)}_\mu + (1 - i\,m\,\varphi)\,d^{(m)}_\mu = 0\,. \tag{78}$$

The solution of this equation, in accord with the Couette symmetry, is of the form

$$d^{(m)}_\mu \sim sinh(\kappa_m\, y)$$

where the inverse length κ_m is determined by

$$\kappa_m^2 = \kappa_0^2\,(1 - i\,m\,\varphi) \tag{79}$$

and consequently

$$\kappa_m = \kappa_0\,(1 + m^2\,\varphi^2)^{1/2}\,(\cos(\alpha_m/2) - i\,\sin(\alpha_m/2))\,,\;\; \cos(\alpha_m) = (1 + m^2\,\varphi^2)^{-1/2}\,. \tag{80}$$

For a weak flow with $|\varphi| << 1$ one has $\kappa_m \approx \kappa_0\,(1 - i\,m\,\varphi/2)$.

The slip boundary condition (51) leads to

$$d^{(m)}_\mu = sinh(\kappa_m\, y)\,(sinh(\kappa_m\, b) + \ell_d\,\kappa_m\, cosh(\kappa_m\, b))^{-1}\;P^{(m)}_{\mu\nu} d^{wall}_\nu = S_m P^{(m)}_{\mu\nu} d^{wall}_\nu\,, \tag{81}$$

where ℓ_d and d^{wall}_ν are recalled as the dipole slip length and the surface induced dipole. Notice that

$$d_\mu = d^{(0)}_\mu + d^{(1)}_\mu + d^{(-1)}_\mu\,.$$

The components of the dipole vector parallel to the velocity and to the gradient direction are

$$d_\parallel = e^x_\mu\, d_\mu = (1/2)\,(S_1 + S_{-1})\,d^{wall}_x + (i/2)\,(S_1 - S_{-1})\,d^{wall}_y \tag{82}$$

and

$$d_\perp = e^y_\mu\, d_\mu = (1/2)\,(S_1 + S_{-1})\,d^{wall}_y - (i/2)\,(S_1 - S_{-1})\,d^{wall}_x\,. \tag{83}$$

Due to the rotation of the particles caused by the flow, one has $d_\perp \neq 0$ even when $d^{wall}_y = 0$, as long as $d^{wall}_x \neq 0$.

When the coupling of the dipole field with the velocity and the angular velocity is ignored, the stationary solution of the relaxation equation (59), where it was assumed that the dipole vector has only a component parallel to the velocity, is of the form

$$d_\parallel = d = d_3\, sinh(y\,\kappa_0)\,,\;\; \kappa_0^2 = \nu^d/D^d\,.$$

Notice that κ_0^{-1} is a characteristic length associated with the dipole diffusion and relaxation. The value of the coefficient d_3 is determined by the boundary condition (61). The result is

$$d_3 = d^{wall}\,(sh_d + \ell_d\,\kappa_0\, ch_d)^{-1}\,,\;\; sh_d = sinh(b\kappa_0)\,,\; ch_d = cosh(b\kappa_0)\,. \tag{84}$$

4.3.2. *Dipole due to surface coupling.* The influence of a flow on the dipole via the boundary layer coupling as described by (48) is discussed next. As before, Φ_μ is approximated by $A_d\, d_\mu$. Then the boundary condition can be rewritten as

$$d_\mu - d_\mu^{wall} = -\ell_d\, n_\nu \nabla_\nu d_\mu \,+ A_d^{-1}\left(C_{dv}\, F_\mu^v + C_{dw}\, \varepsilon_{\mu\nu\lambda}\, n_\nu\, F_\lambda^w\right)\,,\ \ \ell_d = C_d\, D^d\, \nu_0^{-1}\,, \tag{85}$$

with

$$F_\mu^v = p_0^{-1}\, k_\mu^{tan}\,,\ F_\lambda^w = \nu_0^{-1}\, w_0^{-1}\, \Theta^{-1}\, n_\kappa\, J_{\kappa\lambda} = -\nu_0^{-1}\, w_0^{-1}\, D^J\, \nabla_\kappa w_\lambda\,.$$

The last equality applies to the isotropic approximation for the angular momentum diffusion tensor. The boundary condition (85) corresponds to the simpler slip condition (51) with d_μ^{wall} replaced by $d_\mu^{wall} + d_\mu^{walleff}$ where the effective surface dipole is determined by the coupling coefficients C_{dv} and C_{dw}. For the Couette geometry considered here, one has $d_\mu^{walleff} = d^{walleff}\, e_\mu^x$, with

$$d^{walleff} = -A_d^{-1}\left[C_{dv}\, p_0^{-1}\, \eta\left(\gamma + (\eta^{rot}/\eta)\,(\tfrac{1}{2}\gamma + w)\right) + C_{dw}\, \nu_0^{-1} w_0^{-1}\, D^J\, w'\right]\,. \tag{86}$$

For $(\frac{1}{2}\gamma + w) \approx 0$ and $w' \approx 0$ this expression reduces to

$$d^{walleff} \approx -A_d^{-1} C_{dv}\, p_0^{-1}\, \eta\, \gamma.$$

4.3.3. *Flow-induced electric polarization.* Next, the influence of the bulk coupling terms in equation (59) is taken into account, subject to the assumption that the influence of the dipole vector on the flow is small. This means, the solutions given above for the shear rate and for the angular velocity are used as inhomogeneity in the dynamic equation for the dipole vector. Thus the ansatz

$$d = d_2\, sinh(\kappa y) + d_3\, sinh(y\, \kappa_0)\,, \tag{87}$$

is made. For κ see the formula (68). Insertion into (59) and use of (63) and (64) leads to

$$(-\frac{\kappa^2}{\kappa_0^2} + 1)\, A_d\, \nu^d\, d_2 = \kappa\, (L^{dv}\, \gamma_2 + L^{d1}\, w_2)\,.$$

Provided that $\kappa \neq \kappa_0$, one finds

$$d_2 = \kappa\, \tau^d\, (L^{dv}\, \gamma_2 + L^{d1}\, w_2)\left(1 - \frac{\kappa^2}{\kappa_0^2}\right)^{-1}\,. \tag{88}$$

Here $\tau^d = (A_d\, \nu^d)^{-1}$, cf. (25), is the dipole relaxation time. Clearly, the flow-induced dipole coefficient d_2 is non-zero only when at least one of the two bulk coupling coefficients L^{dv} and L^{d1} does not vanish. Instead of (84), the dipole boundary condition (61) now implies

$$d_3 = \left(d^{wall} - d_2\, (sh + \ell_d\, \kappa\, ch)\right)\, (sh_d + \ell_d\, \kappa_d\, ch_d)^{-1}\,. \tag{89}$$

For the special case $d^{wall} = 0$ and $\ell_d = 0$, the flow-induced dipole vector becomes

$$d_\mu = d_\parallel\, e_\mu^x\,,\ \ d_\parallel = d_2\, \left(sinh(\kappa y) - (sh/sh_d)\, sinh(y\, \kappa_0)\right)\,, \tag{90}$$

with d_2 given by (88). The ensuing electric polarization $P_\mu \sim (\rho/m)\, d_\mu$ is parallel to the flow direction and thus difficult to detect experimentally. The angular velocity occurring in the dynamic equation (41), however, also gives rise to a component parallel to the y-direction. When this rotation effect is treated as a perturbation, one finds in lowest order

$$d^{(1)}_{\mu} = \tau^{d}\, \varepsilon_{\mu\nu\lambda}\, w_{\nu}\, d^{(0)}_{\lambda}$$

where $d^{(0)}_{\lambda} \sim e^{x}_{\lambda}$ is the dipole vector considered above. This leads to

$$d^{(1)}_{\mu} = d_{\perp}\, e^{y}_{\mu}\,,\ \ d_{\perp} = \tau^{d}\, w\, d\,, \tag{91}$$

where w and d are given by (64) and (87). Notice that the Couette symmetry is conserved, since w is symmetric whereas d is antisymmetric with respect to the exchange $y \rightarrow -y$.

5. Concluding remarks

In this article, equations governing the non-equilibrium dynamics of the linear and the angular velocities as well as of the vector parallel to the average dipole moment are stated. These equations are based on local conservation and balance laws and on extended constitutive relations for the symmetric and the antisymmetric parts of the pressure tensor and for the flux tensors of the spin and the dipole. The boundary conditions needed to supplement the partial differential equations are derived within the framework of non-equilibrium thermodynamics, following an idea introduced by Ludwig Waldmann. Applications are presented here for the plane Couette flow geometry. The extension to a plane Poiseuille flow as in Brunn (1975), Hess and Koo (1989), Condiff and Dahler (2004), and Heidenreich *et al.* (2007) is straight forward.

Experimental and theoretical information on the phenomenological coefficients characterizing the bulk and the surface behavior are desirable. Kinetic theory (Hess and Waldmann 1966) and a mesoscopic approach based on a generalized Fokker-Planck equation (Hess 1968a, 1976, 1979) provided expressions for some, but not all, of the coefficients occurring in the dynamic equations used here. Computer simulations provide some microscopic insight (Evans and Streett 1978; Hess and Loose 1989; Bonhuis *et al.* 2009; Hansen *et al.* 2010). Further studies along these lines are desirable.

Kinetic theory methods can and have been applied for the elucidation and calculation of surface phenomena in rarefied gases (Waldmann 1976). The study of physical models and the formulation of a microscopic theory for the boundary coefficients of dense fluids remains a challenge.

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