Hydrodynamics of chiral liquids and suspensions

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We obtain hydrodynamic equations describing a fluid consisting of chiral molecules or a suspension of chiral particles in a Newtonian fluid. The stresses arising in a flowing chiral liquid have a component forbidden by symmetry in a Newtonian liquid. For example, a chiral liquid in a Poiseuille flow between parallel plates exerts forces on the plates, which are perpendicular to the flow. A generic flow results in spatial separation of particles of different chirality. Thus even a racemic suspension will exhibit chiral properties in a generic flow. A suspension of particles of random shape in a Newtonian liquid is described by equations which are similar to those describing a racemic mixture of chiral particles in a liquid.

Equations of hydrodynamics express conservation of mass, momentum and energy, and can be written as

\[
\begin{align*}
\partial_t \rho + \nabla \cdot \mathbf{J} &= 0, \\
\partial_t \mathbf{P} + \nabla \cdot \mathbf{J}_E &= 0, \\
\partial_t E + \nabla \cdot \mathbf{E} &= 0.
\end{align*}
\]

(1a) (1b) (1c)

Here \(\partial_t\) and \(\partial_i\) denote time and spatial derivatives, \(\rho\), \(\mathbf{P}\), and \(E\) are correspondingly the densities of mass, momentum and energy, and \(\mathbf{J}\), \(\mathbf{J}_E\) and \(\mathbf{E}\) are the flux densities of mass, energy and momentum (we indicate vector quantities by bold face symbols and second rank tensors by hats). The flux densities can be expressed in terms of the hydrodynamic variables: the pressure \(p(r, t)\), temperature \(T(r, t)\) and the hydrodynamic velocity \(\mathbf{v}(r, t)\), which we define via the equation

\[
\rho \mathbf{v} = \mathbf{J} = \mathbf{P}.
\]

(2)

To lowest order in spatial derivatives we have

\[
\Pi_{ij} = \rho \mathbf{v}_i \mathbf{v}_j + p \delta_{ij} - \eta \mathbf{v}_i \mathbf{v}_j - \frac{2}{3} \delta_{ij} \text{div} \mathbf{v},
\]

(3)

where \(\mathbf{v}_i = \partial_i \mathbf{v} + \partial_i \mathbf{v} - \frac{2}{3} \delta_{ij} \text{div} \mathbf{v}\) is the rate of shear strain, and \(\eta\) and \(\zeta\) are the first and the second viscosities. This leads to the Navier-Stokes equations, which should be supplemented by the equation of state of the fluid and the expression for the energy current in terms of the hydrodynamic variables.

For a dilute suspension of particles in a Newtonian liquid, the basic hydrodynamic equations need to be supplemented by the conservation law for the current of suspended particles,

\[
\partial_t n + \mathbf{v} \cdot \nabla n + \text{div} \mathbf{j} = 0.
\]

(4)

Here \(n(r, t)\) is the density of suspended particles, and \(\mathbf{j}(r, t)\) their flux density (relative to the fluid). To linear order in the gradients of concentration, temperature and pressure the latter can be written as

\[
\mathbf{j} = -D \nabla n - n \lambda_T \nabla T - n \lambda_p \nabla p.
\]

(5)

Equation (4) remains unchanged and can be considered as a definition of the hydrodynamic velocity \(\mathbf{v}\), which is, generally speaking, different from the local velocity \(\mathbf{u}(r, t)\) near an individual particle of the suspension.

There are corrections to the flux densities of various quantities, which are higher orders in spatial derivatives of the hydrodynamic variables (for a review see, for example, Refs. [2] [3]). Moreover, there are nonlocal corrections to the Navier-Stokes equations, which can not be expressed in terms of higher order spatial derivatives of hydrodynamic variables [4, 5, 6, 7].

Several studies focused on the effects of chirality on the motion of suspended particles in hydrodynamic flows [8, 9, 10, 11, 12, 13, 14, 15, 16]. It was shown that non-chiral magnetic colloidal particles can self-assemble into chiral colloidal clusters [17].

In this article, we develop a hydrodynamic description for the case of a suspension containing both right-handed and left-handed chiral particles in a centrosymmetric liquid. We show that in this case the corrections to the Navier-Stokes equations contain new terms, which are associated with the chirality of the particles. The significance of these corrections is that they describe new effects, which are absent in the case of centrosymmetric liquid. Since certain types of hydrodynamic flow lead to separation of particles with different chirality, these corrections are important even in initially racemic suspensions of chiral particles. For simplicity we consider the case of incompressible fluids.

In a given flow an individual particle of the suspension undergoes a complicated motion which depends on the initial position and orientation of the particle. The hydrodynamic equations can be written for quantities which are averaged over the characteristic spatial and temporal scales of such motion.

In the presence of chirality the following contribution to momentum flux density is allowed by symmetry:

\[
\Pi^{\text{ch}}_{ij} = n^{\text{ch}} \alpha \eta \epsilon_{ijk} (\partial_i \mathbf{v}_j + \partial_j \mathbf{v}_i) + \eta \alpha_1 \left[ \mathbf{v}_i \partial_j n^{\text{ch}} + \mathbf{v}_j \partial_i n^{\text{ch}} \right],
\]

(6)

where \(\omega_i(r) = \frac{1}{2} \epsilon_{ijk} \partial_j v_k(r)\) is the flow vorticity, and \(n^{\text{ch}} = (n_+ - n_-)\) is the chiral density, with \(n_+\) and
\(n_\text{--}\) being the volume densities of right- and left-handed particles respectively. Equations 1 should be supplemented by the expression for the chiral current, defined as the difference between the currents of right- and lefthanded particles. Separating it into the convective part, \(v n^{ch}\), and the current relative to the fluid, \(j^{ch}\), we write the continuity equation as

\[
\partial_t n^{ch} + \text{div}(vn^{ch}) + \text{div}j^{ch} = 0.
\]

(7)

Besides the conventional contribution given by Eq. 5 with \(n\) replaced by \(n^{ch}\), the chiral current contains a contribution, \(j^{ch}\), which depends on the flow vorticity:

\[
\tilde{j}_i^{ch} = n[\beta_i \nabla^2 \omega_i + \beta_1 \omega_j V_{ij}],
\]

(8)

where \(n = n_+ + n_-\). The contributions to \(\tilde{j}^{ch}\) containing only \(n \omega_i\) are not allowed as there should be no chiral current in rigidly rotating fluid.

In Eqs. 6 and 7 we keep only the leading terms in the powers of \(\partial_i V_{ij}\), or in the order of spatial derivatives of \(v\). Although these terms are subleading in comparison to those in the conventional hydrodynamic approximation, they describe new effects which are absent in the latter.

Note that according to the Navier-Stokes equations

\[
\nabla^2 \text{curl}(v) = \frac{\rho}{\eta}\{\partial_t \text{curl}(v) + \text{curl}[\nabla^2 \nabla]v\}.
\]

(9)

Thus the first term in Eq. 8 arises either due to non-stationary or non-linear in \(v\) nature of the flow. In particular, in stationary flows and to zeroth order in the Reynolds number \(\nabla^2 \text{curl}(v) = 0\) and this term vanishes.

In spatially inhomogeneous flows the suspended particles rotate, generally speaking, relative to the surrounding fluid. This gives rise to separation of particles of different chirality due to the propeller effect, and to the chiral contribution to the momentum flux, Eq. 6.

The rotation of the particles relative to the fluid arises due to two effects:

i) In the presence of the spatial dependence of vorticity, \(\omega_i(r)\), the angular velocity of a particle is different from \(\omega_i(r)\). This results in Eq. 6 and the first term in Eq. 8.

ii) A non-uniform hydrodynamic flow induces orientational order in suspended particles similar to nematic order in liquid crystals. In the presence of flow vorticity orientation of particles induces their rotation with respect to the surrounding fluid. This contributes both to the chiral stress and the chiral flux. The latter contribution is described by the second term in Eq. 8. The contribution to the chiral part of the stress tensor associated with orientational order was discussed in Ref. 8.

In most cases of practical importance the Reynolds number corresponding to the particle size \(R\) is small. In this regime the coefficients \(\alpha\), \(\alpha_1\), \(\beta\), and \(\beta_1\) in Eqs. 6 and 8 can be obtained by studying the particle motion in the surrounding fluid in the creeping flow approximation [19, 20]. In this approximation the motion of particle immersed in the liquid is of purely geometrical nature (see for example Ref. 20). Dimensional analysis gives an estimate

\[
\alpha \sim \alpha_1 \sim \chi R^4, \quad \beta \sim \chi R^3,
\]

(10)

where \(R\) is the characteristic size of the particles, and the dimensionless parameter \(\chi\) characterizes the degree of chirality in shape of the particles.

The relative magnitudes of the different terms in Eqs. 6 and 8 depend on the particle geometry. For example, particles with the symmetry of the isotropic helicoid [13] can not be oriented in a shear flow. Therefore the second term in Eq. 6 vanishes is this case.

The degree of orientation of the particles can be obtained by balancing the characteristic directional relaxation rate due to the Brownian rotary motion, \(\sim T/\eta R^3\) with \(T\) being the temperature, with the rate of orientation due to the shear flow, \(\sim V_{ij}\). Thus at small shear rates the degree of particle orientation is \(\sim V_{ij} \eta R^3/T\). This leads to the estimate

\[
\beta_1 \sim \chi \eta R^4/T.
\]

(11)

The second term in Eq. 8 is the leading term in the expansion in the rotational Reynolds number \(Pe \sim V_{ij} \eta R^3/T\). At larger Reynolds numbers terms of higher power in \(V_{ij}\) should be taken into account. For \(Pe \gg 1\) the particle orientation becomes strong, and the corresponding contribution to the chiral current can be estimated as

\[
\tilde{j}^{ch} \sim \chi R \omega.
\]

(12)

Equations 10 and 11 are written for the case when there is no external force acting on the particles, e.g. for a suspension of uncharged neutrally buoyant particles. In the presence of an external force \(F\), there will be additional contributions to the chiral flux. The linear in \(F\) contributions can be constructed by contracting the antisymmetric tensor \(e_{ijk}\) with the velocity \(v_i\), force \(F_i\) and two derivatives \(\partial_i\). For example, the following terms exist when \(F\) is constant: \((F \cdot \nabla)\omega, F \times \nabla^2 \nabla, \nabla (F \cdot \omega)\). These terms arise when the orientation of the suspended particles can be characterized by a polar vector. In this case the degree of particle orientation can be estimated as \(\sim R F/T\). Thus the coefficients with which these terms enter the chiral current \(j^{ch}\) are of order as \(\chi R^3/T\). In the case when particles do not have a polar axis the degree of their orientation, and the corresponding contribution to the chiral flux are quadratic in \(F\) for small force.

The chiral contribution to the stress tensor Eq. 6 leads to several new effects. Consider a Poiseuille flow of a chiral liquid between parallel planes separated by a distance \(d\): \(v_x = -\partial_x p (d^2 - 4y^2)/8\eta, v_z = v_y = 0\) (see Fig. 1). with \(\partial_x p\) being the pressure gradient along the flow. If the chiral density is uniform the chiral part of the stress tensor has only two non-vanishing elements, \(\Pi_{yz} = -\alpha n^{ch} \partial_x p/2\). It describes a pair of opposing forces
per unit area exerted by the liquid on the top and bottom planes. These forces are perpendicular to the flow, as shown in Fig. 1. Assuming $n^\text{ch} R^3 \sim 1$ and using Eq. (10) the magnitude of the chiral force per unit area of the plane can be estimated as $\sim \chi R \delta x p$.

If $n^\text{ch}$ is constant in space, then the volume force density generated by the chiral part of the stress tensor is $f_i^\text{ch} = -\partial_j \Pi_{ij}^\text{ch} = -n^\text{ch} \alpha \eta \nabla^2 \omega_i$. Then it is clear from Eq. (9) that $f_i^\text{ch}$ is generated only in nonstationary or nonlinear flows. In the special case of stationary Poiseuille flow the chiral part of the stress tensor does not generate a force density inside the fluid even at large Reynolds numbers. Thus the flow pattern is not affected by the fluid chirality. However, in a generic flow with converging or diverging flow lines the fluid chirality does affect the flow pattern. This is especially evident in flows, which have a mirror symmetry in the absence of chiral corrections. In these cases the chiral contribution to the stress tensor results in mirror asymmetric corrections to the flow velocity. For example a chiral liquid flowing between two surfaces with a varying distance between them, see Fig. 1, will develop a helicoidal component of velocity with non-vanishing vorticity along the flow direction. This can be checked explicitly for the exactly solvable case of stationary Couette flow (§ 23 of Ref. 1).

Another consequence of Eq. (8) is a possibility of separation of particles of different chirality in hydrodynamic flows. It has been observed in numerical simulations [10 11 12 13] and recent experiments [15]. We note that according to Eq. (9) in a stationary flow and in the linear approximation in the shear rate $\partial_i v_j$, we have $\nabla^2 \omega_i = 0$, and the first term in Eq. (8) vanishes. Thus separation chiral isomers in the absence of external forces acting on the particles is possible either in non-linear or in non-stationary flows.

In the practically important case of a stationary Couette flow, the first term in Eq. (8) vanishes for arbitrary Reynolds numbers, and the chiral current arises only due to orientation of the particles. The latter increases with the rotational Péclet number and saturates at $\Pe \gg 1$. In this regime the chiral current becomes linear in the flow vorticity $\omega$, Eq. (12). The linear dependence of $J_{\text{ch}}$ on $\omega$ and saturation of the proportionality coefficient at $\Pe \to \infty$ has been observed numerically in Refs. [10 12].

Separation of particles by chirality can also be achieved by subjecting the particles to an external circularly polarized electric or magnetic field. The orientation of the particles along the field (e.g. due to the presence of a permanent electric or magnetic dipole moment or anisotropy of the polarization matrix) will cause their rotation relative to the surrounding fluid. This will produce a chiral flux along the circular polarization axis due to the propeller effect [21 22] (similarly, a stationary electric or magnetic field will cause separation of particles by chirality in a rotating fluid). We also note that there are other mechanisms of chiral current generation which do not involve transfer of angular or linear momentum from the ac-field to the particles [23]. Chiral separation by circularly polarized magnetic field has been recently observed in the experiments of Refs. [24 25]. The full quantitative analysis of this effect is beyond the scope of this work. Here we restrict the treatment to the experimentally relevant regime of strong and slowly varying fields, where thermal fluctuations can be neglected and the particles are fully polarized along the instantaneous electric field. In this case the problem is of purely geometric nature. The chiral current becomes independent of the viscosity of the fluid and can be expressed in terms of the Berry adiabatic connection [20]. Below we express this adiabatic connection in terms of the resistance matrix of the particle [18]. The latter relates the external force $F$ and torque $\tau$ exerted on the particle to the linear velocity $\delta v$ and angular velocity $\delta \omega$ relative to the fluid,

$$\begin{pmatrix} F \\ \tau \end{pmatrix} = -\begin{pmatrix} \hat{K} & \hat{C} \\ \hat{C} & \hat{\Omega} \end{pmatrix} \begin{pmatrix} \delta v \\ \delta \omega \end{pmatrix}. \tag{13}$$

Here we chose the origin of the reference frame at the reaction center, so that the coupling tensor $\hat{C}$ is symmetric [18]. Since a uniform electric field exerts no force on the particle we immediately obtain the relations,

$$\delta v = -\hat{K}^{-1} \hat{C} \delta \omega, \tag{14a}$$
$$(\tau = -\hat{\Omega} \delta \omega. \tag{14b}$$

where we introduced the notation $\hat{\Omega} = \hat{\Omega} - \hat{C} \hat{K}^{-1} \hat{C}$.

The orientation of the particle relative to the lab frame is described by the three Euler angles, $\phi, \theta$ and $\psi$ [26]. We choose the axes of the body reference frame, $x_1, x_2, x_3$, so that $x_3$ points along the dipole moment of the particle. For fully polarized particles the latter points along the instantaneous direction of the electric field. Thus $\theta$ and $\phi$ coincide with the polar angles of the electric field vector. The value of $\psi$ remains undetermined because the particle can be rotated by an arbitrary angle about $x_3$ without changing its polarization energy. When the orientation
of the electric field changes with time the particle orientation angle about the instantaneous field direction, \( \psi(t) \), also changes. Its time evolution can be determined from the condition that projection of the torque onto the \( x_3 \) axis must vanish. This is clear because the torque \( \tau = d \times E \) is perpendicular to the dipole moment \( d \), which points along \( x_3 \). Writing Eq. (14b) in the body frame, \( \Omega_{31} \omega_1 = 0 \), and expressing \( \omega_1 \) in terms the Euler angles, \( \omega_1 = \dot{\phi} \sin \theta \sin \psi + \dot{\theta} \cos \psi \), etc. we obtain:

\[
\begin{align*}
A_\phi &= -\cos \theta - \frac{\sin \theta}{\Omega_{33}} \left( \Omega_{31} \sin \psi + \Omega_{32} \cos \psi \right), \\
A_\theta &= -\frac{1}{\Omega_{33}} \left( \Omega_{31} \cos \psi + \Omega_{32} \sin \psi \right).
\end{align*}
\]

This defines \( \dot{\psi} \) in terms of \( \dot{\theta} \) and \( \dot{\phi} \). The displacement of the particle can be obtained from Eq. (14a). Instead of presenting the general formulae we focus on the practical case of an ac-field of frequency \( \omega_0 \) circularly polarized in the \( xy \) plane: \( \theta = \pi/2, \phi = \omega_0 t \). In this case it is easy to see that the average velocity along the \( x \) and \( y \) axes vanishes. For the average \( z \)-component of the velocity an elementary calculation gives:

\[
\delta v_z = \frac{\omega_0}{2\Omega_{33}} \text{Tr} \left[ \tilde{K}_{-1} \tilde{C} \begin{pmatrix} -\Omega_{33} & 0 & 0 \\ 0 & -\Omega_{33} & 0 \\ \Omega_{31} & \Omega_{32} & 0 \end{pmatrix} \right],
\]

where the resistance tensor is expressed in the body frame, and \( \chi \) can be viewed as the dimensionless measure of the particle chirality. Since the coupling tensor \( \tilde{C} \) changes sign under inversion it is clear that particles of opposite chirality will move in opposite directions along the \( z \) axis. By order of magnitude the chiral separation velocity \( v_z^{ch} \sim R \omega_0 \), which is consistent with the recent experimental findings [24, 25].

In the regime where the polarization energy in the electric field is smaller than the temperature the chiral current is reduced compared to the above estimate. The leading contribution at weak fields is proportional to the intensity of the ac-radiation [22].

So far we discussed the case where the suspended particles consist of the opposite enantiomers of a single species. However, the effects considered above exist even in suspensions of particles of completely random shape in a non-chiral liquid. In this case the definition of chirality requires clarification. For example one can define the chirality of a particle by considering the direction of its motion in a hydrodynamic shear flow or under the action of an ac-electromagnetic field. Thus the same individual particle can exhibit different chirality with respect to different external perturbations.

The set of Eqs. (13) still holds for a suspension of random particles. In this case the auxiliary quantities \( n^{ch} \) and \( \tilde{J}^{ch} \) are defined in terms of the chiral component of the stress tensor Eq. (6) and correspond to quantities averaged over the random shape of the particles.

Finally, we note that symmetry allows contributions to \( \tilde{J}^{ch} \) that are proportional to the external magnetic field \( B \), for example \( \tilde{J}^{ch} \propto n^{ch} (\nabla \times B) \). We believe that these effects are of fluctuational origin similar to those discussed in Refs. [4, 5, 6, 7] and do not study them in this work.

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