Hydrodynamics of Liquids of Chiral Molecules and Suspensions Containing Chiral Particles

A. V. Andreev,[1] D. T. Son,[2] and B. Spivak[1]
[1]Physics Department, University of Washington, Seattle, Washington 98195, USA
[2]Institute for Nuclear Theory, University of Washington, Seattle, Washington 98195, USA
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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 hydrodynamic velocity and stresses arising in a flowing chiral liquid have components that are 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.

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

$$\partial_t \rho + \partial_i J_i = 0, \tag{1a}$$

$$\partial_t P_i + \partial_j \Pi_{ij} = 0, \tag{1b}$$

$$\partial_t E + \partial_i J_E = 0. \tag{1c}$$

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

$$\rho \mathbf{v} = \mathbf{J} \equiv \mathbf{P}. \tag{2}$$

To lowest order in spatial derivatives we have [1]

$$\Pi_{ij} = \rho v_i v_j + p\delta_{ij} - \eta V_{ij} - \zeta \delta_{ij} \mathrm{div}\mathbf{v}, \tag{3}$$

where $V_{ij} = \partial_j v_i + \partial_i v_j - \frac{2}{3}\delta_{ij}\mathrm{div}\mathbf{v}$ is the rate of shear strain, and η and ζ 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 [1] by the conservation law for the current of suspended particles,

$$\partial_t n + \mathbf{v} \cdot \nabla n + \mathrm{div}\mathbf{j} = 0. \tag{4}$$

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

$$\mathbf{j} = -D\nabla n - n\lambda_T \nabla T - n\lambda_p \nabla p. \tag{5}$$

Equation (2) remains unchanged and can be considered as a definition of the hydrodynamic velocity $\mathbf{v}$, which is, generally speaking, different from the local velocity $\mathbf{u}(\mathbf{r}, t)$ 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 cannot be expressed in terms of higher order spatial derivatives of hydrodynamic variables [4–7].

Several studies have focused on the effects of chirality on the motion of suspended particles in hydrodynamic flows [8–17]. It was shown that nonchiral magnetic colloidal particles can self-assemble into chiral colloidal clusters [18].

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 flows 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 where the right- and left-handed particles are mirror images of each other and are suspended in an incompressible fluid. The extension of our treatment to more general cases is straightforward.

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 the momentum flux density is allowed by symmetry:

$$\Pi_{ij}^{\mathrm{ch}} = n^{\mathrm{ch}}\alpha\eta[\partial_i\omega_j + \partial_j\omega_i] + \eta\alpha_1[\omega_i\partial_j n^{\mathrm{ch}} + \omega_j\partial_i n^{\mathrm{ch}}], \tag{6}$$

where $\omega_i(\mathbf{r}) = \frac{1}{2}\epsilon_{ijk}\partial_j v_k(\mathbf{r})$ is the flow vorticity, and $n^{\mathrm{ch}} = (n_+ - n_-)$ is the chiral density, with n_+ and n_- being the volume densities of right- and left-handed particles, respectively. Eqs. (1)–(6) should be supplemented by the expression for the chiral current, defined as the difference between the currents of right- and left-handed particles. Separating it into the convective part $\mathbf{v}n^{\mathrm{ch}}$ and the current relative to the fluid $\mathbf{j}^{\mathrm{ch}}$, we write the continuity equation as

$$\partial_t n^{\mathrm{ch}} + \mathrm{div}(\mathbf{v}n^{\mathrm{ch}}) + \mathrm{div}\mathbf{j}^{\mathrm{ch}} = 0. \tag{7}$$

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

$$\tilde{j}_i^{\mathrm{ch}} = n[\beta\nabla^2\omega_i + \beta_1\omega_j V_{ij}], \tag{8}$$

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

In accordance with the philosophy underlying hydrodynamics Eqs. (6) and (8) represent the lowest order terms in the powers of $\partial_i v_j$, or in the order of spatial derivatives of $\mathbf{v}$ that display the effects of chirality. These terms are subleading in comparison to those in the conventional hydrodynamic approximation. Their retention is justified because they describe new phenomena absent in conventional hydrodynamics. The first term is reactive and arises from the gradient expansion. The second term is dissipative and represents the leading term in the expansion in the rotational Péclet number [19] [see discussion below Eq. (11)].

Note that according to the Navier-Stokes equations

$$\nabla^2\mathrm{curl}(\mathbf{v}) = \frac{\rho}{\eta}\{\partial_t\mathrm{curl}(\mathbf{v}) + \mathrm{curl}[(\mathbf{v}\nabla)\mathbf{v}]\}. \tag{9}$$

Thus the first term in Eq. (8) arises either due to nonstationary or nonlinear in $\mathbf{v}$ nature of the flow. In particular, in stationary flows and to zeroth order in the Reynolds number $\nabla^2\mathrm{curl}(\mathbf{v}) = 0$ 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 because of two effects:

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

(ii) A nonuniform 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. [9].

In most cases of practical importance the Reynolds number corresponding to the particle size R is small. In this regime the coefficients α, α_1, β, and β_1 in Eqs. (6) and (8) can be obtained by studying the particle motion in the surrounding fluid in the creeping flow approximation [20,21]. In this approximation the motion of a particle immersed in the liquid is of purely geometrical nature (see, for example, Ref. [22]). Dimensional analysis gives an estimate

$$\alpha \sim \alpha_1 \sim \chi R^4, \qquad \beta \sim \chi R^3, \tag{10}$$

where R is the characteristic size of the particles, and the dimensionless parameter χ characterizes the degree of chirality in the shape of the particles.

The second term in Eq. (8) describes the effect of orientation of the particles induced by the hydrodynamic flow. 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

$$\beta_1 \sim \chi\eta R^4/T. \tag{11}$$

Using Eqs. (9)–(11) we can estimate the ratio of the second term in the expression for the chiral current, Eq. (8) to the first one as $\sim \mathrm{Re}\,\eta^2 R/\rho T$, where Re is the Reynolds number. This ratio is much larger than unity at all reasonable even if the particle size is of the order of interatomic scale in the liquid.

The second term in Eq. (8) is the leading term in the expansion in the rotational Péclet number $\mathrm{Pe} \sim V_{ij}\eta R^3/T$: the larger the Péclet number, the more oriented are the particles. As one increases the Péclet number to values of order one or larger, the degree of orientation of particles should saturate. For example, when $\mathrm{Pe} \gg 1$, one can neglect rotational diffusion of the particles, and a particle of an arbitrary shape executes a complicated motion. Averaged over long time scales, the degree of particle orientation becomes of order unity. In this regime the rate of rotation of the particle with respect to the fluid becomes of the order of the shear rate, and expansion to lowest order in V_{ij} is no longer valid.

For $\mathrm{Pe} \gg 1$ the direction of the chiral current is nonuniversal; it depends not only on the shear rate and vorticity but also on the shape of the particle. However, in this regime the dependence of the instantaneous velocity of the particle relative to the fluid on the shear rate and flow vorticity is purely geometrical and linear [8]. Therefore the magnitude of the chiral current can be estimated as

$$\tilde{j}^{\mathrm{ch}} \sim n\chi R\omega. \tag{12}$$

Similarly, the direction of the chiral part of the momentum flux, (orientation of its eigenaxes) is also nonuniversal. However, its magnitude (eigenvalues) remains linear in the vorticity gradients $\partial_i \omega_j$ [23]. Because of saturation of the average particle orientation it can be estimated as

$$\Pi^{\mathrm{ch}} \sim n^{\mathrm{ch}}\alpha\eta[\partial_i\omega_j + \partial_j\omega_i]. \tag{13}$$

In this relation we assumed that the chiral density is spatially uniform.

Equations (6) and (8) 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 $\mathbf{F}$, there will be additional contributions to the chiral flux. The linear in $\mathbf{F}$ contributions can be constructed by contracting the antisymmetric tensor ϵ_{ijk} with the velocity v_i, force F_i, and two derivatives ∂_i. For example, the following terms exist when $\mathbf{F}$ is constant: $(\mathbf{F}\cdot\nabla)\boldsymbol{\omega}$, $\mathbf{F}\times\nabla^2\mathbf{v}$, $\nabla(\mathbf{F}\cdot\boldsymbol{\omega})$. 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 $\sim RF/T$. Thus the coefficients with which these terms enter the chiral current $\mathbf{j}^{\mathrm{ch}}$ 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 $\mathbf{F}$ for small force.

The chiral contribution to the stress tensor Eq. (6) leads to several new effects. A flowing chiral liquid develops stresses and components of hydrodynamic velocity which are forbidden by symmetry in the case of a nonchiral liquid. Since the chiral stress represents a correction to the conventional viscous stress tensor, its influence can be studied perturbatively starting from a given flow of a Newtonian liquid.

Consider a Poiseuille flow 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. If the chiral density is uniform the chiral part of the stress tensor has only two nonvanishing elements, $\Pi_{yz} = \Pi_{zy} = -\alpha n^{\mathrm{ch}}\partial_x p/2$. 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 $n^{\mathrm{ch}}R^3 \sim 1$ and using Eq. (10) the magnitude of the chiral force per unit area of the plane can be estimated as

$$\Pi^{\mathrm{ch}} \sim \chi R\partial_x p. \tag{14}$$

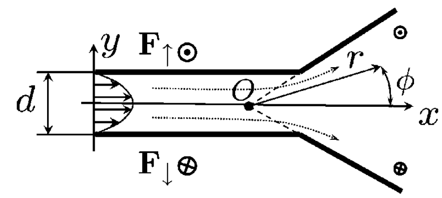

FIG. 1. A chiral liquid in a Poiseuille flow between parallel plates exerts a pair of opposite forces on the plates $\mathbf{F}_\uparrow = -\mathbf{F}_\downarrow$, which are directed into (⊗) and out of (⊙) the page. A flow of a chiral liquid in a converging or diverging channel develops a helicoidal component of velocity directed into and out of the page, as shown at right. The distance to the origin of the channel, point O, is denoted by r. For a Newtonian fluid the flow lines (dotted lines) lie in the plane of the figure.

For spatially uniform n^{ch} the volume force density generated by the chiral part of the stress tensor is $f_i^{\mathrm{ch}} = -\partial_j\Pi_{ij}^{\mathrm{ch}} = -n^{\mathrm{ch}}\alpha\eta\nabla^2\omega_i$. Then it is clear from Eq. (9) that f_i^{ch} is generated only in nonstationary or nonlinear flows. In the special case of a 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 which is perpendicular to the unperturbed flow. The chiral component of the velocity, $\mathbf{v}^{\mathrm{ch}}$, can be obtained by balancing the chiral force density evaluated on the unperturbed flow ($\mathbf{v}_0$) with the viscous force density arising due to chiral correction, $\mathbf{v}^{\mathrm{ch}}$. For an incompressible fluid with a uniform chiral density this gives

$$\alpha n^{\mathrm{ch}}\nabla^2\omega_0 = \nabla^2\mathbf{v}^{\mathrm{ch}}. \tag{15}$$

The chiral correction to the hydrodynamic velocity can be easily found for an exactly solvable flow in a diverging channel (§ 23 of Ref. [1]), see Fig. 1. In this case the velocity of the unperturbed flow is in the radial direction. At large Reynolds numbers $\mathrm{Re} \gg 1$, the vorticity of the unperturbed flow is localized to a narrow angular region $\delta\phi \sim 1/\sqrt{\mathrm{Re}}$ near the boundaries, whereas the flow in the interior of the channel is potential with the velocity $v \sim \mathrm{Re}/r$, r being the distance to the origin of the converging channel. Assuming $n^{\mathrm{ch}}R^3 \sim 1$ and using Eq. (15) we estimate magnitude of the chiral velocity as

$$v^{\mathrm{ch}} \sim \nu\chi\mathrm{Re}^{3/2}\frac{R}{r^2}, \tag{16}$$

where ν is the kinematic viscosity.

Taking the channel width and the particles size to be respectively ~ 1 mm, and $\sim 1\ \mu$m, assuming $\nu \sim 10^{-2}\ \mathrm{cm}^2/\mathrm{s}$, and $\mathrm{Re} \sim 100$ and using Eqs. (14) and (16) we estimate the magnitude of the chiral stress and velocity to be $\Pi^{\mathrm{ch}} \sim 10^{-5}\chi\ \mathrm{dyn/cm}^2$ and $v^{\mathrm{ch}} \sim \chi \times 10^{-2}\ \mathrm{cm/s}$, respectively.

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 [11–14] and recent experiments [16]. 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 nonlinear or in nonstationary 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 $\mathrm{Pe} \gg 1$. In this regime the chiral current becomes linear in the flow vorticity ω, Eq. (12). The linear dependence of $\mathbf{j}_{\mathrm{ch}}$ on ω and saturation of the proportionality coefficient at $\mathrm{Pe} \to \infty$ has been observed numerically in Refs. [11,13].

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 nonchiral liquid. In this case the definition of chirality requires clarification. Some possible measures of chirality have been discussed in Ref. [24]. Another possibility is to 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. In these cases one can relate the degree of particle chirality with the appropriate terms in the generalized mobility tensor [20,21]. We note that the same individual particle can exhibit different chirality with respect to different external perturbations.

The set of Eqs. (1)–(8) still holds for a suspension of random particles. In this case n^{ch} can be introduced as an auxiliary quantity defined in terms of the chiral component of the stress tensor Eq. (6), and corresponds to quantities averaged over the random shape of the particles. The chiral current is given by the continuity equation, and $\tilde{\mathbf{j}}^{\mathrm{ch}}$ can still be written in the form of Eq. (8).

Finally, we note that symmetry allows contributions to $\tilde{\mathbf{j}}^{\mathrm{ch}}$ that are proportional to the external magnetic field $\mathbf{B}$, for example $\tilde{\mathbf{j}}^{\mathrm{ch}} \propto n^{\mathrm{ch}}(\nabla T)^2\mathbf{B}$. We believe that these effects are of fluctuational origin similar to those discussed in Refs. [4–7] and do not study them in this work.

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