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Onsager symmetry principle for a particle moving through a fluid not in equilibrium

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(Received 4 September 1990)

We have shown that the mobility tensor for a particle moving through an arbitrary homogeneous stationary flow satisfies generalized Onsager symmetry relations in which the time-reversal transformation should also be applied to the external forces that keep the system in the stationary state. It is then found that the lift forces, responsible for the motion of the particle in a direction perpendicular to its velocity, have different parity than the drag forces.

It is well known that Onsager relations follow from the time-reversal symmetry principle, which is strictly valid at equilibrium. In its derivation one combines the detailed balance principle and the Onsager regression law, for which fluctuations evolve on the average according to nonequilibrium thermodynamics linear laws. Then one gets the condition that the matrix of phenomenological coefficients L is symmetric:[1]

$$L=\tau L^{\dagger}\tau \; . \tag{1}$$

Here $\dagger$ stands for the Hermitian matrix and τ for the parity. These relations have been corroborated experimentally within acceptable error limits for widely different phenomena, such as thermoelectricity, chemical reactions, heat conduction in anisotropic solids, etc.[2]

The preceding result has been generalized in Ref. 3 to the case in which the system is in a nonequilibrium steady state. For the matrix L, one then obtains the relation

$$L=\tau \bar{L}^{\dagger}\tau \; , \tag{2}$$

where the overbar on L denotes that the time-reversal transformation should also be taken over the external forces responsible for the existence of a stationary state.

This formulation of the Onsager relations comes about as a result of the difference in behavior between fluctuations around equilibrium and nonequilibrium steady states,[4] which could be intuitively illustrated in the following example. Consider that a spontaneous fluctuation occurs in a point of the system, say point 1, and propagates to point 2. In equilibrium this event takes place with probability $P(1\to 2)$, which is equal to $P(2\to 1)$. This result constitutes, essentially, the formulation of the detailed balance principle, which, together with the Onsager regression hypothesis, leads to the Onsager relations (1). Imagine now that fluctuations diffuse in and are convected by an external flow, whose origin is the presence of external "forces" (pressure gradients, motion of boundaries, etc.). In this case, one readily concludes that $P(1\to 2)\neq P(2\to 1)$. This probability, however, will depend on a parameter characterizing the motion of the fluid (shear rate in the case of Couette flow). One then arrives at the result that these probabilities will be the same, provided that the fluid moves in an opposite direction: $P(1\to 2;\gamma)=P(2\to 1;-\gamma)$, γ being the shear rate. This equality formulates the detailed balance principle in the presence of convection and constitutes the basis for the derivation of the generalized Onsager relations (2).

Our purpose in this paper is to provide a specific example of a system away from equilibrium for which the generalized symmetry principle (2) is satisfied. To this end we will study the motion of a particle through a fluid moving due to externally imposed gradients.

Before discussing the problem of the motion of the particle through the fluid, let us first of all specify the nature of the flow in the absence of the particle. We will consider that the stationary velocity of the fluid is given by

$$\mathbf{v}_s(\mathbf{r})=\mathbf{r}\cdot\overleftrightarrow{\beta} \; , \tag{3}$$

where the tensor $\overleftrightarrow{\beta}$ is assumed to be the sum of the elongational $\overleftrightarrow{\beta}_E$ and rotational $\overleftrightarrow{\beta}_R$ contributions:

$$\overleftrightarrow{\beta}=\overleftrightarrow{\beta}_E+\overleftrightarrow{\beta}_R \; . \tag{4}$$

These quantities are given by

$$\begin{aligned} \overleftrightarrow{\beta}_E&=\beta\begin{bmatrix}0&1&0\\1&0&0\\0&0&0\end{bmatrix} , \\ \overleftrightarrow{\beta}_R&=\omega_0\begin{bmatrix}0&-1&0\\1&0&0\\0&0&0\end{bmatrix}=-\omega_0\times \; , \end{aligned} \tag{5}$$

where β and ω_0 are the elongational and rotational rates, respectively, and $\boldsymbol{\omega}_0=\frac{1}{2}\text{rot}\mathbf{v}$. In Eq. (5), $\boldsymbol{\omega}_0\times$ should be understood as an operator. The decomposition (4) may therefore describe a great number of stationary flows ranging from pure elongation ($\omega_0=0$) to pure rotation ($\beta=0$). The case $\beta=\omega_0$ may then be identified as the shear flow.

To arrive at the value for the mobility or the friction on the particle, it is convenient to write the equations of motion in a reference frame corotating with the rotational part of the unperturbed fluid motion in such a way that the flow is purely elongational. In the new frame, the equations of motion for the fluid are

$$\rho\frac{d\mathbf{v}}{dt}+2\rho\boldsymbol{\omega}_0\times\mathbf{v}=-\nabla p^*+\eta\nabla^2\mathbf{v}\ ,$$
$$\nabla\cdot\mathbf{v}=0\ , \qquad (6)$$
$$\text{for } |\mathbf{r}-\mathbf{R}(t)|>a\ .$$

Here ρ is the density, $\mathbf{v}$ the velocity, η the shear viscosity, $\mathbf{R}(t)$ the position vector of the center of mass of the particle, and a the radius of the particle, which is assumed to be spherical. Moreover, $2\rho\boldsymbol{\omega}_0\times\mathbf{v}$ can be identified with the Coriolis force density and $p^*=p-\frac{1}{2}\rho[\omega_0^2r^2-(\boldsymbol{\omega}_0\cdot\mathbf{r})^2]$, with p being the pressure, and the second term comes from the centrifugal force density. Likewise, use has been made of the incompressible nature of the fluid, which is consistent with the form of the stationary flow given through (3)–(5).

The boundary-value problem posed through (6) can be reformulated by introducing an induced force density $\mathbf{F}_{\text{ind}}(\mathbf{r},t)$,[5] accounting for the presence of the sphere inside the fluid. We then extend the flow field within the particle in such a way that the Navier-Stokes equation reads

$$\rho\frac{\partial\mathbf{v}}{\partial t}+\rho\mathbf{v}\cdot\nabla\mathbf{v}+2\rho\boldsymbol{\omega}_0\times\mathbf{v}=-\nabla p^*+\eta\nabla^2\mathbf{v}+\mathbf{F}_{\text{ind}} \quad \text{for all } \mathbf{r}\ . \qquad (7)$$

Due to the assumption of stick boundary conditions on the surface of the sphere, the induced force is taken such that

$$\mathbf{v}(\mathbf{r},t)=\mathbf{u}(t)-[\boldsymbol{\Omega}(t)-\boldsymbol{\omega}_0]\times\mathbf{r},\quad \text{for } |\mathbf{r}-\mathbf{R}(t)|\le a\ , \qquad (8)$$

where $\mathbf{u}(t)$ and $\boldsymbol{\Omega}(t)$ are the translational and rotational velocities of the sphere, respectively. In order to simplify our analysis, we can take the motion of the sphere to be torque free, so that $\boldsymbol{\Omega}=\boldsymbol{\omega}_0$.

Our next step is to linearize the equations of motion in the perturbation $\mathbf{v}-\mathbf{v}_s$. We then obtain

$$\frac{\partial\mathbf{v}}{\partial t}+\rho\overleftrightarrow{\beta}_E\cdot\mathbf{v}+\rho\mathbf{r}\cdot\overleftrightarrow{\beta}_E\cdot\nabla\mathbf{v}+2\rho\boldsymbol{\omega}_0\times\mathbf{v}=-\nabla_p^{**}+\eta\nabla^2\mathbf{v}+\mathbf{F}_{\text{ind}}\ , \qquad (9)$$

where $p^{**}=p^*-\frac{1}{2}\rho\mathbf{r}\cdot\overleftrightarrow{\beta}_E\cdot\overleftrightarrow{\beta}_E\cdot\mathbf{r}$.

In Ref. 6 we have shown that the induced-force method permits one to arrive at the expression for the mobility

$$\mu_{ij}=\frac{a^2}{(2\pi)^3}\int d\boldsymbol{\kappa}\frac{\sin(\kappa a)}{\kappa a}G_{ij}\frac{\sin(\kappa a)}{\kappa a}\ , \qquad (10)$$

where G_{ij} is the propagator

$$\overleftrightarrow{G}=\{(\overleftrightarrow{1}-\hat{\kappa}\hat{\kappa})\cdot[-i\omega\rho+\eta\kappa^2+\rho(\overleftrightarrow{\beta}_E+2\boldsymbol{\omega}_0\times)]\cdot(\overleftrightarrow{1}-\hat{\kappa}\hat{\kappa})\}^{-1}\ , \qquad (11)$$

which follows from (9) and where $\hat{\kappa}$ is the unit vector along the direction of $\boldsymbol{\kappa}$ and $\overleftrightarrow{1}$ the unit tensor. This propagator can be rewritten in the more convenient form

$$\overleftrightarrow{G}=\sum_{j=\pm}(-i\omega\rho+\eta\kappa^2+\rho\lambda_j)^{-1}\mathbf{e}_j^r\mathbf{e}_j^l\ , \qquad (12)$$

where the nonvanishing eigenvalues are given by

$$\lambda_\pm=-\beta\hat{\kappa}_x\hat{\kappa}_y\pm[\beta^2\hat{\kappa}_x^2\hat{\kappa}_y^2+(\beta^2-4\omega_0^2)\hat{\kappa}_z^2]^{1/2}\ , \qquad (13)$$

with $\hat{\kappa}_i$ being the ith component of the unit vector $\hat{\kappa}$. On the other hand, the corresponding left and right eigenvalues are found to be

$$\begin{aligned}\mathbf{e}_\pm^l(\beta,\omega_0)&=\mathbf{e}_\pm^r(\beta,-\omega_0)\\&=\{(\beta-2\omega_0)(1-\hat{\kappa}_x^2)(\hat{\kappa}_z,0,-\hat{\kappa}_x)\\&\quad+[(\beta+2\omega_0)\hat{\kappa}_x\hat{\kappa}_y+\lambda_\pm]\\&\quad\times(0,\hat{\kappa}_z,-\hat{\kappa}_y)\}(n_\pm)^{-1}\ ,\end{aligned} \qquad (14)$$

where $n_\pm$ are the norms that satisfy the orthonormality conditions $\mathbf{e}_i^l\cdot\mathbf{e}_j^r=\delta_{ij}$, $i,j=\pm$. The eigenvector associated with the zero eigenvalue is equal to $\hat{\kappa}$.

To study the time-reversal symmetries of the mobility, we will start from Eq. (10). By using (12)–(14) in (10) the mobility reads

$$\overleftrightarrow{\mu}(\omega;\beta,\omega_0)=\frac{1}{8\pi^3\eta a}\int d\hat{\kappa}\sum_{j=\pm}(\mathbf{e}_j^r\mathbf{e}_j^l)_{\beta,\omega_0}I_j(\beta,\omega_0)\ , \qquad (15)$$

where the integral I_j depends on the inverse penetration lengths $\alpha_j\equiv[(-i\omega+\lambda_j)/\nu]^{1/2}$, with $\text{Re}(\alpha_j)\ge 0$, and its value is

$$I_j=\frac{1}{2a}\int_0^\infty d\kappa\frac{\sin^2(\kappa a)}{\kappa^2+\alpha_j^2}\simeq\frac{\pi}{2}(1-\alpha_j a+\cdots)\ . \qquad (16)$$

Combining (15) and (16), one may conclude that the mobility splits into equilibrium and nonequilibrium contributions:

$$\overleftrightarrow{\mu}(\omega;\beta,\omega_0)=\overleftrightarrow{\mu}_{\text{eq}}+\overleftrightarrow{\mu}_{\text{noneq}}(\omega;\beta,\omega_0)\ , \qquad (17)$$

where $\overleftrightarrow{\mu}_{\text{eq}}=(6\pi\eta a)^{-1}\overleftrightarrow{1}$ and

$$\overleftrightarrow{\mu}_{\text{noneq}}(\omega;\beta,\omega_0)=-(6\pi\eta a)^{-1}\frac{3}{4\pi}\int_0^\pi d\theta\sin\theta\int_0^\pi d\varphi\sum_{j=\pm}(\mathbf{e}_j^r\mathbf{e}_j^l)_{\beta,\omega_0}\alpha_j(\omega;\beta,\omega_0)\ . \qquad (18)$$

To compute $\overleftrightarrow{\mu}_{\text{noneq}}(\omega;-\beta,-\omega_0)$, one may also use (15) with the corresponding expressions for the eigenvalues, the eigenvectors, and α_j. Because our purpose is to analyze the symmetries of $\overleftrightarrow{\mu}_{\text{noneq}}$, let is introduce the change of variable $\tilde{\varphi}=\pi-\varphi$, which is equivalent to making the transformation $\hat{\kappa}_x \rightarrow -\hat{\kappa}_x$. We can show that the diagonal terms of the mobility matrix satisfy

$$\mu_{ii,\text{noneq}}(\omega;\beta,\omega_0)=\mu_{ii,\text{noneq}}(\omega;-\beta,-\omega_0), \quad i=1,2,3 \ , \tag{19}$$

whereas for the nondiagonal elements one has

$$\mu_{ij,\text{noneq}}(\omega;\beta,\omega_0)=-\mu_{ij,\text{noneq}}(\omega;-\beta,-\omega_0) \ , \quad i,j=1,2,3, \quad i\neq j \ . \tag{20}$$

These two equations or the ones corresponding for the friction tensors formulate the Onsager symmetry principle. Notice that they are valid even in the nonstationary case for any flow in the form of (3).

To analyze the symmetries in the stationary case, one can also start from (15), setting $\omega=0$ and taking the real part. The stationary mobility will clearly depend upon the sign of $\beta^2-4\omega_0^2$. These relations can be verified from the explicit expressions for the mobility in the elongational, rotational, and simple shear cases that were given in Ref. 7. Notice that taking the time-reversal transformation is equivalent to a rotation R_π around the y axis.

Let us go further in depth into the physical interpretation of our results. First of all, we should realize that the nonequilibrium contribution to the mobility matrix has nondiagonal terms different from zero. These terms are responsible for the presence of lift forces[7,8] that may give rise to migration phenomena in suspensions, known as the Segré-Silberberg effect.[9] To illustrate our contention, let us consider that the particle moves along the x direction with velocity u_x. According to the equation

$$\mathbf{F}=-\overleftrightarrow{\xi}\cdot(\mathbf{u}-\mathbf{v}_s) \ , \tag{21}$$

where $\overleftrightarrow{\xi}=\overleftrightarrow{\mu}^{-1}$ is the friction tensor which simply follows from (17) and (18), one has

$$F_x^D=-\xi_{xx}(u_x-v_{s,x}) \ , \tag{22}$$

$$F_y^L=-\xi_{yx}(u_x-v_{s,x}) \ . \tag{23}$$

As shown in Ref. 7, when the particle moves through a fluid at rest, $\xi_{yx}=0$; consequently, the lift force F_y^L is not present, and only the drag force F_x^D acts on the particle. Moreover, F_y^L changes its sign when the direction of the flow is inverted. The lift forces are then perpendicular to the velocity relative to the stationary flow, and depend on the inverse penetration lengths. From the symmetry relations (19), (20), (22), and (23) one concludes that the lift force is an $\boldsymbol{\alpha}$ variable, whereas the drag force is a $\boldsymbol{\beta}$ variable.

The situation studied in this paper could be compared, for example, with the phenomenon of heat conduction in anisotropic crystals. In the absence of a magnetic field, the heat-conductivity tensor must be necessarily symmetric. When a magnetic field acts on the system, Onsager relations allow for the existence of an antisymmetric part. These relations are then similar to the ones obtained here [see Eqs. (19) and (20)]. This fact is not surprising, since in both cases (heat conduction and motion of the particle through the fluid) time reversal is performed not only by changing the sign of the momenta of the particles, but by changing the sign of the magnetic field or of the elongational and rotational rates. Our equation (23) relating "fluxes" and "forces" in perpendicular directions is then similar to the ones giving rise to the Righi-Leduc or Hall effects,[10] which are also a consequence of the existence of nondiagonal contributions to the heat conductivity and the resistivity tensors.

In summary, the generalized Onsager relations derived recently in Ref. 3, based on a formulation given by McLennan,[11] have been found to be satisfied for the mobility tensor of a particle moving through a fluid not in equilibrium. These relations assign different parity to the drag and lift forces acting on the particle, and are similar to the ones encountered in thermomagnetic and galvanomagnetic effects. The experimental verification of these relations could be carried out by analyzing the parity of the lift forces. Our results indicate that those forces should be invariant under the transformation $(u_x,\beta,\omega_0)\rightarrow(-u_x,-\beta,-\omega_0)$.

We would like to thank D. Bedeaux and J. W. Dufty for useful discussions. This work was supported by the European Economic Community under Contract No. ST2 0246 and by La Comisión Investigacíon Científica y Técnica of the Spanish Government under Grant No. PB87-0782.

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