IRREVERSIBLE PROCESSES IN A SYSTEM WITH INTERNAL ROTATIONS

PHYSICS

1967

SovietRxiv

Abstract

Full Text

UDC 536.758

PHYSICS

L. A. POKROVSKII

IRREVERSIBLE PROCESSES IN A SYSTEM WITH INTERNAL ROTATIONS

(Presented by Academician N. N. Bogolyubov on 19 XII 1966)

In a rotating liquid (or gas), the mean angular velocity of internal rotations may fail to coincide with the angular velocity of rotation of the liquid. Then a process of exchange of angular momentum between the external and internal degrees of freedom arises, called rotational viscosity, by virtue of which the angular velocities are equalized ([1-4]). In the case of spatial inhomogeneity of the angular velocity, there also arises a diffusion process of transfer of internal angular momentum. Although these processes have little effect on the motion of the liquid, nevertheless there exist phenomena whose consideration is impossible without taking rotational viscosity into account, for example the gyromagnetic effect for a paramagnetic gas and the entrainment of a liquid by a rotating electric and magnetic field. In ([1-4]) the theory of rotational viscosity was developed by the methods of irreversible thermodynamics. In the present work the theory of rotational viscosity is considered by the methods of irreversible statistical thermodynamics.

Let us consider a system of molecules with internal rotational degrees of freedom with Hamiltonian

$$H = \int H(x)\, dx; \tag{1}$$

$H(x)$ is the energy-density operator

$$H(x) = \sum_{\gamma} \left(\frac{1}{2m} \nabla \psi_{\gamma}^{+}(x) \nabla \psi_{\gamma}(x) + R_{\gamma} \psi_{\gamma}^{+}(x) \psi_{\gamma}(x) \right) +$$

$$+\frac{1}{2} \sum_{\gamma_1 \gamma_2, \gamma_1' \gamma_2'} \int dx'\, \Phi_{\gamma_1 \gamma_2, \gamma_1' \gamma_2'}(x - x') \psi_{\gamma_1}^{+}(x) \psi_{\gamma_2}^{+}(x') \psi_{\gamma_2'}(x') \psi_{\gamma_1'}(x) \quad (\hbar = 1), \tag{2}$$

where γ is the set of quantum numbers of the internal state of a molecule, including the internal angular momentum and its projection on the z-axis; m is the mass of the molecule; R_γ are eigenvalues of the operator of internal energy; $\psi_\gamma(x)$ is a second-quantized field function of Bose or Fermi type; $\Phi_{\gamma_1\gamma_2,\gamma_1'\gamma_2'}(x-x')$ are matrix elements of the interaction potential.

To study nonequilibrium processes, we formulate the conservation laws of energy, momentum, number of particles, and internal angular momentum with densities $H(x)$, $\mathbf{p}(x)$, $n(x)$, and $\mathbf{s}(x)$:

$$\dot{H}(x) + \operatorname{div}\mathbf{j}_H(x) = 0, \qquad \dot{\mathbf{p}}(x) + \operatorname{Div} T(x) = 0,$$

$$\dot{n}(x) + \operatorname{div}\mathbf{j}(x) = 0, \qquad \dot{\mathbf{s}}(x) + \operatorname{Div} j_s(x) = I_s(x), \tag{3}$$

where $\mathbf{j}_H(x)$ is the energy flux; $T(x)$ is the momentum-flux tensor; $\mathbf{j}(x)$ is the particle flux; $j_s(x)$ is the tensor of the flux of internal angular momentum; $I_s(x)$ is the source of internal angular momentum. In contrast to the case of spherically symmetric molecules ([5]), $T(x)$ is not symmetric. Therefore the external mo-

the angular momentum $\mathbf{l}(x) = [\mathbf{x} \times \mathbf{p}(x)]$ is not conserved,

$$\dot{\mathbf{l}}(x) + \operatorname{Div} j_l(x) = \mathbf{I}_l(x), \tag{4}$$

where $j_l(x)$ is the flux tensor of the external angular momentum with components $j^l_{\beta\alpha}(x) = e_{\alpha\mu\nu}x_\mu T_{\beta\nu}(x)$ (summation over identical Greek indices is understood, $e_{\alpha\mu\nu}$ is the unit completely antisymmetric tensor); $\mathbf{I}_l(x)$ is the source of the external angular momentum,

$$\mathbf{I}_l(x) = -\frac{1}{2}\sum_{\gamma_1\gamma_2,\gamma_1'\gamma_2'}\int dx'\left[(\mathbf{x}-\mathbf{x}') \times \frac{\partial\Phi_{\gamma_1\gamma_2,\gamma_1'\gamma_2'}(x-x')}{\partial\mathbf{x}}\right]\psi^+_{\gamma_1}(x)\psi^+_{\gamma_2}(x')\psi_{\gamma_2'}(x')\psi_{\gamma_1'}(x). \tag{5}$$

Calculating the time derivative of the density of the internal angular momentum

$$\mathbf{s}(x) = \sum_{\gamma\gamma'}\mathbf{s}_{\gamma\gamma'}\psi^+_\gamma(x)\psi_{\gamma'}(x), \tag{6}$$

where $\mathbf{s}_{\gamma\gamma'}$ are the known matrix elements of the single-particle angular momentum ([9]), and using the condition of conservation of the total angular momentum,

$$[\Phi, \mathbf{s}+\mathbf{s}']_{\gamma_1\gamma_2,\gamma_1'\gamma_2'} + i\left[(\mathbf{x}-\mathbf{x}') \times \frac{\partial\Phi_{\gamma_1\gamma_2,\gamma_1'\gamma_2'}(x-x')}{\partial\mathbf{x}}\right] = 0, \tag{7}$$

where [,] is the commutator, we obtain the last formula from (3) and an explicit expression for $j_s(x)$ and $\mathbf{I}_s(x)$:

$$j_s(x) = \sum_{\gamma_1\gamma_2} \mathbf{j}_{\gamma_1\gamma_2}(x)\, \mathbf{s}_{\gamma_1\gamma_2} + \frac{1}{2i} \sum_{\gamma_1\gamma_2,\gamma_1'\gamma_2'} \int dx'\, (\mathbf{x}-\mathbf{x}')\, [\Phi, \mathbf{s}]_{\gamma_1\gamma_2,\gamma_1'\gamma_2'} \psi^+_{\gamma_1}(x)\psi^+_{\gamma_2}(x')\psi_{\gamma_2'}(x')\psi_{\gamma_1'}(x), \tag{8}$$

$$\mathbf{I}_s(x) = -\mathbf{I}_l(x), \tag{9}$$

where

$$\mathbf{j}_{\gamma_1\gamma_2}(x) = \frac{1}{2im}\left(\psi^+_{\gamma_1}(x)\nabla\psi_{\gamma_2}(x) - \nabla\psi^+_{\gamma_1}(x)\psi_{\gamma_2}(x)\right).$$

Thermodynamic relations for inhomogeneous states can be obtained with the aid of the locally equilibrium ensemble

$$\rho_l = Q_l^{-1} \exp\left\{-\int dx\, \beta(x)(H'(x) - \mu(x)n(x))\right\}, \tag{10}$$

where $H'(x)$ is the energy density in the accompanying frame of reference, the accompanying being carried out both with respect to the mass velocity $\mathbf{v}(x)$ and with respect to the angular velocity $\omega(x)$; $\beta(x)$ is the inverse local temperature; $\mu(x)$ is the chemical potential. The operator $H'(x)$ includes the potential of the centrifugal forces; therefore the transition to the fixed frame of reference is carried out according to the formula

$$H'(x) = H(x) - \mathbf{v}(x)\cdot\mathbf{p}(x) - \omega(x)\cdot\mathbf{s}(x) + \frac{mv^2(x)n(x)}{2}. \tag{11}$$

Substituting (11) into (10), we obtain the locally equilibrium ensemble in the fixed frame of reference

$$\rho_l = Q_l^{-1} \exp\left\{-\int dx\, \beta(x)\left[H(x) - \mathbf{v}(x)\cdot\mathbf{p}(x) - \omega(x)\cdot\mathbf{s}(x) + \left(\frac{mv^2(x)}{2} - \mu(x)\right) n(x)\right]\right\}. \tag{12}$$

Equilibrium ensembles of this type are considered in detail in ([6]).

Let us find the thermodynamic relations for the locally equilibrium ensemble. We introduce the entropy and the entropy density by the formulas

$$S = -\operatorname{Sp}\rho_l \ln \rho_l = \int s(x)\, dx. \tag{13}$$

Varying S with respect to the parameters $\beta(x)$, $\mu(x)$, and $\vec{\omega}(x)$, we obtain

$$\delta S(x) = \beta(x)(\delta u - \vec{\omega}(x) \cdot \delta\langle \mathbf{s}(x)\rangle_l - \mu(x)\delta\langle n(x)\rangle_l), \tag{14}$$

where $\langle ...\rangle_l = Sp(... \rho_l)$ and $u = \langle H'(x) + \vec{\omega}(x)\mathbf{s}(x)\rangle$. Relation (14) is more exact than the analogous equation used in ([3]), since we regard $\vec{\omega}(x)$ as one of the thermodynamic parameters.

The operator (12) does not satisfy the Liouville equation and therefore does not describe nonequilibrium processes. Following ([7],[8]), we shall seek the nonequilibrium statistical operator in the form of a functional of the local integrals of motion $B_i(x,t)$

$$\rho = Q^{-1} \exp\left\{-\sum_i \int B_i(x,t)\, dx\right\},$$

$$B_i(x,t) = F_i(x,t)P_i(x) - \int_{-\infty}^{0} dt_1\, e^{\varepsilon t_1} \left(\frac{\partial F_i(x,t+t_1)}{\partial t_1} P_i(x,t_1) + F_i(x,t+t_1)\dot{P}_i(x,t_1)\right), \tag{15}$$

where $F_1(x,t) = \beta(x,t)$, $F_2(x,t) = -\beta(x,t)\mathbf{v}(x,t)$, $F_3(x,t) = -\beta(x,t)\vec{\omega}(x,t)$, $F_4(x,t) = \beta(x,t)(mv^2(x,t)/2 - \mu(x,t))$, $P_1(x) = H(x)$, $P_2(x) = \mathbf{p}(x)$, $P_3(x) = \mathbf{s}(x)$, and $P_4(x) = n(x)$. The time argument of the operators $P_i(x,t)$ has a different meaning than that of $F_i(x,t)$, and denotes the Heisenberg representation. The statistical operator may be written in the form

$$\rho = Q^{-1} \exp\left\{-\sum_i \int \left[F_i(x,t)P_i(x) - \int_{-\infty}^{0} e^{\varepsilon t_1} \left(\nabla F_i(x,t+t_1) j_i(x,t_1) + \frac{\partial F_i(x,t+t_1)}{\partial t_1} P_i(x,t_1) - \right.\right.\right.$$

$$\left.\left.\left. -\beta(x,t+t_1)\vec{\omega}(x,t+t_1) \cdot \mathbf{I}_s(x,t_1)\right) dt_1\right] dx\right\}, \tag{16}$$

where $j_1(x) = \mathbf{j}_H(x)$, $j_2(x) = T(x)$, $j_3(x) = \mathbf{j}_s(x)$, and $j_4(x) = \mathbf{j}(x)$. We have made use of the conservation laws (3) and have discarded surface integrals. Restricting ourselves to first-order processes, we shall assume that $\langle P_i(x)\rangle = \langle P_i(x)\rangle_l$, where $\langle ...\rangle$ denotes averaging over the ensemble (16). Then the derivatives $\partial F_i/\partial t$ can be calculated with the aid of the equations of reversible hydrodynamics, obtained by averaging the conservation laws over the locally equilibrium ensemble. As a result we obtain

$$\frac{\partial F_i}{\partial t} = \frac{du}{dt}\left(\frac{\partial F_i}{\partial u}\right)_{s,n} + \frac{\partial s}{\partial t}\left(\frac{\partial F_i}{\partial s}\right)_{u,n} + \frac{\partial n}{\partial t}\left(\frac{\partial F_i}{\partial n}\right)_{u,s}, \tag{17}$$

where

$$du/dt = -(u+p)\,\mathrm{div}\,\mathbf{v}, \qquad dn/dt = -n\,\mathrm{div}\,\mathbf{v}, \tag{18}$$

$$ds/dt = -s\,\mathrm{div}\,\mathbf{v}, \qquad d/dt = \partial/\partial t + \mathbf{v}\cdot\nabla.$$

Here $n = \langle n(x)\rangle_l$, $\mathbf{s} = \langle \mathbf{s}(x)\rangle_l$. For brevity we have omitted the signs of averaging over the locally equilibrium ensemble. Substituting (18) into (17) and, after simple but lengthy calculations analogous to the calculations of ([8]), taking (9) into account, we bring the statistical operator to the form

$$\rho = \left\{1 + \frac{1}{\beta}\int dx \int_0^\beta d\lambda \int_{-\infty}^0 dt_1 e^{\varepsilon t_1} \sum_k j^k(x, t_1 + i\lambda) X_k^*(x, t+t_1)\right\}\rho_l, \tag{19}$$

where $j^k(x)$ are the operators of irreversible fluxes,

$$\mathbf{j}^1(x) = \mathbf{j}'_H(x) - \mathbf{j}'(x)h, \qquad \mathbf{j}^2(x) = T'(x) - U\,\{p(x)+$$

$$+\frac{\partial p}{\partial u}\left[H(x) - \vec{\omega}(x)\cdot s(x) - \langle H(x) - \vec{\omega}(x)\cdot s(x)\rangle_l\right]+$$

$$+\frac{\partial p}{\partial s}\cdot(s(x) - \langle s(x)\rangle_l) + \frac{\partial p}{\partial n}\left(n(x) - \langle n(x)\rangle_l\right)\Big\},$$

$$\mathbf{j}^3(x) = \mathbf{j}'_s(x) - \sum_{\gamma\gamma'} \mathbf{j}_{\gamma\gamma'}(x)\left(J_{\gamma\gamma'} - \frac{\langle J(x)\rangle_l}{n}\,\vec{\omega}(x)\delta_{\gamma\gamma'}\right),$$

$\mathbf{j}'_H(x)$, $T'(x)$, and $\mathbf{j}'(x)$ are operators in the co-moving reference frame; $X_j(x, t+t_1)$ are the thermodynamic forces:

$X_1 = \nabla\beta(x, t+t_1)$, $X_2 = \nabla v(x, t+t_1) - \omega(x, t+t_1)$, $X_3 = \nabla\omega(x, t+t_1)$,

which give rise, respectively, to heat conduction, viscous processes, and diffusion of the internal angular momentum; U is the unit tensor; p is pressure; h is the enthalpy per molecule; $\omega(x, t+t_1)$ is the antisymmetric tensor dual to the pseudovector $\vec{\omega}(x, t+t_1)$. The thermodynamic force X_2 is decomposed into the irreducible tensors $\mathrm{div}\,v$, $\frac{1}{2}\,\mathrm{rot}\,v - \vec{\omega}$, and the symmetric traceless tensor $(\nabla v)_{s0}$, corresponding to the processes of bulk, rotational, and shear viscosity. Averaging the fluxes over the statistical ensemble (19), we obtain linear relations between the mean fluxes and the thermodynamic forces

$$\langle j^k(x,t)\rangle = \sum_m L_{km} F_m(x,t), \tag{20}$$

where L_{km} are kinetic coefficients having the form of integrals of the Kubo-formula type. Here we assume that the parameters vary sufficiently slowly in space and time that spatial and temporal dispersion may be neglected. In particular, we obtain expressions for the coefficients of rotational viscosity and diffusion of internal angular momentum in terms of the correlation functions, respectively, of the sources of internal angular momentum and of the irreversible flux of internal angular momentum:

$$\eta_r = \frac{1}{3\beta} \int dx' \int_0^\beta d\lambda \int_{-\infty}^0 dt_1 \, \langle I_s(x) I_s(x', t_1 + i\lambda) \rangle_l, \tag{21}$$

$$D_s = \frac{1}{9\beta} \int dx' \int_0^\beta d\lambda \int_{-\infty}^0 dt_1 \, \langle \mathbf{j}^3(x) : \tilde{\mathbf{j}}^3(x', t_1 + i\lambda) \rangle_l. \tag{22}$$

Analogous relations can also be written for the kinetic coefficients of cross processes, which, in the presence of rotation, exist between heat conduction and diffusion of internal angular momentum, as well as between the various viscous processes.

The method developed is easily generalized to obtain the equations of relaxation hydrodynamics.

In conclusion, the authors express their gratitude to D. N. Zubarev for discussion of the work.

Steklov Mathematical Institute
Academy of Sciences of the USSR

Received
2 XII 1966

REFERENCES

1. V. S. Sorokin, *ZhETF*, **13**, 3069 (1943).

2. Ya. Frenkel, *Kinetic Theory of Liquids*, Moscow–Leningrad, 1945.

3. C. de Groot, P. Mazur, *Nonequilibrium Thermodynamics*, Moscow, 1964.

4. M. M. Shliomis, *ZhETF*, **51**, 258 (1966).

5. P. Martin, J. Schwinger, *Phys. Rev.*, **115**, 1342 (1959).

6. H. Grad, *Comm. Pure Appl. Math.*, **5**, 455 (1952).

7. D. N. Zubarev, *DAN*, **140**, 92 (1961); **162**, 532 (1965); **162**, 794 (1965); **164**, 65 (1965).

8. J. McLennan, *Phys. Fluids*, **4**, 1319 (1961); *Adv. Chem. Phys.*, **5**, (1963).

9. L. D. Landau, E. M. Lifshitz, *Quantum Mechanics*, "Nauka," 1964.

Note: Figure translations are in progress. See original paper for figures.