Reports of the Academy of Sciences of the USSR

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1965

SovietRxiv

Abstract

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Reports of the Academy of Sciences of the USSR

1965. Volume 162, No. 4

PHYSICS

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TRANSPORT PROCESSES IN SYSTEMS OF PARTICLES WITH INTERNAL DEGREES OF FREEDOM

(Presented by Academician N. N. Bogolyubov, 27 XI 1964)

In systems of complex molecules, energy exchange between translational and internal motion may be difficult. Such a system can be regarded as a mixture of gases whose molecules are in different excited states. To study transport phenomena in such systems, it is necessary to formulate the conservation laws separately for each subsystem with specified quantum numbers:

$$\dot{H}_k(x) + \operatorname{div} \mathbf{j}_{H_k}(x) = J_{H_k}(x), \qquad \dot{n}_k(x) + \operatorname{div} \mathbf{j}_k(x) = J_k(x),$$

$$\dot{\mathbf{p}}_k(x) + \operatorname{Div} T_k(x) = \mathbf{f}_k(x), \tag{1}$$

where all quantities refer to the state k; $H_k(x)$ is the energy density; $\mathbf{j}_{H_k}(x)$ is the energy flux; $J_{H_k}(x)$ is the change in the energy of the k-th subsystem per unit time; $n_k(x)$ is the density of particles in state k; $\mathbf{j}_k(x)$ is the particle flux; $J_k(x)$ is the rate of formation of particles in state k; $\mathbf{p}_k(x)$ is the momentum density; $T_k(x)$ is the momentum-density tensor; $\mathbf{f}_k(x)$ is the density of the force of interaction of the k-th component with the others. The total densities of energy, number of particles, and momentum satisfy conservation laws; hence,

$$\sum_k J_{H_k}(x) = 0, \qquad \sum_k J_k(x) = 0, \qquad \sum_k \mathbf{f}_k(x) = 0. \tag{2}$$

In order to write explicitly the operators appearing in (1), one must choose a model of a system of particles with internal degrees of freedom. Let us consider an example of such a model. Denote by y the set of variables $y_1, y_2, \ldots$ describing the internal degrees of freedom of the molecule, and by x the coordinates of its center of mass. We take the Hamiltonian of the system in the form

$$H = \int \Psi^+(x,y) \Big\{ -\frac{1}{2m}\nabla^2 + H_{\text{in}}(y) +$$

$$+\frac{1}{2}\int \Psi^+(x',y')\,\Phi(xy,x'y')\,\Psi(x',y')\,dx'dy' \Big\}\,\Psi(x,y)\,dx\,dy, \tag{3}$$

where $\Phi(xy,x'y') = \Phi(x'y',xy)$ is the energy of interaction between molecules; $H_{\text{in}}(y)$ is the Hamiltonian of the internal degrees of freedom; $H_{\text{in}}(y) \times \varphi_i(y) = E_i\varphi_i(y)$, where E_i, $\varphi_i(y)$ are, respectively, the energy and eigenfunction of internal state i; the Planck constant is set equal to unity.

Introduce second-quantized operators $\Psi_i(x)$, describing subsystems with specified quantum numbers i:

$$\Psi_i(x) = \frac{1}{\sqrt{V}}\sum_k a_{ki}e^{i(kx)}, \qquad \Psi(x,y) = \sum_i \varphi_i(y)\Psi_i(x) \tag{4}$$

and satisfying the permutation relations

$$\begin{gathered}\Psi_i(x)\Psi_j^+(x') \pm \Psi_j^+(x')\Psi_i(x) = \delta_{ij}\delta(x-x'),\\ \Psi_i(x')\Psi_j(x) \pm \Psi_j(x')\Psi_i(x) = 0,\end{gathered} \tag{5}$$

where the plus sign is taken for odd molecular spin, and the minus sign for even spin.

The Hamiltonian (3) can be written in the form

$$H = \sum_i \int \Psi_i^+(x)\left(-\frac{1}{2m}\nabla^2 + E_i\right)\Psi_i(x)\,dx +$$

$$+\frac{1}{2}\sum_{ijkl}\int \Psi_i^+(x)\Psi_j^+(x')\Phi_{ij}^{kl}(x,x')\Psi_k(x')\Psi_l(x)\,dx\,dx', \tag{6}$$

where the function

$$\Phi_{ij}^{kl}(x,x') = \int \varphi_i^*(y)\varphi_j(y')\Phi(xy,x'y')\varphi_k(y')\varphi_l(y)\,dy\,dy'$$

has the symmetry properties $\Phi_{ij}^{kl}(x,x') = \Phi_{ji}^{lk}(x',x)$, $\Phi_{ij}^{kl}(x,x')^* = \Phi_{lk}^{ji}(x,x')$, which follow from the symmetry of $\Phi(xy,x'y')$ with respect to the interchange $x \to x'$, $y \to y'$ and from the Hermiticity of the interaction operator. The Hamiltonian (6) may be regarded as an initial model for a system of particles with internal degrees of freedom. The function $\Phi_{ij}^{kl}(x,x')$ plays the role of the interaction potential between molecules in states k and l, as a result of which they are transformed into molecules in states i and j. One may imagine that a chemical reaction takes place according to the scheme $(k)+(l) \rightleftarrows (i)+(j)$. The Hamiltonian (6) is similar to the Hamiltonian of a gas mixture, with the difference that it takes into account the internal energy of the molecules E_i and the possibility of transitions $k,l \to i,j$ in molecular collisions. The function $\Phi^{kl}_{ij}(x,x')$ can be estimated from the effective cross section of an inelastic collision. An analogous formal scheme for taking account of internal degrees of freedom, but on the basis of the Boltzmann kinetic equation, was developed by Wang Chang, Uhlenbeck, and de Boer ([7,8]).

The operator $\Psi_i(x)$ satisfies the equation of motion

$$i\dot{\Psi}_i(x) = \left\{-\frac{1}{2m}\nabla^2 + E_i\right\}\Psi_i(x) +$$

$$+\frac{1}{2}\sum_{jkl}\int \Psi^+_j(x')\left(\Phi^{kl}_{ij}(x,x') + \Phi^{kl}_{ji}(x',x)\right)\Psi_k(x')\Psi_l(x)\,dx' \quad (\hbar = 1). \quad (7)$$

The number of particles in the state i, $n_i(x) = \Psi^+_i(x)\Psi_i(x)$, is no longer conserved, since in collisions transitions from one internal state to another are possible, and it satisfies the balance equation

$$\dot{n}_i(x) + \operatorname{div}\mathbf{j}_i(x) = J_i(x), \quad (8)$$

where

$$J_i(x) = \frac{1}{2i}\sum_{jkl}\int\{\Psi^+_i(x)\Psi^+_j(x')(\Phi^{kl}_{ij}(x,x') + \Phi^{kl}_{ji}(x',x))\Psi_k(x')\Psi_l(x) -$$

$$-\Psi^+_l(x)\Psi^+_k(x')(\Phi^{kl}_{ij}(x,x')^* + \Phi^{kl}_{ji}(x',x)^*)\Psi_j(x')\Psi_i(x)\}\,dx' \quad (9)$$

is the operator of the rate of the "reaction" of formation of particles in state i. The flux operator $\mathbf{j}_i(x)$ has the usual form. The total density $n(x) = \sum_i n_i(x)$ is conserved, since $\sum_i J_i(x) = 0$. Analogously, one can also construct the other flux operators entering into (1).

The conservation laws (1) can be written in the form of a single equation for quantities depending on two indices,

$$\dot{P}_{mk}(x) + \nabla\cdot\mathbf{j}_{mk}(x) = J_{mk}(x), \quad (10)$$

moreover $\sum_k J_{mk}(x) = 0$, where we have introduced the notation $P_{0k}(x) = H_k(x)$, $P_{1k}(x) = n_k(x)$, $P_{2k}(x) = \mathbf{p}_k(x)$, $j_{0k}(x) = \mathbf{j}_{H_k}(x)$, $j_{1k}(x) = \mathbf{j}_k(x)$, $j_{2k} = T_k(x)$, $J_{0k}(x) = J_{H_k}(x)$, $J_{1k}(x) = J_k(x)$, $J_{2k}(x) = \mathbf{f}_k(x)$.

The density and current operators in (10) may have a more general meaning, for example, they may refer to a system in which chemical reactions occur; then the index k may denote the type of molecules of the reactants and reaction products, and the index m the type of conserved quantities (energy, mass, or momentum).

The formal theory of transport phenomena has been developed by many authors (see ($^{1-5}$) and the review (^{6})). Let us apply the general scheme for constructing the statistical operator (^{5}, ^{10}) to a system with conservation laws (10). The local integrals of motion have the form

$$A_{mk}(x) = P_{mk}(x) + \int_{-\infty}^{0} e^{\varepsilon t}\{\nabla \cdot j_{mk}(x,t) - J_{mk}(x,t)\}\, dt,$$

and the corresponding statistical operator is

$$\rho = Q^{-1}\exp\left\{ -\sum_{mk}\int\left(F_{km}(x)\cdot P_{mk}(x) - \int_{-\infty}^{0} e^{\varepsilon t}\nabla F_{km}(x)\cdot j_{mk}(x,t)\, dt \right.\right. \\ \left.\left. + \int_{-\infty}^{0} e^{\varepsilon t}(F_{km}(x) - F^{0}_{0m}(x))J_{mk}(x,t)\, dt \right) dx \right\}, \tag{11}$$

where $\nabla F_{km}(x)$, $F_{km}(x) - F^{0}_{0m}(x)$ are thermodynamic forces, with $F_{k0}(x) = \beta_k(x)$; $F_{k1}(x) = -\beta_k(x)(\mu_k(x) - m_k v_k^2(x)/2)$; $F_{k2}(x) = -\beta_k(x)\mathbf{v}_k(x)$; $\beta_k(x)$, $\mu_k(x)$, $\mathbf{v}_k(x)$ are the inverse temperature, chemical potential, and mass velocity of the particles of subsystem k.

We shall assume that the thermodynamic forces are small; then, with the aid of (11), we obtain linear relations between the thermodynamic forces and the fluxes:

$$\begin{aligned} \langle j_{mk}(x)\rangle &= \langle j_{mk}(x)\rangle_l \\ &\quad + \sum_{m_1k_1}\int \left\{ L^{k_1m_1}_{km}(x,x')\cdot\nabla F_{k_1m_1}(x') + \mathcal{L}^{k_1m_1}_{km}(xx')\cdot(F_{k_1m_1}(x') - F^{0}_{0m_1}(x'))\right\} dx', \\ \langle J_{mk}(x)\rangle &= \langle J_{mk}(x)\rangle_l \\ &\quad + \sum_{m_1k_1}\int \left\{ \mathcal{L}^{k_1m_1}_{km}(x,x')\cdot\nabla F_{k_1m_1}(x') + \Omega^{k_1m_1}_{km}(x,x')(F_{k_1m_1}(x') - F^{0}_{0m_1}(x'))\right\} dx', \end{aligned} \tag{12}$$

where

$$L_{km}^{k_1 m_1}(x, x') = \int_{-\infty}^{0} e^{\varepsilon t} (j_{km}(x), j_{k_1 m_1}(x', t))\, dt \tag{13}$$

are kinetic coefficients. The brackets in (13) denote correlation functions

$$(j_k(x), j_m(x', t)) = \beta^{-1} \int_0^{\beta} \left\langle j_k(x)(j_m(x', t, i\tau) - \langle j_m(x') \rangle_l) \right\rangle_l \, d\tau,$$

$$j_m(x', t, i\tau) = e^{-\beta^{-1} A \tau} j_m(x', t) e^{\beta^{-1} A \tau}, \qquad A = \sum_{mk} \int F_{km}(x) \cdot P_{mk}(x)\, dx, \tag{14}$$

and the index l denotes averaging over the local ensemble. Analogous expressions are obtained also for $\mathcal{L}_{km}^{k_1 m_1}(x, x')$, $\Omega_{km}^{k_1 m_1}(x, x')$.

For the local production of entropy we obtain a quadratic form in the thermodynamic forces

$$\sigma(x) = \sum_{\substack{km \\ k_1 m_1}} \int \Big\{ \nabla F_{km}(x) L_{km}^{k_1 m_1}(x, x') \nabla F_{k_1 m_1}(x') +$$

$$+ 2(F_{km}(x) - F_{0m}(x)) \mathcal{L}_{km}^{k_1 m_1}(x, x') \nabla F_{k_1 m_1}(x') +$$

$$+ (F_{km}(x) - F_{0m}(x)) \Omega_{km}^{k_1 m_1}(x, x') (F_{k_1 m_1}(x') - F_{0 m_1}(x')) \Big\}\, dx'. \tag{15}$$

If the isotropy of the system is taken into account, then many terms in (15) vanish.

A particular case of the problem considered is irreversible processes in a spatially homogeneous system consisting of weakly interacting subsystems, for example the case of a chemical reaction in a homogeneous phase or of a temperature difference between different components of a mixture. The conservation laws for energy and particle number in these cases have the form $\dot{H}_k = J_{H_k}$, $\dot{N}_k = J_{N_k}$, where H_k and N_k are the energy and the number of particles of the k-th subsystem, with $\sum_k J_{H_k} = 0$, $\sum_k J_{N_k} = 0$. In the general case, when the system may be regarded as a set of weakly interacting subsystems, for example a set of reservoirs connected by capillaries or semipermeable partitions, the conservation laws have the same form; they correspond to the integrals of motion

$$A_{H_k} = H_k - \int_{-\infty}^{0} e^{\varepsilon t} \dot{H}_k(t)\, dt, \qquad A_{N_k} = N_k - \int_{-\infty}^{0} e^{\varepsilon t} \dot{N}_k(t)\, dt \tag{16}$$

and the statistical operator (9)

$$\rho = Q^{-1} \exp\left\{ -\sum_k \beta_k (H_k - \mu_{kN} k) + \sum_k (\beta_k - \beta_0) \int_{-\infty}^{0} e^{\varepsilon t} \dot{H}_k(t)\, dt \right.$$
$$\left. - \sum_k (\beta_k \mu_k - \beta_0 \mu_0) \int_{-\infty}^{0} e^{\varepsilon t} \dot{N}_k(t)\, dt \right\}. \qquad (17)$$

Assuming that the thermodynamic forces $\beta_k - \beta_0$, $\beta_k \mu_k - \beta_0 \mu_0$ are small, we obtain linear relations for the change in the energy and number of particles of the k-th subsystem.

In conclusion I express my gratitude to N. N. Bogoliubov for a valuable discussion.

Received
25 XI 1964

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