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D. N. ZUBAREV

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Abstract

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D. N. ZUBAREV

STATISTICAL OPERATOR FOR NONEQUILIBRIUM SYSTEMS

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For systems in a state of statistical equilibrium, the Gibbs distribution is known, with the aid of which one can in principle calculate the mean value of any dynamical quantity. For irreversible processes no such universal distribution has been found, and in solving problems of the statistical mechanics of nonequilibrium systems one resorts to various approximate methods, for example to the method of the kinetic equation ([1,2]), or to the solution of the Liouville equation with the initial condition of local equilibrium (the method of correlation functions ([3])).

We shall show that one can find a probability distribution which for equilibrium systems goes over into the Gibbs distribution, and for nonequilibrium systems makes it possible to obtain macroscopic equations of diffusion, heat conduction, and hydrodynamics, generally speaking of nonlocal type, in any approximation, and to calculate kinetic coefficients through correlation functions. In the linear approximation, this distribution yields the results of Mori ([3]) and Green ([8]) (see also ([4,5,9])).

The usual construction of statistical ensembles for equilibrium systems is based on Liouville' s theorem that the time derivative of the statistical operator ρ is equal to zero if it is a function of the integrals of motion, and on the assumption that these integrals are the additive integrals of motion: the Hamiltonian operator of the system H, and, for the grand Gibbs ensemble, in addition the operator of the total number of particles N, i.e. $\rho = \rho(H, N)$. We shall likewise proceed from Liouville' s theorem, but we shall need its generalized formulation.

Suppose that we have found operators $A_1(x), A_2(x)$ ..., depending on the coordinate x, which are integrals of motion, i.e. $\dot{A}_1(x) = 0$, $\dot{A}_2(x) = 0, ...$; differentiation with respect to t means, as usual, the operation of commutation with the full Hamiltonian H, which is assumed not to depend on time:

$$\dot{A}_j(x) = \frac{1}{i\hbar}[A_j(x), H] \quad (j = 1, 2, ...).$$

Such operators $A_j(x)$ we shall call local integrals of motion. (In the case of classical mechanics, the quantum Poisson brackets must be replaced by classical ones. Below we shall consider the quantum case; the transition to the classical case presents no difficulties.) Then, if the statistical operator ρ is a functional of $A_j(x)$: $\rho = \rho\{\ldots A_j(x) \ldots\}$, then it is also an integral of motion, i.e.

$$\dot{\rho} = \frac{1}{i\hbar}[H, \rho] = 0$$

(as is well known, the time derivatives of the ordinary operator and of the statistical operator differ in sign).

In constructing the Gibbs ensemble one uses the conservation laws of energy and particle number. We shall also use these conservation laws, but in differential, operator form:

$$\dot{H}(x,t) + \operatorname{div} j_H(x,t) = 0, \qquad \dot{n}(x,t) + \operatorname{div} j(x,t) = 0, \tag{1}$$

where $H(x)$, $n(x)$, $\mathbf{j}_H(x)$, $\mathbf{j}(x)$ are the operators of the energy density, particle-number density, and the densities of the energy and particle fluxes. The form of these operators is assumed known; they are easily found if the Hamiltonian of the system is known,

$$H = \int H(x)\,dx.$$

The operator of the total number of particles is

$$N = \int n(x)\,dx.$$

All operators are considered in the Heisenberg representation; for example:

$$H(x,t) = e^{iHt/\hbar} H(x) e^{-iHt/\hbar}.$$

(For the case of classical mechanics, the Heisenberg representation must be replaced by the action of the evolution operator S_t; see (^{2}).) One could also consider the conservation laws for momentum, angular momentum, and the numbers of particles of different types of molecules, which is important for constructing the complete equations of hydrodynamics. Generalizations of this kind present no difficulty.

Let us note that the operators

$$A_1(x) = H(x) + \int_{-\infty}^{0} \operatorname{div} \mathbf{j}_H(x,t)\,dt, \qquad A_2(x) = n(x) + \int_{-\infty}^{0} \operatorname{div} \mathbf{j}(x,t)\,dt \tag{2}$$

with the boundary condition of absence of sources at $t = -\infty$,

$$\operatorname{div} \mathbf{j}_H(x, -\infty) = \operatorname{div} \mathbf{j}(x, -\infty) = 0,$$

are local integrals of motion, since by virtue of (1)

$$\dot{A}_1(x) = \dot{A}_2(x) = 0.$$

Consequently, the statistical operator $\rho = \rho\{A_1(x), A_2(x)\}$, as a functional of $A_1(x)$, $A_2(x)$, is also an integral of motion by virtue of the generalized Liouville theorem.

We assume that $\rho\{A_1(x), A_2(x)\}$ has the form

$$\rho\{A_1(x), A_2(x)\} = Q^{-1} \exp\left\{-\sum_j \int \alpha_j(x) A_j(x)\, dx\right\} \quad (j = 1, 2), \tag{3}$$

where $\alpha_j(x)$ are certain functions of x; Q is the normalization factor, determined from the probability normalization condition $\operatorname{Sp} \rho = 1$. By analogy with the ordinary grand Gibbs ensemble, we choose

$$\alpha_1(x) = \beta(x) = \frac{1}{T(x)}, \qquad \alpha_2(x) = -\beta(x)\mu(x) = -\frac{\mu(x)}{T(x)},$$

where $T(x)$ is the local temperature and $\mu(x)$ the local chemical potential. Consequently, the statistical operator (3) can be represented in the form

$$\rho = Q^{-1} \exp\left\{-\int \beta(x) \left[H(x) - \mu(x)n(x) + \int_{-\infty}^{0} \{\nabla \mathbf{j}_H(x, t) - \mu(x) \nabla \mathbf{j}(x, t)\}\, dt\right] dx\right\} \tag{4a}$$

or

$$\rho = Q^{-1} \exp\left\{-\int \left[\beta(x)(H(x) - \mu(x)n(x)) - \int_{-\infty}^{0} \{\mathbf{j}_H(x, t) \cdot \nabla\beta(x) - \mathbf{j}(x, t) \cdot \nabla\beta(x)\mu(x)\}\, dt\right] dx\right\}, \tag{4b}$$

where we have integrated by parts and neglected surface integrals. Here Q is the statistical sum, equal to

$$Q = \operatorname{Sp} \exp \left\{ - \int \left[\beta(x)(H(x) - \mu(x)n(x)) - \int_{-\infty}^{0} \{\mathbf{j}_H(x,t) \cdot \nabla\beta(x) - \mathbf{j}(x, t \cdot \nabla\beta(x)\mu(x)\} \, dt \right] dx \right\}. \tag{5}$$

The statistical operator ρ (4a, b) gives the desired statistical distribution, which is also applicable to irreversible processes. We shall call ρ the statistical functional. With its help one can calculate the mean value of any operator $\mathfrak{A}$ by the formula $\overline{\mathfrak{A}} = \operatorname{Sp}(\rho\mathfrak{A})$.

We have not considered changes of the parameters $\beta(x)$ and $\mu(x)$ with time. Generally speaking, they may vary slowly, with a characteristic time of variation much greater than the relaxation time of the statistical distribution (4a, b); ρ can be found for this case as well.

Mori (^{3}) takes as the initial condition for the Liouville equation the so-called "locally equilibrium distribution"

$$\rho_l = Q_l^{-1} \exp \left\{ - \int \beta(x)\{H(x) - \mu(x)n(x)\} \, dx \right\}, \tag{6}$$

which itself is not a solution of the Liouville equation, although for small $\nabla\beta(x)$, $\nabla\mu(x)$ it is close to (4). This is also the reason for the success of Mori' s theory.

Let us introduce notation for the densities of the generalized thermodynamic forces $X_1(x) = \beta^{-1}(x)\nabla\beta(x)$, $X_2(x) = -\beta^{-1}(x)\nabla\beta(x)\mu(x)$, and for the densities of the fluxes conjugate to them $j_1(x) = j_H(x)$, $j_2(x) = j(x)$; then

$$\rho = Q^{-1} \exp \left\{ - \int \beta(x) \left[H(x) - \mu(x)n(x) - \sum_m \int_{-\infty}^{0} (j_m(x,t)X_m(x)) \, dt \right] dx \right\}. \tag{7}$$

If the temperature β^{-1} and the chemical potential μ are constant, then $X_1(x) = X_2(x) = 0$, and the statistical functional (7) becomes the usual Gibbs distribution for the grand ensemble: $\rho = Q^{-1} \exp\{-\beta(H - \mu N)\}$.

The operator ρ (7) is an integral of motion and, consequently, is constant in time. One can, however, introduce the entropy operator S by the relation

$$\rho = \exp\{-S - \Delta S\}, \tag{8}$$

where

$$S = \int \beta(x)\{H(x) - \mu(x)n(x) - \Omega(x)\} \, dx, \tag{8a}$$

$$\Delta S = -\sum_k \int \int_{-\infty}^{0} \{j_k^*(x,t) - \bar{j}_k(x,t)\} \cdot X_k(x)\, dx\, dt \tag{8b}$$

($\Omega(x)$ is the density of the thermodynamic potential), and, consequently, the mean value of the operator ΔS is zero, $\overline{\Delta S} = 0$. The operator S will no longer be an integral of motion, but will increase so that

$$\dot{\bar{S}} = \sum_k \int \beta(x)(\bar{j}_k(x) X_k(x))\, dx \geq 0, \tag{9}$$

where we have used the fact that $\dot{A}_k(x) = 0$. The positivity of (9) can be shown by calculating $\bar{j}_k(x)$ in the linear approximation in $X_m(x)$.

Write the operator ρ in the form

$$\rho = Q^{-1} e^{-(A+B)}, \tag{10}$$

where

$$A = \int \beta(x)\{H(x) - \mu(x) n(x)\}\, dx, \tag{10a}$$

$$B = -\sum_m \int \int_{-\infty}^{0} \beta(x)(j_m(x,t) X_m(x))\, dx\, dt, \tag{10b}$$

and expand $e^{-(A+B)}$ in a series in powers of B, retaining terms through first order:

$$e^{-(A+B)} = e^{-A} - \int_0^1 e^{-A\tau} B e^{A\tau} e^{-A}\, d\tau; \tag{11}$$

then we obtain

$$\bar{\mathbf{j}}_k(x) = -\frac{1}{\beta} \int_0^{\beta} \langle \mathbf{j}_k(x) B(i\hbar\tau) \rangle d\tau, \tag{12}$$

where $\langle ... \rangle$ denotes averaging over the equilibrium Gibbs ensemble.

In deriving (12) we assumed that the mean current densities in the state of local equilibrium are equal to zero. Substituting (10) into (12), we obtain

$$\bar{\mathbf{j}}_k(x) = \sum_m \int L_{km}(x,x') \cdot \mathbf{X}_m(x')\, dx', \tag{13}$$

where

$$L_{km}(x,x') = \int_0^\beta \int_{-\infty}^0 \langle \mathbf{j}_k(x)\,\mathbf{j}_m(x',t+i\hbar\tau)\rangle\,d\tau\,dt \tag{14}$$

is the tensor correlation function between the currents $\mathbf{j}_k(x)$ and $\mathbf{j}_m(x')$, from which the Onsager principle follows (^{6,7}). Formulas (13), (14) coincide with Mori' s formulas (^{3}) if, in the latter, the parameter τ_c is made to tend to infinity. Substituting (13) into (9), we obtain

$$\dot{\bar{S}} = \sum_{k,m} \int \beta(x)\mathbf{X}_k(x)\cdot L_{km}(x,x')\cdot \mathbf{X}_m(x')\,dx\,dx' \geq 0, \tag{15}$$

i.e., with the choice of the local integrals of motion (2), the entropy increases.

The above makes possible a new approach to interpreting the second law of thermodynamics. The choice of the local integrals $A_1(x)$, $A_2(x)$ in (2) is not unique. It is also possible to choose

$$A_1'(x) = H(x) - \int_0^\infty \operatorname{div}\mathbf{j}_H(x,t)\,dt, \qquad A_2'(x) = n(x) - \int_0^\infty \operatorname{div}\mathbf{j}(x,t)\,dt \tag{16}$$

with boundary conditions $\operatorname{div}\mathbf{j}_H(x,\infty) = \operatorname{div}\mathbf{j}(x,\infty) = 0$. Then, taking into account the symmetry $t \to -t$, we obtain

$$\dot{\bar{S}} = -\sum_{k,m} \int \beta(x)\mathbf{X}_k(x)\cdot L_{km}(x,x')\cdot \mathbf{X}_m(x')\,dx\,dx' \leq 0,$$

i.e., the entropy decreases. Thus, it should be assumed that physical meaning is possessed by local integrals of the type (2), but not of the type (16). The method presented can be applied to various concrete problems in the theory of irreversible processes.

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

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