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Abstract

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THE LOCALLY EQUILIBRIUM GIBBS ENSEMBLE AND ITS CONNECTION WITH THE THEORY OF FLUCTUATIONS AND TRANSPORT PHENOMENA

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To determine the thermodynamic functions of nonequilibrium states it is necessary to construct the corresponding statistical ensemble, for example by introducing an auxiliary field that would make the state thermodynamically equilibrium ([1]). However, the inhomogeneity of the temperature, generally speaking, cannot be included by means of an auxiliary field; therefore we shall use the method of locally equilibrium Gibbs ensembles.

Under stationary external conditions (contacts with different thermostats, semipermeable partitions), a locally equilibrium stationary distribution is established in the system; it is necessary to determine the corresponding statistical operator. Let the nonequilibrium state be specified by an inhomogeneous distribution of the energy $E(x)$. Instead of $E(x)$ it is convenient to consider the set of its Fourier components E_q, which form a discrete set. The quantities $E(x)$ and E_q correspond to dynamical variables—the energy-density operator $H(x)$ and its Fourier component $H_q = \int e^{-i(qx)} H(x)\,dx$. The operator $H(x)$ is Hermitian; consequently, $H_q^+ = H_{-q}$. The quantity H_q has the character of a collective variable. For example, for a system of particles with direct interaction,

$$H_q = \sum_k \frac{1}{2m}(\mathbf{k},\mathbf{k}+\mathbf{q})\, a_k^+ a_{k+q} + \frac{1}{2V} \sum_{k_1'+k_2'=k_1+k_2+q} v(k_2'-k_2) a_{k_1}^+ a_{k_2}^+ a_{k_2'} a_{k_1'} . \quad (1)$$

Let us note that for $q = 0$, (1) is the full Hamiltonian of the system H.

Usually the Gibbs statistical ensemble is introduced with the aid of the eigenfunctions of the operator H ([2,3]). To construct the statistical operator for locally equilibrium systems, we shall use the eigenfunctions of the operator $\sum_q \beta_{-q} H_q$. Just as in the equilibrium case the statistical operator is obtained by projection onto states with specified values of H, we shall construct the operator

$$\rho = Q^{-1} \exp\left(-\sum_q \beta_{-q} H_q\right) = Q^{-1} \exp\left\{-\int \beta(x) H(x)\, dx\right\}, \tag{2}$$

which corresponds to the maximum of the informational entropy (^{5})

$$S = -\operatorname{Sp}(\rho \ln \rho) \tag{3}$$

for prescribed

$$\langle H_q \rangle = \operatorname{Sp}(\rho H_q). \tag{4}$$

The quantity

$$\beta(x) = \sum_q \beta_q e^{i(qx)} \tag{5}$$

is the local temperature.

For a multicomponent system with a velocity field, it is necessary, in addition to (1), to take into account the Fourier components of the particle-number density operators $n_\alpha(x)$

and momentum $\mathbf{p}(x)$:

$$\rho = \exp\left\{-\Phi[F_0(x) \dots F_n(x)] - \sum_0^n \int F_k(x) P_k(x)\, dx\right\}, \tag{6}$$

$$F_0(x) = \beta(x), \qquad F_\alpha(x) = -\beta(x)(\mu_\alpha(x) - {}^1/_2 m_\alpha v^2(x)),$$

$$F_n(x) = -\beta(x)\mathbf{v}(x),$$

$$P_0(x) = H(x), \qquad P_\alpha(x) = n_\alpha(x), \qquad P_n(x) = \mathbf{p}(x) \qquad (\alpha = 1, 2, \dots n-1),$$

$\mu_\alpha(x)$ is the chemical potential, $\mathbf{v}(x)$ is the mass velocity.

The quantity

$$\Phi[F_0(x) \dots F_n(x)] = \ln Q$$

has the meaning of a functional generalizing the Massieu-Planck function to inhomogeneous systems. It is related to the entropy by the relation

$$S = \Phi + \sum_{k=0}^{n} \int F_k(x) \langle P_k(x) \rangle \, dx =$$

$$= \ln \mathrm{Sp} \exp \left\{ - \sum_{k=0}^{n} \int F_k(x) (P_k(x) - \langle P_k(x) \rangle) \, dx \right\}. \tag{7}$$

Varying the normalization condition for the operator (6) with respect to $F_k(x)$, and (7) with respect to $\langle P_k(x) \rangle$, we obtain the thermodynamic equalities

$$\delta\Phi / \delta F_k(x) = -\langle P_k(x) \rangle, \qquad \delta S / \delta \langle P_k(x) \rangle = F_k(x),$$

whence follows the relation between the variational derivatives of Φ and the correlation functions

$$\delta^2 \Phi / \delta F_k(x') \delta F_i(x) = -\delta \langle P_i(x) \rangle / \delta F_k(x') = (P_i(x), P_k(x')), \tag{8}$$

$$(P_i(x), P_k(x')) = \int_0^1 \langle P_i(x) e^{-A\tau} (P_k(x') - \langle P_k(x') \rangle) e^{A\tau} \rangle \, d\tau,$$

$$A = \sum_k \int F_k(x) P_k(x) \, dx.$$

To investigate fluctuations in an inhomogeneous state, we introduce a macroscopic distribution function $W \Delta P_{0q} \ldots \Delta P_{nq}$, which gives the probability that the parameters $\ldots P_{0q} \ldots P_{nq} \ldots$ (Fourier components of $P_k(x)$) lie in the region $\ldots \Delta P_{0q} \ldots \Delta P_{nq} \ldots$

$$W \Delta P_{0q} \ldots \Delta P_{nq} = \Omega \Delta P_{0q} \ldots \Delta P_{nq} \exp \left\{ -\Phi - \sum_k \int F_k(x) P_k(x) \, dx \right\}. \tag{9}$$

We now regard the quantities P_{kq} not as dynamical variables, but as ordinary functions. The functional (9) is a generalization of Einstein's macroscopic distribution function (6). The quantity $\Omega \Delta P_{0q} \ldots \Delta P_{nq}$ is the number of microstates in the region $\ldots \Delta P_{0q} \ldots \Delta P_{nq} \ldots$, which can be estimated through the entropy of the microcanonical ensemble $s = \ln \Omega / \Omega_0$, where Ω_0 is a constant inessential for us. We write (9) in the form

$$W = \Omega_0 \exp\left\{ s - S - \sum_k \int F_k(x) \Delta P_k(x)\, dx \right\}, \tag{10}$$

$$\Delta P_k(x) = P_k(x) - \langle P_k(x) \rangle.$$

As a consequence of the equivalence of statistical ensembles, the entropy in the locally equilibrium canonical ensemble is the same function of $\langle P_{0q} \rangle \ldots \langle P_{nq} \rangle$ as the entropy in the locally equilibrium canonical ensemble is of $P_{0q} \ldots P_{nq}$, i.e., S and s are identical functions, but of different variables. Expanding $s - S$ in a functional series, we obtain

$$W = A \exp\left\{ \frac{1}{2} \sum_{ik} \iint \frac{\delta^2 S}{\delta \langle P_i(x_1) \rangle \delta \langle P_k(x_2) \rangle} \Delta P_i(x_1) \Delta P_k(x_2)\, dx_1\, dx_2 \right\}. \tag{11}$$

With the aid of (11) one can investigate fluctuations near a critical point both in a homogeneous and in an inhomogeneous state; for this it is necessary to expand the Fourier coefficients of the second derivative of the entropy in a series in the wave number and to retain several terms.

The statistical operator (6) gives the correct thermodynamic equalities and fluctuations, but does not allow one to study transport processes. Let us note, however, that the operators $P_k(x)$ are defined nonuniquely, only up to a divergence, and we shall make use of this arbitrariness below. The quantities $P_k(x)$ satisfy the conservation laws

$$\dot{P}_k(x,t) + \nabla \cdot j_k(x,t) = 0.$$

All quantities are taken in the Heisenberg representation.

Taking into account the nonuniqueness in the definition of $P_k(x)$, let us choose in their place the quantities $A_k(x)$

$$A_k(x) = P_k(x) + \int_{-\infty}^{0} e^{\varepsilon t} \nabla \cdot j_k(x,t)\, dt = \varepsilon \int_{-\infty}^{0} e^{\varepsilon t} P_k(x,t)\, dt, \tag{12}$$

which are local integrals of motion as $\varepsilon \to 0$. Operation (12) means taking the invariant part of the operator with respect to the motion with Hamiltonian H. The choice (12) means imposing boundary conditions of the retarded type, i.e., causality conditions. An analogous situation occurs in the formal theory of scattering ([7]). Solutions of the advanced type,

$$\varepsilon \int_{0}^{\infty} e^{-\varepsilon t} P_k(x,t)\, dt,$$

are unsuitable, since they would give not an increase but a decrease of the entropy (^{8}). Instead of (12) one could formally take a smoothing in time,

$$\frac{1}{T}\int_{-T}^{0} P_k(x,t)\,dt,$$

but then it would still be necessary to define the integrals by a displacement into the complex plane, which is equivalent to (12).

Replacing in (7) $P_k(x)$ by $A_k(x)$ and omitting surface integrals, we obtain the statistical operator for nonequilibrium stationary processes

$$\rho = Q^{-1}\exp\left\{-\sum_k \int \left(F_k(x)P_k(x) - \int_{-\infty}^{0} e^{\varepsilon t} j_k(x,t)\cdot\nabla F_k(x)\,dt\right)dx\right\}. \tag{13}$$

This expression was obtained in (^{8}), but now we have clarified the meaning of the condition used there that the fluxes (or thermodynamic forces) vanish at $t \to -\infty$. An expression analogous to (13) was later obtained in (^{9}) by another method for the nonstationary case. With the aid of (13), averages are calculated for large systems, i.e., as $V \to \infty$, and we shall always assume that first the limiting transition $V \to \infty$ is performed, and only then $\varepsilon \to 0$.

Expanding (13) in small gradients F_k, we obtain linear relations between the thermodynamic forces and the fluxes and an expression for lo-

of local entropy production

$$\langle j_k(x)\rangle = \langle j_k(x)\rangle_l + \sum_m \int L_{km}(x,x')\cdot\nabla F_m(x')\,dx',$$

$$\sigma(x) = \sum_{km}\int \nabla F_k(x)\cdot L_{km}(x,x')\cdot\nabla F_m(x')\,dx', \tag{14}$$

where

$$L_{km}(x,x') = \int_{-\infty}^{0} e^{\varepsilon t}(j_k(x),\, j_m(x',t))\,dt$$

are the kinetic coefficients (see (10–13)).

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CITED LITERATURE

1. M. A. Leontovich, *Statistical Physics*, Moscow-Leningrad, 1944.
2. I. von Neumann, *Mathematical Foundations of Quantum Mechanics*, 1964.
3. N. N. Bogolyubov, *Lectures on Quantum Statistics*, Kiev, 1949.
4. Yu. A. Krutkov, DAN, No. 1, 1 (1933).
5. E. T. Janes, Information Theory and Statistical Mechanics. In: *Statistical Physics*, 3, 1963, p. 160.
6. R. F. Green, H. B. Callen, Phys. Rev., 83, 1231 (1951).
7. M. Gell-Mann, M. L. Goldberger, Phys. Rev., 91, 398 (1953).
8. D. N. Zubarev, DAN, 140, 92 (1961).
9. J. McLennan, Phys. Fluids, 3, 493 (1960); 4, 1319 (1961).
10. M. S. Green, J. Chem. Phys., 20, 1281 (1952); 22, 398 (1954).
11. H. Mori, Phys. Rev., 112, 1829 (1958).
12. R. Kubo, M. Yokota, S. Nakajima, J. Phys. Soc. Japan, 12, 1203 (1957).
13. G. Chester, Rep. Progr. Phys., 26, 411 (1963).

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