Vol. A58 (1980) ACTA PHYSICA POLONICA No 1

CONNECTION BETWEEN THE NONLINEAR RESPONSE OF A SYSTEM AND THE MAXIMUM OF ENTROPY

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(*Received December 7, 1979*)

Using the maximum entropy formalism we obtained the formulas both for nonlinear and linear response of a system.

1. Introduction

The equilibrium distribution functions and statistical operators for all the Gibbsian ensembles correspond to the maximum of entropy for the assumed different external conditions [1, 2]. The external properties of the Gibbsian ensembles were noticed a long time ago. Indeed, in generalizing the Gibbsian ensembles to the case of quantum statistics, von Neumann started from the extremal properties of entropy [3]. The use of the extremal properties of entropy is a very convenient method for finding the different distribution functions and statistical operators. This method is suitable in both equilibrium and non-equilibrium statistical mechanics [4]. In the present paper, we shall use the extremal properties of the entropy to construct the statistical operator for the nonlinear response of a system.

2. Maximum of entropy

We shall consider the response of a quantum statistical ensemble of a system, with the Hamiltonian $\mathscr{H}(0)$ independent of time t, to the switching on time-dependent external perturbation $V(t)$. The total Hamiltonian of the system, including the external perturbation, is

$$\mathscr{H} = \mathscr{H}(0)+V(t), \tag{1}$$

where $V(t)$ is the operator of interaction of the system with the external classical field.

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The statistical operator $\varrho(t)$ satisfies the von Neumann equation

$$i\hbar \frac{\partial \varrho(t)}{\partial t} = [\mathscr{H}, \varrho(t)]. \tag{2}$$

We assume that at $t = -\infty$ the external perturbation is absent i.e.,

$$V(t = -\infty) = 0 \tag{3}$$

and

$$\delta\langle \mathscr{H}(0)\rangle(t = -\infty) = 0, \tag{4}$$

$$\delta\langle N_j\rangle (t = -\infty) = 0, \tag{5}$$

where

$$\langle \mathscr{H}(0)\rangle(t = -\infty) = \mathrm{Tr}\,[\varrho(t = -\infty)\mathscr{H}(0)], \tag{6}$$

$$\langle N_j\rangle (t = -\infty) = \mathrm{Tr}\,[\varrho(t = -\infty)N_j]. \tag{7}$$

N_j is the operator of a particle number for j type particles. Consequently, at $t = -\infty$ the system is in contact with a thermostat and a particle reservoir, this means that they are characterized by specifying the average energy and average number of particles.

The negative mean of the logarithm of the statistical operator is called the Gibbs entropy

$$S = -\langle \ln \varrho(t)\rangle = -\mathrm{Tr}\,[\varrho(t) \ln \varrho(t)]. \tag{8}$$

We shall show that the nonlinear response of the system corresponds to the maximum of the entropy (8), i.e.,

$$\delta S = 0, \tag{9}$$

$$\delta^2 S < 0 \tag{10}$$

for a given (4) and (5) and when the normalization is conserved

$$\mathrm{Tr}\,[\varrho(t)] = 1. \tag{11}$$

We think that expressions (9) and (10) can be regarded as specific "boundary conditions" of statistical mechanics.

We find the extremum of the functional (8) under the supplementary conditions (4), (5) and (11). Following the usual method, we seek the absolute extremum of the functional

$$L[\varrho(t)] = -\mathrm{Tr}\,[\varrho(t) \ln \varrho(t)] - \beta\,\mathrm{Tr}\,[\varrho(t = -\infty)\mathscr{H}(0)]$$
$$+(1+\beta\Omega)\,\mathrm{Tr}\,[\varrho(t)] + \beta \sum_j \mu_j\,\mathrm{Tr}\,[\varrho(t = -\infty)N_j], \tag{12}$$

where β, μ_j and $1+\beta\Omega$ are Lagrange multipliers determined from the conditions (4), (5) and (11).

If the Hamiltonian (1) depends explicitly on time, the von Neumann equation (2) can be formally integrated with the help of the evolution operator $U(t, -\infty)$, a unitary operator satisfying the equation

$$i\hbar \frac{\partial U(t, -\infty)}{\partial t} = (\mathscr{H}(0) + V(t))U(t, -\infty), \tag{13}$$

where

$$U^{\dagger}(t, -\infty)U(t, -\infty) = 1 \tag{14}$$

and the initial condition

$$e^{i\mathscr{H}(0)t/\hbar}U(-\infty, -\infty) = 1. \tag{15}$$

The statistical operator at time t has the form

$$\varrho(t) = U(t, -\infty)\varrho(t = -\infty)U^{\dagger}(t, -\infty). \tag{16}$$

Substituting (14) and (16) into functional (12) and using the cyclic invariance of the trace, we obtain

$$\begin{aligned} L[\varrho(t)] = &-\mathrm{Tr}\,[\varrho(t)\ln\varrho(t)] + (1+\beta\Omega)\,\mathrm{Tr}\,[\varrho(t)] \\ &-\beta\,\mathrm{Tr}\,[\varrho(t)U(t, -\infty)\mathscr{H}(0)U^{\dagger}(t, -\infty)] \\ &+\beta\sum_j \mu_j\,\mathrm{Tr}\,[\varrho(t)U(t, -\infty)N_j U^{\dagger}(t, -\infty)]. \end{aligned} \tag{17}$$

From the requirement that the first variation of this functional vanishes

$$\delta L[\varrho(t)] = 0 \tag{18}$$

we find

$$\varrho(t) = \exp\{-\beta[U(t, -\infty)\,(\mathscr{H}(0) - \sum_j \mu_j N_j - \Omega)U^{\dagger}(t, -\infty)]\}, \tag{19}$$

which coincides with the statistical operator in the case of nonlinear response of the system [4, 5].

We now prove that (19) corresponds to the maximum entropy (8). Let $\varrho'(t)$ be a normalized statistical operator corresponding to the same average energy as (6)

$$\mathrm{Tr}\,[\varrho'(t = -\infty)\mathscr{H}(0)] = \mathrm{Tr}\,[\varrho(t = -\infty)\mathscr{H}(0)] \tag{20}$$

and to the same average particles' numbers as (7)

$$\mathrm{Tr}\,[\varrho'(t = -\infty)N_j] = \mathrm{Tr}\,[\varrho(t = -\infty)N_j] \tag{21}$$

but arbitrary in other respects. Putting (19) into the inequality

$$-\mathrm{Tr}\,[\varrho' \ln \varrho'] \leqslant -\mathrm{Tr}\,[\varrho' \ln \varrho] \tag{22}$$

which follows from the obvious inequality

$$\ln x \geqslant 1 - \frac{1}{x}, \qquad x > 0,$$

we obtain

$$-\mathrm{Tr}\,[\varrho'(t) \ln \varrho'(t)] \leqslant -\mathrm{Tr}\,[\varrho'(t) \ln \varrho(t)]$$
$$= -\beta\Omega + \beta\,\mathrm{Tr}\,[\varrho'(t) U(t, -\infty) \mathscr{H}(0) U^{\dagger}(t, -\infty)]$$
$$-\beta \sum_j \mu_j \,\mathrm{Tr}\,[\varrho'(t) U(t, -\infty) N_j U^{\dagger}(t, -\infty)]$$
$$= -\beta\Omega + \beta\,\mathrm{Tr}\,[\varrho'(t = -\infty)\mathscr{H}(0)] - \beta \sum_j \mu_j \,\mathrm{Tr}\,[\varrho'(t = -\infty) N_j]$$
$$= -\beta\Omega + \beta\,\mathrm{Tr}\,[\varrho(t = -\infty)\mathscr{H}(0)] - \beta \sum_j \mu_j \,\mathrm{Tr}\,[\varrho(t = -\infty) N_j]$$
$$= -\beta\Omega + \beta\,\mathrm{Tr}\,[\varrho(t) U(t, -\infty) \mathscr{H}(0) U^{\dagger}(t, -\infty)]$$
$$-\beta \sum_j \mu_j \,\mathrm{Tr}\,[\varrho(t) U(t, -\infty) N_j U^{\dagger}(t, -\infty)] = -\mathrm{T_r}\,[\varrho(t) \ln \varrho(t)], \tag{23}$$

where we use the conditions (11), (14), (20) and (21) for ϱ and ϱ'.

Thus, the statistical operator (19) corresponds to the maximum entropy (8) for a given average energy and average particle number at the time $t = -\infty$. We assumed the contact with a thermostat and a particle reservoir as the initial condition at $t = -\infty$, and the studied the evolution of the system as if it were isolated from all external influences apart from the classical force field $V(t)$.

The mean value of any dynamic variable A is equal to

$$\langle A \rangle(t) = \mathrm{Tr}\,[\varrho(t) A]. \tag{24}$$

Substituting (19) into this expression (24) and using the cyclic invariance of the trace as well as the relation

$$U(t, -\infty) f(A) U^{\dagger}(t, -\infty) = f(U(t, -\infty) A U^{\dagger}(t, -\infty)), \tag{25}$$

where $f(A)$ — arbitrary function of the operator A, we obtain

$$\langle A \rangle(t) = \mathrm{Tr}\,[U(t, -\infty)\varrho_0 U^{\dagger}(t, -\infty) A]$$
$$= \mathrm{Tr}\,[\varrho_0 U^{\dagger}(t, -\infty) A U(t, -\infty)], \tag{26}$$

where

$$\varrho_0 = \exp\,[-\beta(\mathscr{H}(0) - \sum_j \mu_j N_j - \Omega)] \tag{27}$$

is the statistical operator of the grand canonical distribution.

At the time $t = -\infty$ using the relation (25) and substituting the obvious condition

$$\varrho(t = -\infty) = U(-\infty, -\infty)\varrho(t = -\infty)U^{\dagger}(-\infty, -\infty) \tag{28}$$

into expression (19), we have

$$\varrho(t = -\infty) = \varrho_0. \tag{29}$$

3. Evolution operator

The evolution in time of the mean value $\langle A\rangle(t)$ of any dynamic variable A is determined by the equation (13). Let us assume that the first term of the Hamiltonian (1), $\mathscr{H}(0)$, is the zero-order Hamiltonian, and the second, $V(t)$, is the perturbation Hamiltonian, which we can regard as "small". It is convenient to multiply Eq. (13) by $\exp(i\mathscr{H}(0)t/\hbar)$ on the left and transform it to

$$i\hbar\frac{\partial}{\partial t}[e^{i\mathscr{H}(0)t/\hbar}U(t)] = \tilde{V}(t)e^{i\mathscr{H}(0)t/\hbar}U(t), \tag{30}$$

where

$$\tilde{V}(t) = e^{i\mathscr{H}(0)t/\hbar}V(t)e^{-i\mathscr{H}(0)t/\hbar} \tag{31}$$

is the perturbation energy operator in the Heisenberg picture. Integrating Eq. (30) over t from $-\infty$ to t, taking the initial condition (15) into account, we obtain the solution (30) in the form of an ordered P-exponential

$$U(t, -\infty) = e^{-i\mathscr{H}(0)t/\hbar}P\exp\left\{\frac{1}{i\hbar}\int_{-\infty}^{t} V(t')dt'\right\}, \tag{32}$$

where P is the time-ordering operators [6].

In the first approximation, we obtain

$$U(t, -\infty) = e^{-i\mathscr{H}(0)t/\hbar}\left\{1+\frac{1}{i\hbar}\int_{-\infty}^{t}\tilde{V}(t')dt'\right\}. \tag{33}$$

Substituting (33) in (26) we get

$$\langle A\rangle(t) = \langle A\rangle(0)+\int_{-\infty}^{\infty}\langle\langle\tilde{A}(t)\,|\tilde{V}(t')\rangle\rangle dt', \tag{34}$$

where

$$\tilde{A}(t) = e^{i\mathscr{H}(0)t/\hbar}Ae^{-i\mathscr{H}(0)t/\hbar}; \tag{35}$$

$$\langle\langle A(t)\,|B(t')\rangle\rangle = \Theta(t-t')\frac{1}{i\hbar}\langle[A(t), B(t')]\rangle(0) \tag{36}$$

is the retarded two-time Green function and

$$\langle \ldots \rangle(0) = \mathrm{Tr}\,[\ldots \varrho_0]. \tag{37}$$

Formula (34) describes the linear retarded response of the average values of an operator A to the switching on of a perturbation $V(t)$ for a quantum-statistical ensemble and is analogous to the known Kubo formulas [7].

4. *Conclusion*

The most important conclusion of this paper is that the statistical operator for non-linear response of a system corresponds to the maximum of the entropy for a given average energy and average particle number at the time $t = -\infty$.

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