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Statistical Mechanical Theory of the Nonlinear Steady State

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By making use of perturbation techniques, we develop a theory of the nonlinear steady state. We find that the linear term of a mechanical equation such as the Langevin equation is not responsible for the nonlinear terms of its expectation values at the nonequilibrium state arbitrarily far from the thermal equilibrium. The nonlinear steady state is formulated in the two cases where the microscopic conservation law exists and where it does not exist. The expressions for the expectation values of the physical quantities at the steady state are obtained as the functions of other physical quantities which are regarded as the parameters of the steady state. The stability and the instability of the steady state are discussed. A difference in the character of the instability of the steady state from that of the stationary state is discussed. It is noted that the first expansion coefficient should not exhibit an anomaly for instabilities of the steady state. The relation between the mechanical forces appearing in our approach and the corresponding thermal forces is discussed. The variational principle which is valid for the open system is developed.

KEY WORDS: Steady state; nonlinear; stability; instability; balance equation; open system; variational principle.

1. INTRODUCTION

In a previous paper$^{(1)}$ (referred to as I hereafter) we developed a general method to deal with the nonequilibrium states of a many-body system, including states far from thermal equilibrium state. We discussed a general

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method of describing the system by means of one-body variables, e.g., the mean number density $n(\mathbf{r}, t)$ in space–time, at a state arbitrarily far from thermal equilibrium. As a result, it is possible for us to discuss the many-body system in terms of a set of variables with much fewer degrees of freedom than the total number. Under certain conditions we can describe the system in terms of single-particle distributions in coordinate space at all times. The complete thermal equilibrium state, which is determined by the homogeneous number density and also by the total energy, is an example. It is obvious that all states of a many-body system are not always a functional of the single-particle distribution function in coordinate space. There are the other variables, e.g., the energy density. The distinctions among various situations correspond to those among the external conditions or the histories of the system, as discussed in I.

The method developed in I is, however, rather formal and it is hard to apply to individual problems directly. One of the most interesting phenomena at the nonequilibrium states of the many-body system is the situation at the steady state.⁽²⁾ The main purpose of this paper is to investigate the steady state, using the method developed in I. The steady state is defined as a state with constant time rates of change of physical quantities or with constant currents. Thus the steady state is a nonequilibrium state. Furthermore, the steady state is a state of the "open" system. How can we deal with the steady state, and how can we calculate the expectation values of physical quantities at the steady state from first principles? These basic questions about the steady state remain unsolved. We shall discuss this problem in this paper. We do not restrict ourselves to the state near the thermal equilibrium state, because we think that the nonequilibrium state far from thermal equilibrium must have different aspects from those of the state near thermal equilibrium. An example is given in Section 5. We shall discuss the instability of the steady state.

The basic idea developed in I is as follows. To characterize the nonequilibrium state uniquely, we first assume the existence of a thermal equilibrium state of an isolated system. Next we apply an external perturbation to the system to bring the system to a nonequilibrium state from an initial thermal equilibrium state. There are not always well-defined external perturbations. This is the reason why we have to choose a suitable set of the dynamic or the thermodynamic variables to describe the system more and more reliably within restricted degrees of freedom. Thus we use a set of imaginary external fields which act on a set of mechanical operators. We think that the theory of nonequilibrium statistical mechanics which might be established may not have complete correspondence with physical reality. One way to avoid this insufficiency in the theory is to choose measurable quantities such as the particle current or the energy current as the independent variables instead of the conjugate fields of these quantities.

To attain the steady state, a certain limiting procedure is necessary, since we discuss this with the aid of an isolated system which is allowed to be infinitely large after having been disturbed by the external perturbations. The observed system is one of the subsystems of the total system. This subsystem is steady with time since the characteristic relaxation time of the total system becomes infinitely large when the system becomes infinitely large. This formal approach does not prevent us from applying our method to the actual phenomena. The surroundings of the actual system correspond to the remaining parts of our isolated system, which provide the stationary currents.

The next section is devoted to general remarks on the theory developed in I. In Section 3 we discuss the steady state. It will be seen that the introduction of a new variable instead of the conjugate variable of the external force makes it easy for us to formulate the steady state. In Section 4 we discuss the expectation values of physical quantities at the steady state as a function of the "flux," which is not the mechanical variable. In Section 5 we discuss the stability and the instability of the steady state. It is noted that the instability of a steady state has a different character from that of a thermal equilibrium state. In Section 6 we discuss the relation between the external perturbations and the corresponding "thermal" forces. In Section 7 we discuss the variational principle which is valid for the steady state.

2. GENERAL THEORY

In a previous paper(1) we developed a general method for extracting a "relevant internal field" in a many-body system with the aid of the solution of the density matrix of the Liouville equation in the presence of the external perturbations.(3) As was discussed in I, we have to disturb the system to attain a nonequilibrium state if we use a thermal equilibrium state as an initial reference state. Then the nonequilibrium state is determined by the external perturbation

$$\Sigma(\mathbf{r}, t) \tag{1}$$

which acts on a single-body operator $\hat{o}(\mathbf{r})$, and by an initial state. We do not restrict Σ by specifying that it should actually exist, since we intend to discuss the actual phenomena plausibly, by choosing a suitable set of measurable quantities. The interactions between an observed system and its surroundings might be very complicated and the nonequilibrium state depends on these complicated interactions. For instance, the material properties of a container are responsible for the time dependence of the temperature of the hot water in it, while its final equilibrium temperature does not depend on the material properties of the container. This fact tells us that we should be careful to consider the mechanisms of the interactions between the observed system and its surroundings. But we are not interested in dealing with such complicated interactions with the surroundings. We will describe the effects of surroundings, when it is necessary to do so, by choosing a set of measurable quantities as the independent variables. This means that we may specify a state as the state with "x strength of the heat current" and with "y strength of the particle current" and so on.

Our approach to the nonequilibrium state is as follows. The perturbational Hamiltonian is written

$$H_1 = \hat{\sigma}\Sigma(t) \tag{2}$$

Thus an expectation value $\alpha(t)$ of a physical quantity $\hat{\alpha}$ is described as

$$\alpha(t) = \alpha(\Sigma(t'); t > t') \tag{3}$$

For the properly chosen set of expectation values α we can describe Σ as a function of α:

$$\Sigma = \Sigma(\alpha) \tag{4}$$

Thus we have assumed that α and Σ are single valued in (4). Finally, we can determine another expectation value $\alpha_1(t)$ of a physical quantity $\hat{\alpha}_1$ by making use of (3) and (4) as follows;

$$\alpha_1 = \alpha_1(\alpha) \tag{5}$$

These are our basic procedures to describe the nonequilibrium state by measurable quantities. It is natural to give an expectation value α of a physical quantity $\hat{\alpha}$ by

$$\alpha(t) = \mathrm{Tr}\, \rho(t)\hat{\alpha} \tag{6}$$

where $\rho(t)$ is the density matrix that satisfies the equation of motion

$$\dot{\rho}(t) = (1/i\hbar)[H_0 + H_1(t), \rho(t)] \tag{7}$$

where the dot stands for time derivative, H_0 is the unpurturbed Hamiltonian, and

$$[A, B] = AB - BA \tag{8}$$

Let us expand (3) and (4) as follows:(1,4)

$$\begin{aligned} \alpha(t) &= \int \frac{\delta\alpha(t)}{\delta\Sigma(t_1)}\bigg|_{\Sigma=0} \Sigma(t_1)\, dt_1 \\ &\quad + \frac{1}{2}\int \frac{\delta^2\alpha(t)}{\delta\Sigma(t_1)\,\delta\Sigma(t_2)}\bigg|_{\Sigma=0} \Sigma(t_1)\Sigma(t_2)\, dt_1\, dt_2 + \cdots \\ &= \int G_0(t; t_1)\Sigma(t_1)\, dt_1 + \tfrac{1}{2}\int G_0(t; t_1, t_2)\Sigma(t_1)\Sigma(t_2)\, dt_1\, dt_2 + \cdots \\ &\quad + \frac{1}{n!}\int G_0(t; t_1, t_2, \ldots, t_n)\Sigma(t_1)\Sigma(t_2)\cdots\Sigma(t_n)\, dt_1 \cdots dt_n + \cdots \end{aligned} \tag{9}$$

$$\begin{aligned}\Sigma(t) &= \int \frac{\delta\Sigma(t)}{\delta\alpha(t_1)}\bigg|_{\alpha=0} \alpha(t_1)\, dt_1 + \frac{1}{2}\int \frac{\delta^2\Sigma(t)}{\delta\alpha(t_1)\,\delta\alpha(t_2)}\bigg|_{\alpha=0} \alpha(t_1)\alpha(t_2) \\ &\quad \times dt_1\, dt_2 + \cdots \\ &= \int K_0(t; t_1)\alpha(t_1)\, dt_1 + \tfrac{1}{2}\int K_0(t; t_1, t_2)\alpha(t_1)\alpha(t_2)\, dt_1\, dt_2 + \cdots \\ &\quad + \frac{1}{n!}\int K_0(t; t_1, t_2, \ldots, t_n)\alpha(t_1)\alpha(t_2)\cdots\alpha(t_n)\, dt_1\, dt_2 \cdots dt_n \\ &\quad + \cdots \end{aligned} \tag{10}$$

Let us define the quantities

$$G(t; t_1, \ldots, t_n) \equiv \delta^n\alpha(t)/\delta\Sigma(t_1)\cdots\delta\Sigma(t_n) \tag{11}$$

$$K(t; t_1, \ldots, t_n) \equiv \delta^n\Sigma(t)/\delta\alpha(t_1)\cdots\delta\alpha(t_n) \tag{12}$$

Then we obtain the relations among these quantities

$$\int G(t; t')K(t'; t_1)\, dt' = \int K(t; t')G(t'; t_1)\, dt' = \delta(t - t_1) \tag{13}$$

$$K(t; t_1, t_2) = -\int K(t; t')G(t'; t_1', t_2')K(t_1', t_1)K(t_2'; t_2)\, dt_1'\, dt_2'\, dt' \tag{14}$$

$$\begin{aligned}K(t; t_1, t_2, t_3) = 3\int & K(t; t')G(t'; t_1', t_2')K(t_1'; t_1)K(t_2'; t_2'') \\ & \times G(t_2''; t_2''', t_3')K(t_2'''; t_2)K(t_3'; t_3)\, dt'\, dt_1'\, dt_2' \\ & \times dt_2'''\, dt_2'' - \int K(t; t')G(t'; t_1', t_2', t_3')K(t_1'; t_1) \\ & \times K(t_2'; t_2)K(t_3'; t_3)\, dt_1'\, dt_2'\, dt_3'\, dt' \end{aligned} \tag{15}$$

and so on. These relations immediately follow if we perform a variation of (13) so as to get (14) and perform a variation of (14) so as to get (15) and so on. The above relations also hold if we replace G and K by K and G, respectively. Next we examine the expansion of (5):

$$\begin{aligned}\alpha_1(t) &= \int \frac{\delta\alpha_1(t)}{\delta\alpha(t_1)}\bigg|_{\alpha=0} \alpha(t_1)\, dt_1 + \frac{1}{2!}\int \frac{\delta^2\alpha_1(t)}{\delta\alpha(t_1)\,\delta\alpha(t_2)}\bigg|_{\alpha=0} \\ &\quad \times \alpha(t_1)\alpha(t_2)\, dt_1\, dt_2 + \cdots \\ &= \int M_0(t; t_1)\alpha(t_1)\, dt_1 + \frac{1}{2!}\int M_0(t; t_1, t_2)\alpha(t_1)\alpha(t_2)\, dt_1\, dt_2 + \cdots \\ &\quad + \frac{1}{n!}\int M_0(t; t_1, \ldots, t_n)\alpha(t_1)\alpha(t_2)\cdots\alpha(t_n)\, dt_1 \cdots dt_n + \cdots \end{aligned} \tag{16}$$

Let us define the quantities

$$M(t; t_1, \ldots, t_n) \equiv \delta^n\alpha_1(t)/\delta\alpha(t_1)\cdots\delta\alpha(t_n) \tag{17}$$

Our task is to rewrite (17) in terms of G, K, and

$$G_1(t;\, t_1, \ldots, t_n) \equiv \delta^n \alpha_1(t)/\delta\Sigma(t_1)\cdots\delta\Sigma(t_n) \tag{18}$$

We obtain

$$M(t;\, t_1) = \int \frac{\delta\alpha_1(t)}{\delta\Sigma(t')}\,\frac{\delta\Sigma(t')}{\delta\alpha(t_1)}\,dt' = \int G_1(t;\, t')K(t';\, t_1)\,dt' \tag{19}$$

$$\begin{aligned} M(t;\, t_1, t_2) = \frac{\delta M(t;\, t_1)}{\delta\alpha(t_2)} &= \int \frac{\delta G_1(t;\, t_1')}{\delta\alpha(t_2)}\,K(t_1';\, t_1)\,dt_1' \\ &\quad + \int G_1(t;\, t')\,\frac{\delta K(t';\, t_1)}{\delta\alpha(t_2)}\,dt' \\ &= \int G_1(t;\, t_1', t_2')K(t_1';\, t_1)K(t_2';\, t_2)\,dt_1'\,dt_2' \\ &\quad + \int G_1(t;\, t')K(t';\, t_1, t_2)\,dt' \end{aligned} \tag{20}$$

$$\begin{aligned} M(t;\, t_1, t_2, t_3) &= \int G_1(t;\, t_1', t_2', t_3')K(t_1';\, t_1)K(t_2';\, t_2)K(t_3';\, t_3) \\ &\quad \times dt_1'\,dt_2'\,dt_3' + 3\int G_1(t;\, t_1', t_2')K(t_1';\, t_1)K(t_2';\, t_2, t_3) \\ &\quad \times dt_1'\,dt_2' + \int G_1(t;\, t_1')K(t_1';\, t_1, t_2, t_3)\,dt_1' \end{aligned} \tag{21}$$

and so on.

It is interesting to know some aspects on the nonlinear terms of the expansion (16). We put

$$\hat{\alpha}_1(t) = \int \theta(t;\, t')\hat{\alpha}(t')\,dt' + \hat{f}(t) \tag{22}$$

where the time-dependent operators are defined by the Heisenberg representation (27). We denote the expectation value of $\hat{f}(t)$ at a nonequilibrium state by $f(t)$. Then we get[2]

$$\alpha_1(t) = \int \theta(t;\, t')\alpha(t')\,dt' + f(t) \tag{23}$$

Thus we get

$$M(t;\, t_1) = \theta(t;\, t_1) + \delta f(t)/\delta\alpha(t_1)$$

hence we get

$$M(t;\, t_1, t_2) = \delta^2 f(t)/\delta\alpha(t_1)\,\delta\alpha(t_2) \tag{24}$$

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[2] If we use the Heisenberg representation (27) for the operator, the expectation value of the operator at a nonequilibrium state is given by making use of $q(t)$ defined in the next section instead of $\rho(t)$. When $q(t)$ depends on time it seems that (23) does not follow from (22) directly. But the results derived below are correct.

We can readily write down explicit forms of G_0 and G_{10} as[3]

$$G_0(t; t_1,\ldots, t_n) = (1/i\hbar)^n P\theta(t - t_1)\cdots\theta(t_{n-1} - t_n) \times \langle[\cdots[[\hat{\alpha}(t), \hat{\sigma}(t_1)], \hat{\sigma}(t_2)]\cdots]\rangle_0 \tag{25}$$

$$G_{10}(t; t_1,\ldots, t_n) = (1/i\hbar)^n P\theta(t - t_1)\cdots\theta(t_{n-1} - t_n) \times \langle[\cdots[[\hat{\alpha}_1(t), \hat{\sigma}(t_1)], \hat{\sigma}(t_2)]\cdots]\rangle_0 \tag{26}$$

where the symbol P denotes the summation over all permutations of the arguments $(t_1,\ldots, t_n)$ and

$$A(t) = \{\exp[-i(H_0/\hbar)t]\}A \exp[i(H_0/\hbar)t] \tag{27}$$

$$\theta(t) = \begin{cases} 1 & t > 0 \\ 0 & t < 0 \end{cases} \tag{28}$$

and $\langle\cdots\rangle_0$ denotes the ensemble average at a reference state described by H_0.

Since $M(t; t_1,\ldots, t_n)$ $(n > 2)$ does not contain any contributions from $\hat{\alpha}(t)$ explicitly, it follows that we may put $\hat{\alpha}_1(t) \rightarrow \tilde{f}(t)$ in (26) to compute $G_{10}(t; t_1,\ldots, t_n)$ $(n \geqslant 2)$ for M. Furthermore, if we choose $\tilde{f}(t)$ so that the contribution from $\tilde{f}(t)$ to $G_{10}(t; t')$ vanishes, the nonlinear terms of the expansion (16) do not contain $G_{10}(t; t')$. Anyhow, the contributions from the first term on the right-hand side of (22) to the nonlinear terms of the expansion (16) have to be cancelled out at each order of the expansions. If we choose $\hat{\alpha}_1(t)$ as $(d/dt)\hat{\alpha}(t)$ in (22), then (22) becomes equivalent[1] to the Mori equation of generalized Brownian motion.[5] Thus we have discussed the relation between the linear Mori equation and the nonlinear equation of motion for the expectation value of the physical quantity referring to the variable of the Mori equation.

3. STEADY STATES

In this section we shall discuss the steady state. The first attempt at nonequilibrium statistical mechanics by means of the density matrix in the case of a system where the well-defined external perturbation does not exist was done by Mori[6] and also by Kubo *et al.*[7] These authors used the modified density matrix for the initial ensemble. Later Kadanoff and Martin[8] discussed this problem by making use of a time-dependent perturbation which is switched off at time zero. The above two approaches are equivalent to one another. They only seem to be different because of their different quantum mechanical representations. Our approach is also consistent with these approaches. The only difference is that our imaginary external perturbation depends on time in an arbitrary way[9] and therefore we cannot get the local canonical distribution function, which was used by the above authors.

The absence of the local canonical distribution function is not essential to the final results in our approach. This is because the existence of a local canonical distribution function and the existence of a set of local parameters such as the local temperature and the local chemical potential are different things in the case of the nonequilibrium states. For practical reasons it might be convenient to assume that the local parameters can be well defined even at a state far from thermal equilibrium. This can be expected to hold well at the steady state, since the steady state does not change with time and therefore we may define the parameters in order to describe it very well.

Now we put $\alpha \equiv \sigma$ in (9). Let us first discuss only the first term of (9):

$$\sigma(t) = \int G_0(t; t_1)\Sigma(t_1)\,dt_1 \tag{29}$$

If

$$\left| \int G_0(t; t_1)\,dt_1 \right| < \infty \tag{30}$$

then it follows that there is no steady state when Σ is finite. This is true, since $\dot{\sigma}$ is constant and does not vanish at the steady state. Inequality (30) can be satisfied except at the critical point, if we assume the existence of the stationary state.[3] If the system is too large to relax to a thermal equilibrium state within a time interval comparable with the microscopic relaxation time, the small but macroscopic subsystem behaves as if it is steady with time. To attain a steady state, we assume that the total system is much larger than the observed subsystem. This assumption enables us to derive a relation between the force Σ and the flux $\dot{\sigma}$ at the steady state, using a certain limiting procedure to be mentioned later. Let us introduce the quantity

$$q(t) = \{\exp[-(H_0/i\hbar)t]\}\rho(t)\exp[(H_0/i\hbar)t] \tag{31}$$

Then $q(t)$ satisfies the equation of motion

$$\dot{q}(t) = (1/i\hbar)[\mathscr{H}_1(t), q(t)] \tag{32}$$

where

$$\mathscr{H}_1(t) = \{\exp[-(H_0/i\hbar)t]\}H_1(t)\exp[(H_0/i\hbar)t] \tag{33}$$

We assume that

$$q(-\infty) = \rho(-\infty) = \rho_0 \tag{34}$$

where ρ_0 is the density matrix for a thermal equilibrium state described by H_0. Then (2) is written

$$\mathscr{H}_1(t) = \hat{\sigma}(t)\Sigma(t) \tag{35}$$

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[3] The meaning of the stationary state in this paper is that there is no current or no change in physical quantities with time. Thus the stationary state contains a thermal equilibrium state with inhomogeneities in space as well as without inhomogeneities in space.

Let us introduce an operator $\hat{I}(t) = (d/dt)\hat{\sigma}(t)$; then (35) is written[4]

$$\mathscr{H}_1(t) = \int_0^t \hat{I}(t')\,dt'\,\Sigma(t), \qquad \Sigma(-\infty) = 0 \tag{36}$$

We can expand the expectation value $I(t)$ of $\hat{I}(t)$ as follows:

$$I(t) = \sum_n \frac{1}{n!}\int L_0(t; t_1,\dots, t_n)\Sigma(t_1)\cdots\Sigma(t_n)\,dt_1\cdots dt_n \tag{37}$$

where

$$\begin{aligned} L_0(t; t_1,\dots, t_n) &= (1/i\hbar)^n \mathrm{P}\theta(t - t_1)\cdots\theta(t_{n-1} - t_n) \\ &\quad \times \left\langle\cdots\left[\left[\hat{I}_1(t), \int_{-\infty}^{t_1} \hat{I}(t_1')\,dt_1'\right], \int_{-\infty}^{t_2} \hat{I}(t_2')\,dt_2'\right]\cdots\right]\right\rangle_0 \end{aligned} \tag{38}$$

If Σ is the electric field, $\hat{I}(t)$ is the current operator. Thus we put $\hat{\sigma} = e\sum_i x_i$, where e is the electric charge and x_i is the position of the ith electron. The $L_0(t; t_1)$ reduces to the well-known formula(3,10) for the electrical conductivity. The nonlinear response to the external electric field was discussed by Bernard and Callen.(11),5 For more general discussions, let us assume that the external perturbation $\Sigma(t)$ depends also on spatial position, i.e., $\Sigma = \Sigma(\mathbf{r}, t)$. We get

$$\mathscr{H}_1(t) = \int\left[\int_{-\infty}^{t} \dot{\sigma}(\mathbf{r}, t')\,dt'\right]\Sigma(\mathbf{r}, t)\,d\mathbf{r} \tag{39}$$

instead of (36). If the operator $\hat{\sigma}(\mathbf{r}, t)$ satisfies the continuity equation

$$\dot{\sigma}(\mathbf{r}, t) = -\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}, t) \tag{40}$$

(39) becomes

$$\begin{aligned} \mathscr{H}_1(t) &= -\int\int d\mathbf{r}\,dt'\,\boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r}, t')\Sigma(\mathbf{r}, t) \\ &= -\int\int d\mathbf{r}\,dt'\,\boldsymbol{\nabla}\cdot(\hat{\mathbf{j}}(\mathbf{r}, t')\Sigma(\mathbf{r}, t)) + \int\int_{-\infty}^{t} d\mathbf{r}\,dt'\,\hat{\mathbf{j}}(\mathbf{r}, t)\cdot\boldsymbol{\nabla}\Sigma(\mathbf{r}, t) \end{aligned} \tag{41}$$

If we choose $\Sigma \equiv 0$ at the space boundary, then the first term vanishes and we get

$$\begin{aligned} \mathscr{H}_1(t) &= \int\int \hat{\mathbf{j}}(\mathbf{r}, t')\cdot\boldsymbol{\nabla}\Sigma(\mathbf{r}, t)\,dt'\,d\mathbf{r} = -\int\int \hat{\mathbf{j}}(\mathbf{r}, t')\cdot\mathbf{F}(\mathbf{r}, t)\,dt'\,d\mathbf{r} \\ &= \int \mathbf{Q}(\mathbf{r}, t)\cdot\mathbf{F}(\mathbf{r}, t)\,d\mathbf{r} \end{aligned} \tag{42}$$

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[4] Strictly speaking, (36) has to contain the term $-\hat{\sigma}(-\infty)\,\Sigma\,(t)$. But such a term would not contribute to the following results, if we assume that G_0 given by (25) vanishes when we put one or more than one of the arguments $(t_1, t_2,\dots, t_n)$ to be $-\infty$.(1)

[5] The responses of our physical quantities are essentially equivalent to those of Ref. 11. For other work on nonlinear responses of physical quantities see Ref. 12.

where

$$\hat{Q}(\mathbf{r}, t) \equiv -\int_{-\infty}^{t} \hat{\mathbf{j}}(\mathbf{r}, t')\, dt' \tag{43}$$

Thus we get

$$J(\xi) = \sum_{n} \frac{1}{n!} \int L_0(\xi; \xi_1, \ldots, \xi_n) F(\xi_1) \cdots F(\xi_n)\, d\xi_1\, d\xi_2 \cdots d\xi_n \tag{44}$$

$$L_0(\xi; \xi_1, \ldots, \xi_n) = \left(\frac{1}{i\hbar}\right)^n \mathrm{P}\theta(\xi - \xi_1) \cdots \theta(\xi_{n-1} - \xi_n) \langle [\cdots[\hat{J}(\xi), \hat{Q}(\xi)], \ldots, \hat{Q}(\xi_n)] \rangle_0 \tag{45}$$

where we have introduced an abbreviation: $(\xi) \equiv (\mathbf{r}, t, \nu)$ $(\nu = 1, 2, 3)$; ν denotes the components of the vectors **Q**, **j**, and **F**; $\xi > \xi'$ means $t > t'$; and the integrations over ξ contain summations over ν. The J terms denote the components of **j**.

We expect the existence of the integral

$$\int L_0(t; t_1, t_2, \ldots, t_n)\, dt_1 \cdots dt_n \tag{46}$$

for the existence of the steady state, This is, however, not equivalent to the assumption of the existence of the integral

$$\int G_0(t; t_1, \ldots, t_n)\, dt_1 \cdots dt_n \tag{47}$$

The latter is for the existence of a stationary state, hence for a thermal equilibrium state, and we expect it to hold more generally than the former integral. We are dealing with an isolated system. Thus it is necessary to make a certain limiting procedure to attain a steady state. Let the space–time dependence of the field F in (44) be given by

$$F(\xi) = F_\nu \exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t) \tag{48}$$

Then we get

$$J(\xi) = \sum_{n} \frac{1}{n!} \int L_0(\xi; \xi_1, \ldots, \xi_n) \exp[i\mathbf{k}\cdot(\mathbf{r}_1 + \cdots + \mathbf{r}_n) - i\omega(t_1 + \cdots + t_n)] \times F_{\nu_1} \cdots F_{\nu_n}\, d\xi_1 \cdots d\xi_n \tag{49}$$

$$= \sum_{\{\nu_i\}} \sum_{n} \frac{1}{n!} \mathscr{L}_0(\nu; \nu_1, \ldots, \nu_n, \mathbf{k}, \omega) F_{\nu_1} \cdots F_{\nu_n} \tag{50}$$

where

$$\mathscr{L}_0(\nu; \nu_1, \ldots, k, \omega) \equiv \int L_0(\xi; \xi_1, \ldots, \xi_n) \times \exp[i\mathbf{k}\cdot(\mathbf{r}_1 + \cdots + \mathbf{r}_n) - i\omega(t_1 + \cdots + t_n)] \times d\mathbf{r}_1\, d\mathbf{r}_2 \cdots d\mathbf{r}_n\, dt_1\, dt_2 \cdots dt_n \tag{51}$$

To attain the steady state, we take the limit

$$\mathscr{L}_0(\nu;\nu_1,\ldots,\nu_n) = \{\lim_{\omega\to 0}\{\lim_{\mathbf{k}\to 0}\{\lim_{V\to\infty} \mathscr{L}_0(\nu;\nu_1,\ldots,\nu_n,\mathbf{k},\omega)\}\}\} \tag{52}$$

where V is the volume of the system. If we take the limit $\omega \to 0$ before we take the limit $k \to 0$, $\mathscr{L}_0$ will vanish, since the system reaches a stationary state where no current exists.

If the system consists of N identical atoms interacting by spherical interatomic potentials, we may choose the energy current and the particle current as the independent variables for a steady state. Then the perturbation Hamiltonian is written as

$$H_1 = \int \hat{\mathscr{H}}_0(\mathbf{r})\tilde{\beta}(\mathbf{r},t) + \int \hat{N}(\mathbf{r})x(\mathbf{r},t) \tag{53}$$

$$x \equiv \tilde{\beta}(\mathbf{r},t)X(\mathbf{r},t) \tag{54}$$

where $\hat{\mathscr{H}}_0(\mathbf{r})$ and $\hat{N}(\mathbf{r})$ are the Hamiltonian density and the particle density whose Heisenberg representations obey the microscopic conservation laws:

$$\dot{\hat{\mathscr{H}}}_0(\mathbf{r},t) + \nabla\cdot\mathbf{j}_\epsilon(\mathbf{r},t) = 0 \tag{55}$$

$$\dot{\hat{N}}(\mathbf{r},t) + \nabla\cdot\mathbf{j}(\mathbf{r},t) = 0 \tag{56}$$

where $\mathbf{j}_\epsilon$ and $\mathbf{j}$ are the energy current and the particle current, respectively. Then the conjugate forces are $-\nabla\tilde{\beta}(\mathbf{r},t)$ and $-\nabla x = -(\nabla\tilde{\beta})X - \tilde{\beta}(\nabla X)$, respectively. The $\tilde{\beta}$ is the deviation of the inverse temperature scaled by the temperature of the initial stated, and X is the local chemical potential. Although this follows from a solution of the Liouville equation for the thermal equilibrium state,$^{(8)}$ it seems appropriate to think that this is the definition of these quantities in the nonequilibrium state.

It may seem that there is no appearance of the "thermal" forces in the theory. This is, however, not true. This problem will be discussed in Section 6.

4. EXPECTATION VALUES OF PHYSICAL QUANTITIES AT STEADY STATE

Now we can discuss the expectation values of physical quantities at the steady state. Let α_1 be the expectation value of the physical quantity $\hat{\alpha}_1$. We put the expectation value α_{10} of $\hat{\alpha}_1$ at a thermal equilibrium state to be zero, $\alpha_{10} = 0$, for simplicity. Then it is necessary to determine the parameters which characterize the nonequilibrium state. We choose them the "fluxes" I (or J). In the limit of vanishing I the system reaches a thermal equilibrium state and α_1 vanishes. Using (22), we obtain

$$\alpha_1(t) = \int M_0(t;\, t')\alpha(t')\, dt' \tag{57}$$

$$M_0(t;\, t') = \int G_{10}(t'\tau)K_0(\tau;\, t')\, d\tau \tag{58}$$

for small α. Hence if we put $\theta(t;\, t') \equiv M_0(t;\, t')$ in (22), we obtain

$$\tilde{f}(t) = \hat{\alpha}_1(t) - \int M_0(t;\, t')\hat{\alpha}(t')\, dt' \tag{59}$$

As was noted above, we may replace $\hat{\alpha}(t)$ by $\tilde{f}(t)$ to obtain $M_0(t;\, t_1, \ldots, t_n)$ $(n \geqslant 2)$ and therefore $G_{10}(t;\, t_1, \ldots, t_n)$. For instance, we may use

$$G'_{10}(t;\, t_1) \equiv (1/i\hbar)\theta(t - t')\langle[\tilde{f}(t), \hat{\sigma}(t_1)]\rangle_0 \equiv 0 \tag{60a}$$

$$G'_{10}(t;\, t_1, t_2) \equiv (1/i\hbar)^2 \mathrm{P}\theta(t - t_1)\theta(t_1 - t_2)\langle[[\tilde{f}(t), \hat{\sigma}(t_1),]\, \hat{\sigma}(t_2)]\rangle_0 \tag{60b}$$

$$\begin{aligned} G'_{10}(t;\, t_1, t_2, t_3) \equiv{} & (1/i\hbar)^3 \mathrm{P}\theta(t - t_1)\theta(t_1 - t_2)\theta(t_2 - t_3) \\ & \times \langle[[[\tilde{f}(t), \hat{\sigma}(t_1)], \hat{\sigma}(t_2)], \hat{\sigma}(t_3)]\rangle_0 \end{aligned} \tag{60c}$$

instead of $G_{10}(t;\, t_1)$, $G_{10}(t;\, t_1, t_2)$, and $G_{10}(t;\, t_1, t_2, t_3)$ so as to compute $M_0(t;\, t_1, t_2, \ldots, t_n)$ $(n \geqslant 2)$. The lowest order of the expectation value α_1 at a steady state is written

$$\begin{aligned} \alpha_1^{(1)}(t) = (1/i\hbar) \int_{-\infty}^{t} dt' \, & \langle[\hat{\alpha}_1(t), \int_{-\infty}^{t'} \hat{I}(\tau')\, d\tau']\rangle_0 \\ & \times C_0(t';\, t'')I(t'')\, dt'' \end{aligned} \tag{61}$$

where we have introduced a quantity C_0 as the inverse matrix of

$$(1/i\hbar)\theta(t - t')\langle[\hat{I}(t), \int_{-\infty}^{t'} \hat{I}(t'')\, dt'']\rangle_0 \tag{62}$$

The second-order term is written

$$\begin{aligned} \alpha_1^{(2)}(t) = \tfrac{1}{2}(i\hbar)^{-2} \int & \mathrm{P}\theta(t - t_1')\theta(t_1' - t_2') \\ & \times \langle[[\tilde{f}(t), \int_{-\infty}^{t_1'} \hat{I}(\tau_1)\, d\tau_1], \int_{-\infty}^{t_2'} \hat{I}(\tau_2)\, d\tau_2]\rangle_0 \\ \times\, & C_0(t_1';\, t_1)C_0(t_2';\, t_2)I(t_1)I(t_2)\, dt_1'\, dt_2'\, dt_1\, dt_2 \end{aligned} \tag{63}$$

In this way we get the formal expansion

$$\begin{aligned} \alpha_1(t) &= \sum_n \alpha_1^{(n)}(t) \\ &= \sum_n \frac{1}{n!} \int R_{10}(t;\, t_1, t_2, \ldots, t_n)I(t_1) \cdots I(t_n) dt_1 \cdots dt_n \end{aligned} \tag{64}$$

In (64), $\alpha_1(t)$ may contain more than two arguments:

$$\alpha_1(t, t', \dots, t^{(l)}) = \sum_n \frac{1}{n!} \int R_{10}(t, t', \dots, t^{(l)}; t_1, \dots, t_n) I(t_1) \cdots I(t_n)\, dt_1 \cdots dt_n \tag{65}$$

As the steady state, we should put I to be constant in (64) or (65). Thus we get

$$\alpha_1(t, t', \dots, t^{(l)}) = \sum_n \frac{1}{n!} \mathscr{R}_{10}^{(n)}(t, t', \dots, t^{(l)}) I^n \tag{66}$$

where

$$\mathscr{R}_{10}^{(n)} = \int R_{10}(t', \dots, t^{(l)}; t_1, \dots, t_n)\, dt_1 \cdots dt_n \tag{67}$$

Since $\mathscr{R}_{10}^{(n)}$ may possess the translation symmetry with respect to time, we can put

$$\mathscr{R}_{10}^{(n)}(t, \dots, t^{(l)}) = \mathscr{R}_{10}^{(n)}(t - T, \dots, t^{(l)} - T)$$

By choosing $T = t$, we get

$$\mathscr{R}_{10}^{(n)}(t, \dots, t^{(l)}) = \mathscr{R}_{10}^{(n)}(0, \dots, t^{(l)} - t)$$

Equation (64) has the more general form

$$\alpha_1(\xi) = \sum_n \frac{1}{n!} \int R_{10}(\xi; \xi_1, \dots, \xi_n) I(\xi_1) \cdots I(\xi_n)\, d\xi_1 \cdots d\xi_n \tag{68}$$

In (67) the same limiting procedure as in (52) has to be taken.

5. STABILITY AND INSTABILITY OF THE STEADY STATE

In Section 2 we have assumed that Σ and α are single valued. Such an assumption also has been made for the relation between the "flux" I (or J) and the "force" Σ (or F). These assumptions are necessary in order that the state of the system can be determined uniquely by half of these conjugate variables. Generally speaking, however, it is not correct to expect that Σ and α are always single valued. This is due to the fact that we observe phase transitions in the many-body system. It is also known that the flux-force relation may become many valued.(13) We shall discuss some general properties of the instability of the steady state.

Let us consider the expansions

$$J_\nu = \sum_{\{\nu_i\}} \sum_n (1/n!) \mathscr{L}_0(\nu, \nu_1, \dots, \nu_n) F_{\nu_1} \cdots F_{\nu_n} \tag{69}$$

$$F_\nu = \sum_{\{\nu_i\}} \sum_n (1/n!) \mathscr{R}_0(\nu, \nu_1, \dots, \nu_n) J_{\nu_1} \cdots J_{\nu_n} \tag{70}$$

where $\mathscr{L}_0$ in (69) is given by (52) and we have assumed that

$$\mathscr{L}_0(\nu; \nu_1,..., \nu_n) = \mathscr{L}_0(\nu_1; \nu,..., \nu_n) \tag{71}$$

The $\mathscr{R}_0$ is the quantity which corresponds to K_0. Generally speaking, we can expect that the lowest order of $\mathscr{R}_0$, i.e., $\mathscr{R}_0(\mu, \nu)$, in (70) does not vanish in the case of the steady state. If $\mathscr{R}_0(\mu, \nu)$ vanishes, spontaneous polarizations of the fluxes will occur without any external disturbances in an isolated system. Then we have no stationary state, hence no thermal equilibrium state of the isolated system. In the case of the stationary state no such a restriction to the relation between σ and Σ seems to exist, since we can choose equivalently σ and σ + const as the thermodynamic variables. In the case of a quantum mechanical system care must be taken since the phase of the wave function also provides extra mechanical degrees of freedom. The instability with regard to the spontaneous polarization of the phase of the wave function, seen in the superconductivity and the superfluidity, causes a spontaneous polarization of the flux. In this case $\mathscr{R}_0(\mu, \nu)$ vanishes and the above postulate does not hold. Hence we do not consider the polarization of phases of the wave function. From above discussion the instability of a steady state occurs at finite values of the force F and the flux J. This does not mean that all components of the flux have to have finite values, but one of them may have a finite value at least.

For simplicity let us consider the relations written in the following form:

$$J = \sum_n (1/n!)\mathscr{L}_0{}^{(n)}F^n \tag{72}$$

$$F = \sum_n (1/n!)\mathscr{R}_0^{(n)}J^n \tag{73}$$

Then $\mathscr{L}_0$ and $\mathscr{R}_0$ are the functions of the other components of the flux or the force, in general. We further make a simplification that other components of the flux or the force are zero. Then $\mathscr{R}_0^{(1)}$ does not vanish. Thus the possibility of appearance of the instability of the steady state depends on the properties of the higher-order terms of the expansion (73). To illustrate this, we retain the first three terms of the expansion (73):

$$F = \mathscr{R}_0^{(1)}J + \tfrac{1}{2}\mathscr{R}_0^{(2)}J^2 + (1/3!)\mathscr{R}_0^{(3)}J^3 \tag{74}$$

If $\mathscr{R}_0^{(2l)}$ ($l = 1, 2,...$) identically vanish due to the symmetry of the system, we have to consider the following form:

$$F = \mathscr{R}_0^{(1)}J + (1/3!)\mathscr{R}_0^{(3)}J^2 + (1/5!)\mathscr{R}_0^{(5)}J^5 \tag{75}$$

When

$$J = J^* = \{-3\mathscr{R}_0^{(2)} \pm 3[(\mathscr{R}_0^{(2)})^2 - \tfrac{2}{3}\mathscr{R}_0^{(1)}\mathscr{R}_0^{(3)}]^{1/2}/\mathscr{R}_0^{(3)} \tag{76}$$

$\partial F/\partial J$ vanishes for (74), and when

$$J^2 = (J^*)^2 = \{-4!\,\mathscr{R}_0^{(3)} \pm 4!\,[\tfrac{1}{4}\mathscr{R}_0^{(3)} - \tfrac{1}{6}\mathscr{R}_0^{(1)}\mathscr{R}_0^{(5)}]^{1/2}\}/2\mathscr{R}_0^{(5)} \tag{77}$$

$\partial F/\partial J$ vanishes for (75). The right-hand sides of (74) and (75) possess maxima F_+ and minima F_- corresponding to each J^*. Then J is a many-valued function of F in the region $F_- < F < F_+$, and the steady state is unstable for a fixed force F $(F_- < F < F_+)$. For the same reason that $\mathscr{R}_0^{(1)}$ does not vanish because of the existence of a stationary state, we also expect that $F_+F_- > 0$ if the coefficient $\mathscr{R}_0^{(n)}$ does not contain other components of the flux. If $F_+F_- < 0$, then $F = 0$ in (74) or (75) gives many real roots for J and the stationary state $J = 0$ is no longer stable. The analogous discussion also holds for (72). In this case F is a many-valued function of J and the steady state is unstable for a fixed flux J.

6. BALANCE EQUATIONS

As was discussed earlier, there is no well-defined mechanical force referring to the "thermal" disturbance, in general. Thus it is important to discuss the relation between the mechanical forces which we have used for our procedures for the nonequilibrium state and the "thermal" forces which arise from the "nonstationariness" of the system. Let us consider (9) for $\alpha \equiv \sigma$. This equation shows how the expectation value σ of the conjugate quantity of a field Σ polarizes as a function of Σ. Next consider (10) for $\alpha \equiv \sigma$. This equation, although it is equivalent to (9), can be interpreted as showing how the field induced by the polarizing quantity σ in the system balances with the applied external field Σ. Thus we can interpret (10) as a balance equation between the external field and the internal field:

$$\Sigma(t) = \Sigma_{\text{int}}(t) \tag{78}$$

This concept of an internal field makes it easy to understand the "thermal" force, which arises from the inhomogeneity in the system. We have used imaginary external fields to attain a nonequilibrium state. Thus it seems that the system is driven to a nonequilibrium state or an equilibrium state by the mechanical perturbations. However, this difficulty can be removed in the following way. Let us assume that a system is in a thermal equilibrium state in the presence of an external perturbation. Next we switch off the external perturbation; then the system is in a nonequilibrium state at this time and will be driven to a thermal equilibrium state by the "thermal" force Σ_{th}. It is easy to see that the "thermal" force must be equal to the right-hand side of (10).

This is due to the fact that we may apply another mechanical field $\Sigma'(t)$ which cancels the applied external field Σ:

$$\Sigma - \Sigma' = 0 \tag{79}$$

instead of switching off Σ. Thus we can think of the system being driven to a thermal equilibrium state by Σ'. Since we expect to observe the same phenomena under these two situations, we conclude from (79) and (10)

$$\Sigma_{\text{th}} = \Sigma' = \text{rhs of } (10) \tag{80}$$

which drives the system to a thermal equilibrium state.

7. VARIATIONAL PRINCIPLE

In a previous paper we developed a variational principle for the stationary state. The primary advantage of the variational principle developed in I is that we can distinguish an external field from an internal field and can make clear the external conditions of the system. A formal theory can be constructed in the case of the steady state as in the case of the stationary state.

By making use of (72) and (73) we can obtain variational functions

$$\Psi(J, F) = JF - \sum_n [\mathscr{L}_0^{(n)}/(n+1)!]F^{n+1} \tag{81}$$

$$\Phi(J, F) = JF - \sum_n [\mathscr{R}_0^{(n)}/(n+1)!]J^{n+1} \tag{82}$$

Then if the flux J is fixed and plays the role of an external parameter, the state of the system appears so as to give the extremum value of Ψ:

$$(\partial/\partial F)\Psi(J, F) = 0 \tag{83}$$

If the force F is fixed, the state of the system appears so as to give the extremum value of Φ:

$$(\partial/\partial J)\Phi(J, F) = 0 \tag{84}$$

It can be found that Ψ and Φ are generalized functions due to Onsager.(14) We denote the extremum values of Ψ and Φ by Ψ_0 and Φ_0, respectively. Thus we get

$$\Psi_0 = \sum_n \left(\frac{1}{n!} - \frac{1}{(n+1)!}\right)\mathscr{L}_0^{(n)}F^{n+1}, \qquad F = F(J) \tag{85}$$

$$\Phi_0 = \sum_n \left(\frac{1}{n!} - \frac{1}{(n+1)!}\right)\mathscr{R}_0^{(n)}J^{n+1}, \qquad J = J(F) \tag{86}$$

We also find

$$d\Psi_0 = F(J)\,dJ, \qquad d\Phi_0 = J(F)\,dF$$

or

$$F(J) = d\Psi_0/dJ, \qquad J(F) = d\Phi_0/dF \tag{87}$$

The above integral forms for the relation between J and F are similar to those in the case of the stationary state.(1) Since the steady state is not an equilibrium state, we cannot use the variational principle which is used for the stationary state in I. If this variational principle is used, then the most probable state is the thermal equilibrium state and no flux exists. If we use the closed system, the most probable state is the thermal equilibrium state due to the second law of thermodynamics. Hence the variational principle developed in this section is essentially valid for the open system, which we have characterized as a subsystem in a closed system.

The variational functions (81) and (82) have following physical meanings. We can interpret (73) as a balance equation between the external force and the internal force

$$F = F_{\mathrm{in}} \equiv \sum_{n} (1/n!)\mathscr{R}_0^{(n)} J^n \tag{88}$$

for the same reason as in the case of (78). Then we get

$$\Psi(J, F) = \int_0^J \{F - F_{\mathrm{in}}(J')\}\, dJ' \tag{89}$$

Thus $\Psi(J, F)$ gives the total "work" done by the fixed external force F and by the induced internal force $F_{\mathrm{in}}(J)$ to make the flux polarize from zero to a finite value J. Such an interpretation also holds for Φ. The dimensions of this "work" are [energy/time]; hence this is not the true work. More detailed analyses of the properties of these variational functions and also of the variational principle itself will be made in future work.

ADDENDUM

Recently K. Kawasaki and J. D. Gunton [*Phys. Rev. A* **8**:2048 (1973)] also discussed the nonlinear steady state. They studied transport phenomena for the steady state and obtained interesting results, using projection operator techniques and the local canonical distribution function to establish the nonequilibrium state. As was shown in I, our approach seems to give a different definition of the projection operator for the linear Mori equation from the definition determined by the local equilibrium assumption.(5) Thus our approach may lead to different results from theirs.

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