

## Nonadiabatic response theory: The case of volume change

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Using the field-theoretical formalism, nonequilibrium thermodynamics is discussed where the volume  $V(t)$  is changing with time. The time-dependent boundary condition on the wave function is handled by introducing the time-independent mode variables, thus leading to the time-independent Fock space. The correct representation of the second quantized Hamiltonian is derived which depends explicitly on both  $V(t)$  and  $\dot{V}(t)$ . This leads to two kinds of force operators,  $X_1^0(t)$  (pressure) and an extra term  $X_2(t)$ . The adiabatic expansion of the increase  $\Delta E(t)$  of internal energy is performed and it is shown that  $X_2(t)$  has no effect up to the leading nonequilibrium correction. The resulting form of  $\Delta E(t)$  ensures that the correction is positive, thus proving the principle of maximum-minimum work.

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### I. INTRODUCTION

Nonequilibrium thermodynamics based on the field-theoretical formulation can be a first-principles study of the dynamical phenomenon of the macroscopic system and has been widely discussed along this line. However, most of the investigations concern the evaluation of kinetic coefficients and the nonequilibrium thermodynamic relation itself has been little studied. One of the reasons for this is that the thermodynamic relation involves the energy, free energy, or thermodynamic potentials which are the generating functional of various Green's functions and the field-theoretical development of the generating functional has not been thoroughly achieved.

As a first step the internal energy of the system is studied in this paper as a function of time in the presence of some time-dependent external parameters. As a parameter we focus on the volume of the system, which is assumed to be changing slowly with time.

The purpose of the present paper is thus to derive an explicit expression of the first nonequilibrium correction, due to volume change, to the equilibrium thermodynamic formula for the increase  $dE$  in the energy of the system  $E$ . Let us recall here the general expression for  $dE$ , with obvious notations,

$$dE = dQ - p dV + \mu dN - \mathbf{M} \cdot d\mathbf{H} + \dots \quad (1.1)$$

As is well known, Eq. (1.1) is the change of energy when the increase on the right-hand side is due to the process which is infinitely slow, i.e., adiabatic, in the sense that at each instant of time the system can be assumed to be in the equilibrium state. On the right-hand side of (1.1), the term  $dQ$  or  $\mu dN$  cannot be solely expressed as a change of the parameters in the Hamiltonian of the system. They are also closely related to the *state* of the system and environment. The terms  $-\mathbf{M} \cdot d\mathbf{H}$ , on the other hand, comes from the parameter (magnetic field  $\mathbf{H}$ ) change appearing in the *Hamiltonian* of the system, whereas  $-p dV$  is due to the change of the *boundary condition* imposed on the system. Therefore various terms on the right-hand side of (1.1) have different origins and

they have to be studied separately.

The first nonadiabatic correction to (1.1) has been studied in general terms in Ref. [1] in the case where the process is induced by the time-dependent external parameters  $\alpha_i(t)$  ( $i=1, 2, \dots, l$ ) contained in the Hamiltonian. Here the adiabatic expansion is defined to be the one in powers of the time derivative  $\dot{\alpha}_i(t) \equiv d\alpha_i(t)/dt$ ; expansion in terms of the number of dots is called the adiabatic expansion. The system is assumed to be in the equilibrium at  $t = -\infty$  and is brought into the nonequilibrium state by  $\alpha_i(t)$ . Then the result of Ref. [1] is that, up to the lowest correction term,

$$\begin{aligned} \Delta E(t) &\equiv E(t) - E_0 \\ &= \sum_i \int_{-\infty}^t dt' X_i(\alpha(t'), \beta') \dot{\alpha}_i(t') \\ &\quad + \sum_{i,j} \int_{-\infty}^t dt' Y_{ij}(\alpha(t'), \beta') \dot{\alpha}_i(t') \dot{\alpha}_j(t'), \end{aligned} \quad (1.2)$$

or

$$\begin{aligned} dE(t) &= \sum_i X_i(\alpha(t), \beta) d\alpha_i(t) \\ &\quad + \sum_{i,j} Y_{ij}(\alpha(t), \beta) \dot{\alpha}_i(t) d\alpha_j(t). \end{aligned} \quad (1.3)$$

Here  $E(t)$  is the energy at time  $t$ ,  $E_0 = E(-\infty)$ ,  $\beta(\beta')$  is the equilibrium temperature at time  $t(t')$ . Note that  $X_i$  or  $Y_{ij}$  is the average taken over the equilibrium state in which the system lies at each instant of time if the process is adiabatic. Explicit expressions of  $X_i$  or  $Y_{ij}$  have been given in Ref. [1] but the important conclusion is that  $Y_{ij}$  is a positive-definite matrix. The positivity of  $Y_{ij}$  leads to the increase in internal energy which is known as the principle of maximum-minimum work done by the external system. The principle states that the work done by the system (or by the external environment) to the environment (or to the system) takes the maximum (or minimum) value when the process is adiabatic. The above statement can be translated into the one about the change of the internal energy of the system, of course.

Note that this principle can be a basis for the proof of the second law of thermodynamics.

The nonadiabatic correction to  $-p dV$  is discussed below. It requires a substantial amount of work, as will become clear in what follows. As has been pointed out, in order to study the case of time-dependent volume  $V(t)$ , we have to work with the time-dependent boundary conditions. If the boundary is expressed as the infinite potential wall, then as the wall moves the Hilbert space itself changes and we are faced with difficulty from the start in formulating the problem. The difficulty is avoided in Sec. II by introducing, instead of a field operator at space point  $\mathbf{x}$ , the coordinate corresponding to the mode index  $n_j$ , which is time independent. Thus we are led to the time-independent Fock space and the second quantized Hamiltonian is defined on this space. The main results of our investigation are summarized below.

(1) By introducing the mode variable, the second quantized Hamiltonian is derived in (2.20), which contains, besides  $V(t)$ , the term explicitly depending on  $\dot{V}(t)$ .

(2) Up to the lowest-order nonequilibrium correction,  $\Delta E(t)$  is given in (4.13), which is written in terms of the normal term  $X_1^0(t)$  of (3.14) and the extra term  $X_2(t)$  defined in (3.15). However, it turns out that the term  $X_2(t)$  has no contribution to  $\Delta E(t)$  to this order (see Sec. VI).

Our conclusion is therefore that, up to the order considered,

$$\Delta E(t) = -p dV + Y \dot{V} dV, \quad (1.4)$$

$$Y \geq 0, \quad (1.5)$$

where  $Y$  is given in (6.12), which is written in terms of  $X_1^0(t)$  only. Then the principle of maximum-minimum work for the volume change is proved from first principles. Our derivation in this paper is rather formal but the explicit diagrammatical calculation of  $Y$  can be done once the Hamiltonian of the system is known.

The importance of the discussion on the nonequilibrium correction to the equilibrium formula need not be stressed here again since it is a starting point of the whole formalism of the nonequilibrium thermodynamics.

## II. SECOND QUANTIZATION OF SCHRÖDINGER EQUATION WITH TIME-DEPENDENT BOUNDARY

We consider the interacting spinless  $N$ -particle system confined in a volume whose size is changing in time. The Hamiltonian is assumed to take the form

$$\mathcal{H} = \sum_{k=1}^N \mathcal{T}(\mathbf{x}_k) + \frac{g}{2} \sum_{k \neq l (=1)}^N \mathcal{V}(\mathbf{x}_k, \mathbf{x}_l), \quad (2.1)$$

where  $\mathcal{T}(\mathbf{x}_k) \equiv -(\hbar^2/2m)\nabla_k^2$  is the kinetic energy and  $\mathcal{V}$  is the time-independent potential energy of the interaction between two particles with  $g$  the coupling constant. The variable  $\mathbf{x}_k$  denotes the spatial coordinate of the  $k$ th particle. The following discussion hold for general multiparticle interactions  $\mathcal{V}(\mathbf{x}_k, \mathbf{x}_l, \dots, \mathbf{x}_m)$  but we restrict ourselves to (2.1) just for simplicity. Spin variables are

also easily incorporated. The Schrödinger equation is given by

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}_1 \cdots \mathbf{x}_N, t) = \mathcal{H} \Psi(\mathbf{x}_1 \cdots \mathbf{x}_N, t), \quad (2.2)$$

with appropriate boundary conditions [2].

To deal with varying volume  $V(t)$  we take a standpoint that the system is enclosed by perfectly rigid walls that move to cause the change in volume. In this case the many-particle Schrödinger equation should be solved with time-dependent boundary conditions [3]. Namely, the  $N$ -body wave function  $\Psi$  satisfies

$$\Psi(\mathbf{x}_1 \cdots \mathbf{x}_N, t) = 0 \quad (2.3)$$

if any one of  $\mathbf{x}_k$  is not included in the volume  $V(t)$ . Since the introduction of mode variables which are time independent is essential in our argument, we reproduce in what follows necessary steps on the pathway to the second quantized form of (2.2) and (2.3). Another method of second quantization, which is much more concise than the presentation below, is given in Appendix A.

To solve the Schrödinger equation with time-dependent boundary conditions, we first expand  $\Psi$  in terms of a complete set of function  $\psi_E(\mathbf{x}, t)$  at any instant of time that satisfies the boundary condition. The choice of the complete set is not unique, of course, but we restrict ourselves below to the following bases which are particularly convenient:

$$\psi_E(\mathbf{x}, t) = \prod_{j=1}^3 \left[ \frac{2}{L_j(t)} \right]^{1/2} \sin \left[ \frac{n_j \pi x_j}{L_j(t)} \right] \\ (j=1, 2, 3; n_j=1, 2, \dots, \infty), \quad (2.4)$$

where  $E = (n_1, n_2, n_3)$ ,  $\mathbf{x} = (x_1, x_2, x_3)$ , and we have assumed that the system is in a big box with sides  $L_i(t)$  ( $i=1, 2, 3$ ). The expansion of  $\Psi(\mathbf{x}_1 \cdots \mathbf{x}_N, t)$  is thus given by

$$\Psi(\mathbf{x}_1 \cdots \mathbf{x}_N, t) \\ = \sum_{E'_1, \dots, E'_N} C(E'_1 \cdots E'_N, t) \psi_{E'_1}(\mathbf{x}_1, t) \cdots \psi_{E'_N}(\mathbf{x}_N, t). \quad (2.5)$$

We call this expansion the *mode expansion* and  $\psi_E$  the mode function. The important fact here is that the mode is specified by the time-dependent index  $n_j$  as has been stressed in the Introduction. We sometimes call  $E$  or  $n_j$  themselves the *mode (indices)* in what follows.

We put this expression into (2.2), multiply by  $\psi_{E'_1}(\mathbf{x}_1, t) \cdots \psi_{E'_N}(\mathbf{x}_N, t)$ , and integrate over  $\mathbf{x}_1 \cdots \mathbf{x}_N$  inside  $V(t)$ . Then we get a set of equations for the coefficients  $C$ 's:

$$i\hbar \frac{\partial C(E_1 \cdots E_N, t)}{\partial t} = \sum_{k=1}^N \sum_W \left\langle E_k \left| \mathcal{T} - i\hbar \frac{\partial}{\partial t} \right| W \right\rangle_t C(E_1 \cdots E_{k-1} W E_{k+1} \cdots E_N, t) \\ + \frac{g}{2} \sum_{k \neq l (=1)}^N \sum_W \sum_{W'} \langle E_k E_l | \mathcal{V} | WW' \rangle_t C(E_1 \cdots E_{k-1} W E_{k+1} \cdots E_{l-1} W' E_{l+1} \cdots E_N, t), \quad (2.6)$$

where, using an over dot for the time derivative,

$$\left\langle E_k \left| \mathcal{T} - i\hbar \frac{\partial}{\partial t} \right| W \right\rangle_t = \left\langle E_k \left| \mathcal{T} - i\hbar \dot{V} \frac{\partial}{\partial V} \right| W \right\rangle_t = \int^{V(t)} d\mathbf{x} \psi_{E_k}(\mathbf{x}, t) \left[ \mathcal{T}(\mathbf{x}) - i\hbar \frac{\partial}{\partial t} \right] \psi_W(\mathbf{x}, t), \quad (2.7)$$

$$\langle E_k E_l | \mathcal{V} | WW' \rangle_t = \int^{V(t)} d\mathbf{x} \int^{V(t)} d\mathbf{x}' \psi_{E_k}(\mathbf{x}, t) \psi_{E_l}(\mathbf{x}', t) \mathcal{V}(\mathbf{x}, \mathbf{x}') \psi_W(\mathbf{x}, t) \psi_{W'}(\mathbf{x}', t). \quad (2.8)$$

There are some important differences here compared with the case of the time-independent boundary condition. Indeed, we notice that the mode function depends on  $t$  leading to the appearance of the term  $\langle E_k | i\hbar(\partial/\partial t) | W \rangle_t$ . But the concept of *mode* itself is independent of time.

We have to incorporate the statistics of particles. For simplicity we temporarily restrict our argument to noninteracting bosons, but a similar discussion applies for interacting bosons or fermions. The wave function  $\Psi$  is symmetric under the interchange of the coordinates. Then the symmetry of  $C$  under interchange of mode indices follows, namely,

$$C(\cdots E_i \cdots E_j \cdots, t) = C(\cdots E_j \cdots E_i \cdots, t). \quad (2.9)$$

We arrange all the levels (specified by three-component vectors  $\mathbf{n}$ ) available for  $E_i$  in an appropriate order and

call these levels state 1, state 2, etc. Suppose that, in any one of the sets  $(E_1 \cdots E_N)$ ,  $(E'_1 \cdots E'_N)$ ,  $\dots$ , the state 1 occurs  $n_1$  times, the state 2 occurs  $n_2$  times, and so on. Then we notice that, even if  $(E_1 \cdots E_N)$ ,  $(E'_1 \cdots E'_N)$ ,  $\dots$ , are different from each other, coefficients  $C$  for all these sets have the same value  $C(11 \cdots 22 \cdots, t)$ , where there are  $n_1$  ones and  $n_2$  twos, etc., which we call  $\bar{C}(n_1 n_2 \cdots n_\infty, t)$ .

Introducing the normalized coefficient  $f$ ,

$$f(n_1 n_2 \cdots n_\infty, t) = \left[ \frac{N!}{n_1! n_2! \cdots n_\infty!} \right]^{1/2} \times \bar{C}(n_1 n_2 \cdots n_\infty, t), \quad (2.10)$$

(2.6) can be written as follows (for the noninteracting case),

$$i\hbar \frac{\partial f(n_1 n_2 \cdots n_\infty, t)}{\partial t} = \sum_i \left\langle i \left| \mathcal{T} - i\hbar \frac{\partial}{\partial t} \right| i \right\rangle_t n_i f(n_1 n_2 \cdots n_\infty, t) \\ + \sum_{i \neq j} \left\langle i \left| \mathcal{T} - i\hbar \frac{\partial}{\partial t} \right| j \right\rangle_t \sqrt{n_i(n_j+1)} f(n_1 \cdots n_i-1 \cdots n_j+1 \cdots n_\infty, t). \quad (2.11)$$

Here the summation over  $i$  or  $j$  implies the summation over the states.

Let us introduce *time-independent* operators that satisfy

$$[\varphi_i, \varphi_j^\dagger] = \delta_{i,j}, \quad [\varphi_i, \varphi_j] = [\varphi_i^\dagger, \varphi_j^\dagger] = 0, \quad (2.12)$$

where  $i, j$  corresponds to the mode of expansion (2.5).

The eigenstate  $|n_j\rangle$  for the number operator  $\varphi_j^\dagger \varphi_j$  becomes

$$\varphi_j^\dagger \varphi_j |n_j\rangle = n_j |n_j\rangle \quad (n_j = 0, 1, 2, \dots, \infty). \quad (2.13)$$

Then the *time-independent* abstract state vector is defined as

$$|n_1 n_2 \cdots n_\infty\rangle = |n_1\rangle |n_2\rangle \cdots |n_\infty\rangle. \quad (2.14)$$

We now rewrite (2.11) as the equation of motion for the

state vector

$$|\Psi(t)\rangle \equiv \sum_{n_1 n_2, \dots, n_\infty} f(n_1 n_2 \cdots n_\infty, t) |n_1 n_2 \cdots n_\infty\rangle.$$

Noting the relation

$$[(n'_i+1)n'_j]^{1/2} |n'_1 \cdots n'_i+1 \cdots n'_j-1 \cdots n'_\infty\rangle \\ = \varphi_i^\dagger \varphi_j |n'_1 n'_2 \cdots n'_\infty\rangle, \quad (2.15)$$

we finally arrive at

$$i\hbar \frac{\partial |\Psi(t)\rangle}{\partial t} = \sum_{i,j} \left\langle i \left| \mathcal{T} - i\hbar \frac{\partial}{\partial t} \right| j \right\rangle_t \varphi_i^\dagger \varphi_j |\Psi(t)\rangle. \quad (2.16)$$

This is the second quantized Schrödinger equation for a free boson system with a moving wall. The case where

the interaction potential  $\mathcal{V}$  is present and where the particles are fermions can be discussed in a similar manner. We find that a set of equations (2.6) with the statistics of particles included is equivalent to the following second quantized equation:

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = H(t)|\Psi(t)\rangle, \quad (2.17)$$

$$H(t) = \sum_{i,j} \left\langle i \left| \mathcal{T} - i\hbar\frac{\partial}{\partial t} \right| j \right\rangle_t \varphi_i^\dagger \varphi_j + \frac{g}{2} \sum_{i,j,k,l} \langle ij|\mathcal{V}|kl\rangle_t \varphi_i^\dagger \varphi_j^\dagger \varphi_l \varphi_k, \quad (2.18)$$

$$[\varphi_i, \varphi_j^\dagger]_{\pm} = \delta_{ij}, \quad [\varphi_i, \varphi_j]_{\pm} = [\varphi_i^\dagger, \varphi_j^\dagger]_{\pm} = 0, \quad (2.19)$$

where  $[\ , ]_+$  denotes the anticommutator for a fermion and  $[\ , ]_-$  the commutator for a boson. We stress here again that the operators and abstract space (Hilbert space) have been introduced time-independently.

Now we specify the system to be considered. For this purpose the mode function (2.4) is employed with  $L_2$  and  $L_3$  independent of time for simplicity. Keeping in mind that  $\langle i | (\partial/\partial t) | j \rangle_t$  becomes the integration of  $\psi_i(\mathbf{x}, t) \partial \psi_j(\mathbf{x}, t) / \partial t$ , which is the products of trigonometric functions inside  $V(t)$ , we get

$$H(t) = H(V(t), \dot{V}(t)) = \sum_{\mathbf{n}} \hbar\omega_{\mathbf{n}}(t) \varphi_{\mathbf{n}}^\dagger \varphi_{\mathbf{n}} - i\hbar \frac{\dot{V}(t)}{V(t)} \sum_{\mathbf{n}, \mathbf{n}'} f_{\mathbf{n}\mathbf{n}'} \varphi_{\mathbf{n}}^\dagger \varphi_{\mathbf{n}'} + \frac{g}{2} \sum_{\mathbf{n}_1, \dots, \mathbf{n}_4} \langle \mathbf{n}_1 \mathbf{n}_2 | \mathcal{V} | \mathbf{n}_4 \mathbf{n}_3 \rangle_t \varphi_{\mathbf{n}_1}^\dagger \varphi_{\mathbf{n}_2}^\dagger \varphi_{\mathbf{n}_3} \varphi_{\mathbf{n}_4}, \quad (2.20)$$

where

$$\hbar\omega_{\mathbf{n}}(t) = \sum_{j=1}^3 \frac{1}{2m} \left[ \frac{\hbar n_j \pi}{L_j(t)} \right]^2, \quad (2.21)$$

$$f_{\mathbf{n}\mathbf{n}'} = (-1)^{n_1 - n_1'} \frac{2n_1 n_1'}{n_1^2 - n_1'^2} (1 - \delta_{n_1 n_1'}) \delta_{n_2 n_2'} \delta_{n_3 n_3'}. \quad (2.22)$$

We have also recovered the mode index  $\mathbf{n} = (n_1, n_2, n_3)$  for  $E$  (or  $i$ ). The operator  $\varphi_{\mathbf{n}}^\dagger$  or  $\varphi_{\mathbf{n}}$  does not depend on time so that time-independent Hamiltonian contains  $t$  only through  $V(t)$  and  $\dot{V}(t)$  because the potential  $\mathcal{V}$  is assumed to be time independent. The term proportional to  $\dot{V}(t)$ , which is Hermitian, of course, because  $f_{\mathbf{n}\mathbf{n}'}$  is an antisymmetric matrix, describes the effect of mixing among different modes brought about by the moving wall.

The second quantized Hamiltonian given by (2.20) is our first result of the present paper describing the system confined in a box with sides  $L_1(t), L_2, L_3$ .

### III. EXPRESSION FOR INCREASE IN ENERGY

Let us assume that the system described by the Hamiltonian (2.20) is in a thermal equilibrium at initial time  $t_I$  and then evolves into a nonequilibrium state following the Schrödinger equation under the time-dependent Hamiltonian (2.20). For such a case we derive below the

expression for the increase in energy at time  $t$   $[\Delta E(t)]$  compared with that of the initial time.

First, define the time evolution operator for the state in Schrödinger representation. Using the time order operation, it is given by

$$U(t, t') = T \exp \left\{ -\frac{i}{\hbar} \int_{t'}^t ds H(V(s), \dot{V}(s)) \right\}. \quad (3.1)$$

Differentiation the Hamiltonian in the Heisenberg picture with  $t$  we get

$$\frac{\partial}{\partial t} U(t, t_I)^\dagger H(t) U(t, t_I) = U(t, t_I)^\dagger \frac{\partial H(t)}{\partial t} U(t, t_I). \quad (3.2)$$

This leads us, by integration, to the formula

$$U(t, t_I)^\dagger H(t) U(t, t_I) = H(t_I) + \int_{t_I}^t dt' U(t', t_I)^\dagger \times \frac{\partial H(t')}{\partial t'} U(t', t_I). \quad (3.3)$$

Now the expectation value of any operator  $O$  is defined as

$$\langle O \rangle_t = \text{Tr}[\rho_I U(t, t_I)^\dagger O U(t, t_I)], \quad (3.4)$$

where  $\rho_I$  is the initial equilibrium density matrix. We choose in what follows  $\rho_I$  which represents the grand canonical ensemble.

$$\rho_I = e^{-\beta H_I} / \text{Tr} e^{-\beta H_I}, \quad (3.5)$$

$$H_I = H(t_I) - \mu N. \quad (3.6)$$

Here we have assumed  $\dot{V}(t_I) = 0$ ,  $N$  is the number operator,  $T = (k\beta)^{-1}$  denotes the initial temperature, and  $\mu$  is the chemical potential.

Operator  $O$  in (3.4) can explicitly depend on  $t$ , which is called kinematical time development [for example, the explicit dependence on  $V(t)$  and  $\dot{V}(t)$  if  $O$  is the Hamiltonian]. The dynamical time evolution, on the other hand, is the one caused by the Hamiltonian.

The increase in energy  $\Delta E(t)$  is given by using (3.3) as

$$\Delta E(t) = \langle H(t) \rangle_t - \langle H(t_I) \rangle_{t_I} \quad (3.7)$$

$$= \int_{t_I}^t dt' \text{Tr} \left\{ \rho_I U(t', t_I)^\dagger \frac{\partial H(t')}{\partial t'} U(t', t_I) \right\} \quad (3.8)$$

$$= \int_{t_I}^t dt' \text{Tr} \{ \rho_I U(t', t_I)^\dagger \times [ \dot{V}(t') X_1(t') + \ddot{V}(t') X_2(t') ] \times U(t', t_I) \}, \quad (3.9)$$

where

$$X_1(t) = \frac{\partial H(V(t), \dot{V}(t))}{\partial V(t)}, \quad (3.10)$$

$$X_2(t) = \frac{\partial H(V(t), \dot{V}(t))}{\partial \dot{V}(t)}. \quad (3.11)$$

The operator  $X_1$  is related to the usual pressure operator, while  $X_2$  is an operator which appears because  $H$  depends

explicitly on  $\dot{V}$ . It is one of our main purposes in this paper to prove that  $X_2$  has no effect up to next leading term in the adiabatic expansion (see Sec. VI).

The similar discussion to get the expression (3.8) or (3.9) has already been made in Ref. [1] by another approach. The crucial difference from the corresponding expression in Ref. [1] is the appearance of the term  $X_2$ . This is the operator corresponding to the force exerted on the system by the external parameter if it has non-vanishing second time derivative  $\ddot{V}$ .

Before closing this section we show below explicit forms of  $X_1(t)$  and  $X_2(t)$ . They are the force operators conjugate to  $\dot{V}$  and  $\ddot{V}$ , respectively, and are given as follows:

$$X_1(t) = \sum_n \frac{\partial \hbar \omega_n(t)}{\partial V(t)} \varphi_n^\dagger \varphi_n + \frac{g}{2} \sum_{n_1, \dots, n_4} \frac{\partial \mathcal{V}_{n_1 n_2 n_4 n_3}}{\partial V(t)} \varphi_{n_1}^\dagger \varphi_{n_2}^\dagger \varphi_{n_3} \varphi_{n_4} \quad (3.12)$$

$$+ \frac{i \hbar \dot{V}(t)}{V(t)^2} \sum_{n, n'} f_{nn'} \varphi_n^\dagger \varphi_{n'} \quad (3.13)$$

$$\equiv X_1^0(t) - \frac{\dot{V}(t)}{V(t)} X_2(t), \quad (3.14)$$

$$X_2(t) = - \frac{i \hbar}{V(t)} \sum_{n, n'} f_{nn'} \varphi_n^\dagger \varphi_{n'}. \quad (3.15)$$

Here the definition of  $X_1^0(t)$  and the simplified notation may be clear. The conventional operator of pressure is  $X_1^0(t)$ , as will be shown below. Both  $X_1(t)$  and  $X_2(t)$  are Hermitian operators, of course.

#### IV. ADIABATIC EXPANSION

Now we concentrate on the adiabatic expansion of  $\Delta E(t)$  assuming that the time variation of  $V(t)$  is small. For this purpose we expand  $\Delta E(t)$  according to the total number of dots (time derivatives) in each term of expansion. The first few terms are given by  $V$ ,  $\dot{V}$ ,  $(\dot{V})^2$ ,  $(\ddot{V}, \dot{V}\dot{V}, (\dot{V})^3)$  etc.

In the expression (3.9),  $U(t', t_I)$  is seen to depend on  $V(s)$  and  $\dot{V}(s)$  in the interval  $t_I < s < t$ . We expand  $V(s)$  and  $\dot{V}(s)$  in  $U(t', t_I)$  as follows:

$$V(s) = V(t') + \dot{V}(t')(s - t') + \dots, \quad (4.1)$$

$$\dot{V}(s) = \dot{V}(t') + \dots. \quad (4.2)$$

Of course, we can take another expansion scheme, but in what follows we will see that the above choice turns out to be particularly suited for our purpose in this paper.

Up to the order  $\dot{V}$ , the expansion of  $H(V(s), \dot{V}(s))$  in  $U(t', t_I)$  is given as

$$\begin{aligned} H(V(s), \dot{V}(s)) &= H(V(t'), \dot{V}(t')) + \frac{\partial H(V(t'), \dot{V}(t'))}{\partial V(t')} \dot{V}(t')(s - t') + \dots \\ &= H(V(t'), 0) + \dot{V}(t') X_2(t') + X_1^0(t') \dot{V}(t')(s - t') + \dots \end{aligned} \quad (4.3)$$

The  $U(t', t_I)$  becomes

$$\begin{aligned} U(t', t_I) &= T \prod_{i=1}^M U(t_i, t_{i-1}) \\ &= T \prod_{i=1}^M \left[ 1 - \frac{i}{\hbar} \Delta t H(t_i) \right] \\ &= \prod_{i=1}^M \left[ 1 - \frac{i}{\hbar} \Delta t H(V(t'), 0) \right] \\ &\quad + \sum_{k=1}^M \left[ \prod_{i=k+1}^M \left[ 1 - \frac{i}{\hbar} \Delta t H(V(t'), 0) \right] \right] \left[ -\frac{i}{\hbar} \Delta t \dot{V}(t') \{ (t_k - t') X_1^0(t') + X_2(t') \} \right] \\ &\quad \times \left[ \prod_{i=1}^{k-1} \left[ 1 - \frac{i}{\hbar} \Delta t H(V(t'), 0) \right] \right] + \dots, \end{aligned} \quad (4.4)$$

where we have discretized the time interval into  $M$  steps of size  $\Delta t$ .

Let us introduce

$$U'(t_1, t_2) = \exp \left[ -\frac{i}{\hbar} (t_1 - t_2) H(V(t'), 0) \right], \quad (4.5)$$

which realizes the time evolution with volume fixed to the value  $V(t')$ . Thus we get

$$U(t', t_I) = U'(t', t_I) - \frac{i}{\hbar} \int_{t_I}^{t'} dt'' U'(t', t'') \dot{V}(t') \{ (t'' - t') X_1^0(t') + X_2(t') \} U'(t'', t') U'(t', t_I) + \dots, \quad (4.6)$$

where the relation  $U''(t'', t_I) = U''(t'', t')U'(t', t_I)$  has been used. From (3.9), (3.14), (3.15), and (4.6), up to the order ( $\dot{V}(t')^2, \ddot{V}(t')$ ), the following expression for  $\Delta E(t)$  is obtained:

$$\begin{aligned} \Delta E(t) = & \int_{t_I}^t dt' \dot{V}(t') \text{Tr} \{ \rho_I U'(t', t_I)^\dagger X_1^0(t') U'(t', t_I) \} \\ & + \int_{t_I}^t dt' \frac{i}{\hbar} \dot{V}(t')^2 \int_{t_I}^{t'} dt'' \text{Tr} \{ \rho_I U'(t', t_I)^\dagger [ U'(t', t'') ((t'' - t') X_1^0(t') + X_2(t'')) U'(t', t''), X_1^0(t') ] U'(t', t_I) \} \\ & + \int_{t_I}^t dt' \left[ \ddot{V}(t') - \frac{\dot{V}(t')^2}{V(t')} \right] \text{Tr} \{ \rho_I U'(t', t_I)^\dagger X_2(t') U'(t', t_I) \} . \end{aligned} \quad (4.7)$$

From now on we taken  $t_I = -\infty$  in order to discuss the adiabatic expansion where the time derivative of  $V(t')$  is assumed to be a small quantity. This is natural: in order to get finite energy increase  $\Delta E$ , the infinite time interval is required because the rate of the change in volume  $V$  is very slow.

Let us discuss the operator

$$\text{Tr} \{ \rho_I U'(t', t_I)^\dagger \cdots U'(t', t_I) \}$$

appearing in the above formula. The time evolution operator  $U'(t', t_I)$  is the adiabatic limit of  $U(t', t_I)$  in the sense that we have made all the derivatives of  $V(t')$  go to zero [see (4.1)–(4.5)]. The expectation value in the form

$$\text{Tr} \{ \rho_I U'(t', t_I)^\dagger O U'(t', t_I) \} = \text{Tr} \{ U'(t', t_I) \rho_I U'(t', t_I)^\dagger O \}$$

can be interpreted as a thermal *equilibrium* average at time  $t'$ ,  $\text{Tr} \{ \rho_{\text{eq}}(t') O \}$ . The state characterized by  $\rho_{\text{eq}}(t')$  is obtained from  $\rho_I$  by an adiabatic change effected by  $U'$ .

This is more clearly seen by the following argument. The adiabatic expansion defined in a more precise manner is the following:

$$\begin{aligned} V(s) - V(t_I) & \equiv \alpha(s) \\ & = e^{\epsilon s} \bar{\alpha}(s) \\ & = e^{\epsilon s} [ \bar{\alpha}(t') + \dot{\bar{\alpha}}(t')(s - t') + \cdots ] , \end{aligned} \quad (4.8)$$

where  $\epsilon$  is a positive infinitesimal quantity which is taken to be zero after all the calculations.  $\alpha(s)$  and  $\dot{\alpha}(s)$  can be rewritten by

$$\alpha(s) = e^{\epsilon(s-t')} \alpha(t') + e^{\epsilon(s-t')} \dot{\alpha}(t')(s - t') + \cdots , \quad (4.9)$$

$$\dot{\alpha}(s) = \dot{V}(s) = e^{\epsilon(s-t')} \dot{\alpha}(t') + \cdots . \quad (4.10)$$

Expanding  $U(t', t_I)$  according to the order of time derivative of not  $V$  but  $\alpha$ , then  $U'(t', t_I)$  becomes

$$U'(t', t_I) = T \exp \left[ -\frac{i}{\hbar} \int_{t_I}^{t'} ds H(V(t_I) + e^{\epsilon(s-t')} \alpha(t'), 0) \right] . \quad (4.11)$$

Remembering the fact that  $V(t_I) + e^{\epsilon(s-t')} \alpha(t')$  changes its value from  $V(t_I)$  to  $V(t')$  at an infinitely slow rate as  $t$  evolves from  $t_I (= -\infty)$  to  $t'$ , we are allowed to interpret  $U'(t', t_I)$  as the adiabatic limit of  $U(t', t_I)$ . Therefore by a standard argument (see, for example, Ref. [1]) about the adiabatic theorem,  $\rho_{\text{eq}}(t')$  represents an equilibrium state characterized by parameters which take different values from that characterizing  $\rho_I$ . Here  $\rho_{\text{eq}}(t')$  corresponds to the grand canonical distribution of certain temperature  $T' = (k\beta')^{-1}$  and chemical potential  $\mu'$  into which the system has developed through the adiabatic change of the external parameter  $V(t)$ . The precise discussion of  $\rho_{\text{eq}}(t')$  is given in Sec. V.

The above observation about  $\rho_{\text{eq}}(t')$  will become more transparent if we rewrite (3.4) as

$$\langle O \rangle_t = \text{Tr} \{ U(t, t_I) \rho_I U(t, t_I)^\dagger O \} \quad (4.12)$$

from the start and assume that we trace again the process of preceding adiabatic expansion of  $U(t, t_I)$ . Then we arrive at the same result (4.7) but in this case  $U'(t', t_I)$  appears in the combination  $U'(t', t_I) \rho_I U'(t', t_I)^\dagger$ , which is the density matrix at time  $t'$ . In this form the state represented by the density matrix changes adiabatically which allows us to apply the adiabatic theorem to our result. Although this type of argument based on (4.12) is a simple repetition of (4.7), which is obtained in the Heisenberg representation (operator evolves in time), it is given in the Schrödinger picture and we recall here that the adiabatic theorem is usually formulated in the Schrödinger representation since it is a statement about the change of the levels of Hamiltonian.

Now employing the notation

$$\langle \cdots \rangle_{\text{eq}t'} = \frac{\text{Tr} \{ e^{-\beta' [H(V(t'), 0) - \mu' N]} \cdots \}}{\text{Tr} e^{-\beta' [H(V(t'), 0) - \mu' N]} ,$$

we rewrite (4.7) as

$$\begin{aligned} \Delta E(t) = & \int_{t_I}^t dt' \dot{V}(t') \langle X_1^0(t') \rangle_{\text{eq}t'} \\ & + \int_{t_I}^t dt' \frac{i}{\hbar} \dot{V}(t')^2 \int_{t_I}^{t'} dt'' \{ (t'' - t') \chi_{11}''(t'' - t', V(t')) + \chi_{21}''(t'' - t', V(t')) \} \\ & + \int_{t_I}^t dt' \left[ \ddot{V}(t') - \frac{\dot{V}(t')^2}{V(t')} \right] \langle X_2(t') \rangle_{\text{eq}t'} . \end{aligned} \quad (4.13)$$

Here we have defined

$$\begin{aligned}\chi''_{11}(t''-t', V(t')) &= \langle [\hat{X}_1^0(t''), \hat{X}_1^0(t')] \rangle_{\text{eq}t'}, \\ \chi''_{21}(t''-t', V(t')) &= \langle [\hat{X}_2(t''), \hat{X}_1^0(t')] \rangle_{\text{eq}t'},\end{aligned}\quad (4.14)$$

where

$$\hat{X}(s) = U'(s, t')^\dagger X(t') U'(s, t'). \quad (4.15)$$

In (4.13), at every instant  $t'$  of the time integration, all the averages are taken at equilibrium thermal state which is obtained by an infinitely slow change of the volume  $V(s)$  from  $s = t_I$  to  $t'$ . We arrived at this picture because we have chosen the expansion scheme (4.1) and (4.2).

Equation (4.13) is our main result of the paper. The first line describes the adiabatic limit, that is, the equilibrium thermodynamics, while the second and third lines represent the leading nonequilibrium correction to the equilibrium thermodynamics.

## V. EQUILIBRIUM THERMODYNAMICS

In this section we examine the first line of (4.13), or

$$\Delta E(t) = - \int_{V(t_I)}^{V(t)} dV p(V), \quad (5.1)$$

where  $-p(V(t')) = \langle X_1^0(t') \rangle_{\text{eq}t'}$ . The expression  $p(V)$  is interpreted as the pressure of the system. Indeed noting that  $X_1^0(t) = \partial H(V(t), 0) / \partial V(t)$ , we see that

$$\begin{aligned}-p(V) &= - \frac{1}{\beta'} \frac{\partial}{\partial V(t')} \bigg|_{\mu', T'} \ln \{ \text{Tre}^{-\beta' [H(V(t'), 0) - \mu' N]} \} \\ &= \frac{\partial \Omega}{\partial V(t')} \bigg|_{\mu', T'},\end{aligned}\quad (5.2)$$

where  $\Omega$  is the thermodynamic potential. The calculation of  $\Omega$  is to be done for the system described by the time-independent Hamiltonian  $H(V(t'), 0)$  for fixed volume  $V(t')$ ,

$$H(V(t'), 0) = \int^{V(t')} d\mathbf{x} \varphi^\dagger(\mathbf{x}) \left[ -\frac{\hbar^2 \nabla^2}{2m} \right] \varphi(\mathbf{x}) + \frac{g}{2} \int^{V(t')} d\mathbf{x} \int^{V(t')} d\mathbf{y} \varphi^\dagger(\mathbf{x}) \varphi^\dagger(\mathbf{y}) \mathcal{V}(\mathbf{x} - \mathbf{y}) \varphi(\mathbf{y}) \varphi(\mathbf{x}), \quad (5.3)$$

where

$$\begin{aligned}[\varphi(\mathbf{x}), \varphi^\dagger(\mathbf{y})]_{\pm} &= \delta(\mathbf{x} - \mathbf{y}), \\ [\varphi(\mathbf{x}), \varphi(\mathbf{y})]_{\pm} &= [\varphi^\dagger(\mathbf{x}), \varphi^\dagger(\mathbf{y})]_{\pm} = 0.\end{aligned}\quad (5.4)$$

Here, using  $\psi$  defined in (2.4), we have introduced  $\varphi^{(\dagger)}(\mathbf{x}) = \sum_i \varphi_i^{(\dagger)} \psi_i(\mathbf{x}, t')$  from which follows the boundary condition  $\varphi^{(\dagger)}(\mathbf{x}) = 0$  for  $\mathbf{x}$  on the walls.

Now let us discuss the calculation of the equilibrium parameters  $\beta'$  and  $\mu'$ .

(1)  $\beta'$ : There are several ways of calculating  $\beta'$  [4]. The most straightforward way is to use the conservation of entropy in the adiabatic process. Let  $S(E(t))$  the entropy of the system which is in the equilibrium at time  $t$ . It is written as a functional of the energy. Then we have the relation

$$S(E(t)) = S(E(t')). \quad (5.5)$$

Now the energy  $E(t')$  at time  $t'$  is regarded as a function of  $E(t)$  and take the derivative of both sides of (5.5) keeping all other parameters fixed. Then we get

$$\begin{aligned}\beta(t) &= \frac{\partial S(E(t)) / k}{\partial E(t)} \\ &= \frac{\partial S(E(t')) / k}{\partial E(t')} \frac{\partial E(t')}{\partial E(t)} \\ &= \beta(t') \left[ 1 + \frac{\partial \Delta E}{\partial E(t)} \right],\end{aligned}\quad (5.6)$$

where we have written  $E(t') = E(t) + \Delta E$ . This is the formula for the temperature shift. To get  $\Delta E$  as a function of  $E(t)$  can be done in principle and is a straightforward

task in a diagrammatic language if the perturbation in  $\mathcal{V}$  is performed.

(2)  $\mu'$ : The chemical potential is determined by using the number conservation; by using the expression of energy as a functional of  $\mu$  and  $\beta$ , we get

$$N = \frac{\partial E(t, \mu, \beta)}{\partial \mu} = \frac{\partial E(t', \mu', \beta')}{\partial \mu'}. \quad (5.7)$$

Assuming that  $\beta'$  has been obtained, (5.7) enables us to calculate  $\mu'$ .

As is usually done, we are allowed to change the boundary condition to a periodic one without changing the result of calculation as long as our system is of macroscopic size. In this sense (5.2) is a reproduction of the usual expression of the pressure in equilibrium thermodynamics. Indeed, for the noninteracting case, it is easy to show the well-known expression (for example, see Chap. 2 of Ref. [2])

$$p(t') = \frac{1}{4\pi^2} \left[ \frac{2m}{\hbar^2} \right]^{3/2} \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta'(\varepsilon - \mu') - \kappa}}, \quad (5.8)$$

where  $\kappa = 1$  for the Bose system while  $\kappa = -1$  for the Fermi system. Indeed, this result does not depend on which boundary condition has been used in the calculation.

## VI. NONEQUILIBRIUM CORRECTION

In this section we discuss the second and the third lines of (4.13). First, it is easy to see that the third line should vanish. To see this, consider the Feynman rule for  $\langle X_2(t') \rangle_{\text{eq}t'}$ . Let us define the noninteracting part of our Hamiltonian  $H(V(t'), 0) - \mu' N$ ,

$$H_0 = \sum_n \hbar \omega_n(t') \varphi_n^\dagger \varphi_n - \mu' N, \quad (6.1)$$

and the corresponding density matrix,

$$\rho_0 = e^{-\beta H_0} / \text{Tr} e^{-\beta H_0}. \quad (6.2)$$

Then we notice that

$$\text{Tr}\{\rho_0 AB \cdots C\} = \text{real}, \quad (6.3)$$

where  $A, B, \dots, C$  represents  $\varphi_n^\dagger$  or  $\varphi_n$ . This is simply because the contractions (propagators) are real;

$$\varphi_n^\dagger \varphi_m^\bullet = f_{\beta'}(\omega_n) \delta_{nm}, \quad (6.4)$$

$$\varphi_n^\bullet \varphi_m^\dagger = [1 + \kappa f_{\beta'}(\omega_n)] \delta_{nm},$$

where

$$f_{\beta'}(\omega_n) = \frac{1}{e^{\beta'(\hbar\omega_n - \mu')} - \kappa}. \quad (6.5)$$

Calculating  $\langle X_2(t') \rangle_{\text{eq}'}$  by perturbation in terms of interaction  $\mathcal{V}$ , which is also real, we end up with the sum of the terms each of which is represented by a diagram. These terms are real except for the overall factor  $i$  coming from the definition of  $X_2(t')$  given in (3.15). Therefore  $\langle X_2(t') \rangle_{\text{eq}'}$  is a pure imaginary quantity. This contradicts the fact that  $\Delta E$  is real; therefore  $\langle X_2(t') \rangle_{\text{eq}'}$  vanishes. Noting that  $f_{n'n'}$  is zero if  $n = n'$  [see (2.22)] it is a trivial task to confirm  $\langle X_2(t') \rangle_{\text{eq}'} = 0$  for noninteracting systems. We have also confirmed this fact by a direct calculation up to first order of  $\mathcal{V}$ .

More generally,

$$\langle AB \cdots C \rangle_{\text{eq}' } \equiv \text{Tr}\{e^{-\beta'[H(V(t'),0) - \mu'N]} AB \cdots C\} \\ = \text{real} \quad (6.6)$$

if  $AB \cdots C$  are  $\varphi_n^\dagger$  or  $\varphi_n$ . This will be used in Appendix B.

Next we go to the last term in the second line of (4.13) and evaluate the expression

$$\int_{t'}^\infty dt'' \Theta(t' - t'') \chi_{21}''(t'' - t', V(t')) \\ = iP \int_{-\infty}^\infty \frac{d\omega}{2\pi} \frac{\chi_{21}(\omega)}{\omega} + \frac{1}{2} \chi_{21}(\omega=0), \quad (6.7)$$

where

$$\chi_{21}''(t'' - t', V(t')) = \int_{-\infty}^\infty \frac{d\omega}{2\pi} \chi_{21}(\omega, V(t')) e^{-i\omega(t'' - t')} \\ (6.8)$$

and  $P$  denotes the Cauchy's principal value integral. The simplified notation  $\chi_{21}(\omega, V(t')) \equiv \chi_{21}(\omega)$  is employed in what follows. Note that we have used the fact that  $\chi_{21}(t'' - t', V(t'))$  is a function of  $t'' - t'$  and  $V(t')$  as is clear from its definition (4.14). The following properties of  $\chi_{21}$  are crucial in our argument:

$$\chi_{21}(\omega) = \chi_{21}(-\omega), \quad (6.9)$$

$$\chi_{21}(\omega=0) = 0. \quad (6.10)$$

This is proved in Appendix B [see (B4) and (B14)]. Thus the expression (6.7) also vanishes.

The only remaining contribution from the second and third lines of (4.13) is thus

$$\int_{t'}^\infty dt'' \Theta(t' - t'') (t'' - t') \chi_{11}''(t'' - t', V(t')) \\ = iP \int_{-\infty}^\infty \frac{d\omega}{2\pi} \frac{\chi_{11}(\omega)}{\omega^2} - \frac{i}{2} \frac{d\chi_{11}(\omega)}{d\omega} \Big|_{\omega=0}. \quad (6.11)$$

Here the definition of  $\chi_{11}(\omega)$  is the same as (6.8). Taking into account the fact that  $\chi_{11}(\omega) = -\chi_{11}(-\omega)$  [see (B6)], the first integral on the right-hand side of (6.11) vanishes. Now the second and third lines of (4.13) of the entire first-order correction of nonequilibrium thermodynamics to the equilibrium one becomes

$$\int_{-\infty}^t dt' \dot{V}(t')^2 Y(t') \\ \text{with} \quad (6.12)$$

$$Y(t') = \frac{1}{2\hbar} \frac{d\chi_{11}(\omega, V(t'))}{d\omega} \Big|_{\omega=0}.$$

The function  $Y(t')$  is proved to be positive as follows. Let us observe a well-known fact [5] that

$$\omega \chi_{11}(\omega) \geq 0, \quad (6.13)$$

then we reach the conclusion that

$$\frac{d\chi_{11}(\omega, V(t'))}{d\omega} \Big|_{\omega=0} = \lim_{\omega \rightarrow 0} \frac{\chi_{11}(\omega)}{\omega} \\ = \lim_{\omega \rightarrow 0} \frac{\omega \chi_{11}(\omega)}{\omega^2} \geq 0, \quad (6.14)$$

because  $\chi_{11}(\omega=0) = 0$  by (B6).

We have assumed above that  $\chi_{11}''(\omega)$  is continuous at  $\omega=0$ . However, strictly speaking, this property depends on detailed form of Hamiltonian (and the dimension of space). For example, if  $\chi_{11}''(t'' - t', V(t'))$  has a long-time tail as  $t'' \rightarrow +\infty$  then  $Y$  can be negative or even negatively infinite depending on the shape of the tail. Our precise statement is thus there is one-to-one correspondence between non-negativeness of  $Y$  and the continuity of  $\chi_{11}''(\omega)$  at  $\omega=0$ , which may be checked experimentally.

## VII. FIRST-ORDER NONEQUILIBRIUM THERMODYNAMICS

The results of the preceding section can be summarized as follows:

$$\Delta E(t) = - \int_{V(t')}^{V(t)} dV p(V) \\ + \int_{V(t')}^{V(t)} dV \dot{V} Y(V) + \cdots \quad (7.1)$$

or

$$dE = -p dV + Y \dot{V} dV + \cdots \quad (7.2)$$



with positive  $Y$ . The positivity of the second term of the right-hand side of (7.2) implies that the work done by the movement of a rigid wall or the work exerted by the system is minimized or maximized when the velocity of the movement goes to zero, which is known as the principle of maximum-minimum work. The above results provides the proof of this theorem for thermally isolated interacting quantum system up to the lowest order of nonadiabatic change of the volume. The term  $Y\dot{V}dV$  represents the excess energy stored in the system when the wall shows the nonadiabatic movement.

From (4.14), it is a straightforward task to calculate  $\chi''_{11}$  and  $\chi''_{21}$  by perturbation in terms of interaction  $\mathcal{V}$ . Such a calculation can be carried out by use of the standard diagrammatic rule of the nonequilibrium process [4,6,7]. From this calculation, we have found that  $\chi''_{11}$  and  $\chi''_{21}$  equal to zero up to the first order of interaction  $\mathcal{V}$ . This implies that  $Y=0$  for free (ideal) gas and supports our previous result that  $\chi''_{21}=0$  in full order.

We observe here the following important fact;  $Y$  receives nonvanishing value starting from the second order of interaction, the very order in which the coupling constant appears squared and the contribution can be positive definite. This implies that the restoration of the equilibrium is accomplished by the *scattering among particles*, which results in the redistribution of the energy supplied (or taken out) by the moving walls. The detailed diagrammatic evaluation of  $Y$  is planned to be published in a separate paper.

For the discussion of free case, we have to assume an infinitesimally small interaction which brings the system into the equilibrium state. Under this assumption, our nonadiabatic expansion is justified and each coefficient of the expansion depends on the small interaction term. Then the following question arises: at which order of adiabatic expansion does the first nonzero coefficient appear in the limit where the interaction vanishes? We do not have the answer yet, but if the maximum-minimum principle applies for the ideal gas, the first nonzero nonequilibrium correction to  $\Delta E$  has to be positive.

### VIII. CLASSICAL LIMIT

The limit  $\hbar \rightarrow 0$  leads us to the classical nonequilibrium thermodynamics for the present case. Since the limit can

be straightforwardly taken using the well-known technique, we show only the essential steps and the resulting expressions. Let us define the states

$$|\mathbf{x}_1 \cdots \mathbf{x}_N\rangle = \frac{1}{\sqrt{N!}} \varphi^\dagger(\mathbf{x}_1) \cdots \varphi^\dagger(\mathbf{x}_N) |0\rangle \quad (N=1,2,\dots,\infty), \quad (8.1)$$

where

$$\varphi(\mathbf{x})|0\rangle = 0, \quad \langle 0|0\rangle = 1. \quad (8.2)$$

These states form a normalized complete set, or

$$\begin{aligned} (\mathbf{x}_1 \cdots \mathbf{x}_N | \mathbf{x}'_1 \cdots \mathbf{x}'_M) \\ = \delta_{NM} \frac{1}{N!} \sum_P \delta(\mathbf{x}_1 - \mathbf{x}'_{P_1}) \cdots \delta(\mathbf{x}_N - \mathbf{x}'_{P_N}), \end{aligned} \quad (8.3)$$

where  $(\mathbf{x}'_{P_1} \cdots \mathbf{x}'_{P_N})$  is one of the permutations of  $(\mathbf{x}'_1 \cdots \mathbf{x}'_N)$  and  $\sum_P$  implies the summation over all these permutations. Now the correspondence between the classical expression  $O_{cl}(\mathbf{p}, \mathbf{x})$  and the quantum operator  $O$  in the second quantized representation [written by  $\varphi^\dagger(\mathbf{x})$  and  $\varphi(\mathbf{x})$ ] is defined starting from the following identity, which holds for any  $O$ :

$$\begin{aligned} O \left[ \frac{\hbar}{i} \frac{\partial}{\partial \mathbf{x}_l}, \mathbf{x}_l \right] (\mathbf{x}_1 \cdots \mathbf{x}_N | \mathbf{x}'_1 \cdots \mathbf{x}'_N) \\ \equiv (\mathbf{x}_1 \cdots \mathbf{x}_N | O | \mathbf{x}'_1 \cdots \mathbf{x}'_N). \end{aligned} \quad (8.4)$$

Here  $O((\hbar/i)(\partial/\partial \mathbf{x}_l), \mathbf{x}_l)$  is the first quantized expression of  $O$ . We simply replace  $(\hbar/i)(\partial/\partial \mathbf{x})$  inside  $O$  by  $\mathbf{p}$ , which leads to  $O_{cl}(\mathbf{p}, \mathbf{x})$  in the limit  $\hbar \rightarrow 0$ . For example, if the density matrix  $\rho$  is chosen for  $O$ , corresponding classical quantity  $O_{cl}(\mathbf{p}, \mathbf{x})$  defined above becomes the classical distribution function  $f(\mathbf{p}, \mathbf{q})$  itself.

Using this classical correspondence to an operator, we can show

$$\langle O \rangle_{eqt'} \rightarrow \sum_N \frac{1}{N!} \frac{1}{h^{3N}} \int d\mathbf{p}_1 \cdots d\mathbf{p}_N \int d\mathbf{q}_1 \cdots d\mathbf{q}_N f(\mathbf{p}, \mathbf{q}) O_{cl}(\mathbf{p}, \mathbf{q}) \equiv \langle O \rangle_{eqt'}^{cl} \quad (\hbar \rightarrow 0), \quad (8.5)$$

where

$$\begin{aligned} f(\mathbf{p}, \mathbf{q}) = \exp \left[ -\beta' \sum_j \frac{\mathbf{p}_j^2}{2m} \right. \\ \left. -\beta' \frac{g}{2} \sum_{k \neq l (=1)} \mathcal{V}(\mathbf{q}_k, \mathbf{q}_l) + \beta' \mu' N \right]. \end{aligned} \quad (8.6)$$

In the classical limit ( $\hbar \rightarrow 0$ ) the expectation value of

$X_1^0(t')$  and the commutator  $\chi_{11}(\omega)/\hbar$  is replaced by

$$\langle X_1^0(t') \rangle_{eqt'} \rightarrow \langle X_1^0(t') \rangle_{eqt'}^{cl}, \quad (8.7)$$

$$\chi_{11}(\omega)/\hbar \rightarrow \omega \beta \Phi_{11}(\omega), \quad (8.8)$$

where  $\Phi_{11}$  is the classical correlation function,

$$\Phi_{11}(\omega) = \int_{-\infty}^{\infty} d(t'' - t') e^{i\omega(t'' - t')} \langle \hat{X}_1^0(t'') \hat{X}_1^0(t') \rangle_{\text{eqt}'}^{\text{cl}}. \quad (8.9)$$

In this expression,  $\hat{X}_1^0(t'')$  is obtained by  $\hat{X}_1^0(t')$  through the Liouville time evolution formula with the volume taking fixed value  $V(t')$ . Note that from (8.5) it is easy to see that time displacement  $\langle \hat{O} \rangle = (i/\hbar) \langle [H, O] \rangle$  becomes the classical Liouville time displacement

$$\left\langle \sum_i \left[ -\frac{\partial H_{\text{cl}}}{\partial p_i} \frac{\partial}{\partial q_i} + \frac{\partial H_{\text{cl}}}{\partial q_i} \frac{\partial}{\partial p_i} \right] O_{\text{cl}}(\mathbf{p}, \mathbf{q}) \right\rangle^{\text{cl}}$$

in the limit  $\hbar \rightarrow 0$ . As a result, we get the classical version of (7.1) with

$$-p(V(t')) = \langle X_1^0(t') \rangle_{\text{eqt}'}^{\text{cl}}, \quad (8.10)$$

$$\begin{aligned} Y(V(t')) &= \frac{1}{2} \frac{d}{d\omega} (\omega \beta' \Phi_{11}(\omega)) \Big|_{\omega=0} \\ &= \frac{1}{2} \beta' \Phi_{11}(0). \end{aligned} \quad (8.11)$$

Here we have assumed that  $\Phi_{11}(0)$  is finite (see the discussion at the end of Sec. VI).

## IX. DISCUSSION

We have discussed and obtained the explicit formula of the first-order nonequilibrium correction to the equilibrium formula  $\Delta E = -p dV$  and have shown that it is indeed positive in conformity with the maximum-minimum work principle. Several comments concerning our results are in order.

(1) *Internal entropy increase.* Due to the increase in the energy by the nonadiabatic process, the internal entropy  $\Delta S$  increases correspondingly. It is an easy task to calculate  $\Delta S$  using our formula for  $\Delta E$ , (6.11). The explicit formula of  $\Delta S$  has been given in Ref. [1], which takes the usual form,

$$\Delta S(t) = \frac{\Delta E^{\text{NA}}(t)}{T(t)}, \quad (9.1)$$

where  $\Delta E^{\text{NA}}(t)$  is the nonadiabatic part of  $\Delta E(t)$ ,

$$\Delta E^{\text{NA}}(t) = Y(t) \dot{V}(t) \Delta V(t), \quad (9.2)$$

and  $T(t)$  is the equilibrium temperature at  $t$ .

(2) *The term  $dQ$  or  $\mu dN$ .* Needless to say, the nonequilibrium thermodynamics will not become a closed theory before all the factors are taken into account that lead to the time dependence of the energy. As has been stated in the Introduction,  $dQ$  or  $\mu dN$  depend on the state of both the system and environment, which is controlled not only by the Hamiltonian but by the initial condition specifying the state at some initial time  $t_I$ . Once the initial state, i.e., the initial density matrix, is fixed for the whole system including both the object system and the environment, and if the time dependence of the whole system is studied by using the Hamiltonian of the whole system, then the expectation value of the Hamiltonian of the system, i.e., object system, determines  $dQ$  which is flowing into (out of) the object system. This part leads of course to the increase (decrease) of the entropy besides the internal part of the entropy discussed in (1)

above. For the term  $\mu dN$  we have also to consider the subsystem using the number-conserving Hamiltonian of the whole system with some given initial state. The investigation of the  $dQ$  or  $\mu dN$  term in field-theoretical terminology is now underway.

(3) *Time-dependent Ginzburg-Landau-type equation for pressure.* Just as in Ref. [1], we can derive the time-dependent Ginzburg-Landau (TDGL) equation of the pressure  $\langle X_1^0(t) \rangle$  by performing the time-dependent Legendre transformation from  $V(t)$  to  $\langle X_1^0(t) \rangle$ . However, recall here that  $X_1(t)$  in (3.10), hence  $X_1^0(t)$ , is defined by the difference of the energy due to the small change of the boundary; therefore it contains the information just near the boundary. In the equilibrium case it is the pressure of the entire system since the pressure is unique everywhere. The local pressure in the nonequilibrium case can best be defined by introducing the local metric tensor  $g_{ij}(\mathbf{x})$  and by defining the (energy)-momentum tensor  $t_{ij}(\mathbf{x})$  by varying  $g_{ij}(\mathbf{x})$  and then taking the limit  $g_{ij}(\mathbf{x}) \rightarrow \delta_{ij}$  (Kronecker delta). The derivation of the TDGL equation for the local pressure will be an interesting subject.

(4) *Far from equilibrium.* We emphasize here that our results do not say anything about the nonequilibrium correction when it is far from the equilibrium process. In particular, the maximum-minimum work principle, or the law of the increase of entropy, may not be true for the highly nonadiabatic process; indeed, we know various phenomena showing nonequilibrium ordered structure which is apparently realized by the decrease of entropy.

## APPENDIX A

In this appendix (the derivation presented in this appendix was suggested by B. Sakita, to whom we are very thankful), another proof of (2.18) is presented which is more concise and more general than the one given in the text. For simplicity, we first take the noninteracting Hamiltonian of the Bose system.

Let us introduce the Bose operator  $\phi(\mathbf{x}, t)$  satisfying the equal-time commutation relation

$$[\phi(\mathbf{x}, t), \phi^\dagger(\mathbf{x}', t)] = \delta(\mathbf{x} - \mathbf{x}'). \quad (\text{A1})$$

Using the complete set of base function  $\psi_n(\mathbf{x}, t)$  satisfying the boundary condition and the annihilation operator  $\varphi_n$ , which obeys the relation (2.12), we can write

$$\phi(\mathbf{x}, t) = \sum_n \varphi_n \psi_n(\mathbf{x}, t). \quad (\text{A2})$$

One of the example of  $\psi_n(\mathbf{x}, t)$  is (2.4). Since  $\phi$ 's form a complete set as operators like  $\varphi$ 's, we can introduce the wave function as

$$\Psi(\mathbf{x}_1 \cdots \mathbf{x}_N, t) = \langle 0 | \phi(\mathbf{x}_1, t) \cdots \phi(\mathbf{x}_N, t) | \Psi \rangle. \quad (\text{A3})$$

Here the vacuum state is defined to be annihilated by  $\varphi_n$ .

Let us consider the left-hand side of the Schrödinger equation (2.2),

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{x}_1 \cdots \mathbf{x}_N, t) = i\hbar \sum_i \left\langle 0 \left| \phi(\mathbf{x}_1, t) \cdots \frac{\partial}{\partial t} \phi(\mathbf{x}_i, t) \cdots \phi(\mathbf{x}_N, t) \right| \Psi \right\rangle + \left\langle 0 \left| \phi(\mathbf{x}_1, t) \cdots \phi(\mathbf{x}_i, t) \cdots \phi(\mathbf{x}_N, t) \frac{\partial}{\partial t} \right| \Psi \right\rangle. \quad (\text{A4})$$

Now using the following relation, which is derived from (A1)

$$i\hbar \frac{\partial}{\partial t} \phi(\mathbf{x}_i, t) = [\phi(\mathbf{x}_i, t), H_t], \quad (\text{A5})$$

where

$$H_t = i\hbar \int d\mathbf{x} \phi^\dagger(\mathbf{x}, t) \frac{\partial}{\partial t} \phi(\mathbf{x}, t). \quad (\text{A6})$$

It is easy to see that the first term on the right-hand side of (A4) reduces to the following expression:

$$\begin{aligned} \sum_i \langle 0 | \phi(\mathbf{x}_1, t) \cdots [\phi(\mathbf{x}_i, t), H_t] \cdots \phi(\mathbf{x}_N, t) | 0 \rangle \\ = \langle 0 | \phi(\mathbf{x}_1, t) \cdots \phi(\mathbf{x}_i, t) \cdots \phi(\mathbf{x}_N, t) H_t | \Psi \rangle. \end{aligned} \quad (\text{A7})$$

Here we have used the relation  $\langle 0 | H_t = 0$ . In the same way, we utilize the relation

$$-\frac{\hbar^2}{2m} \nabla_i^2 \phi(\mathbf{x}_i, t) = [\phi(\mathbf{x}_i, t), H_f], \quad (\text{A8})$$

where

$$H_f = \int d\mathbf{x} \phi^\dagger(\mathbf{x}, t) \left[ -\frac{\hbar^2}{2m} \nabla^2 \right] \phi(\mathbf{x}, t), \quad (\text{A9})$$

and find that the right-hand side of the Schrödinger equation (2.2) becomes

$$\begin{aligned} \sum_i \left[ -\frac{\hbar^2}{2m} \nabla_i^2 \right] \langle 0 | \phi(\mathbf{x}_1, t) \cdots \phi(\mathbf{x}_N, t) | \Psi \rangle \\ = \langle 0 | \phi(\mathbf{x}_1, t) \cdots \phi(\mathbf{x}_N, t) H_f | \Psi \rangle. \end{aligned} \quad (\text{A10})$$

Then the Schrödinger equation reduces to

$$e^Y X e^{-Y} = X + [X, Y] + \frac{1}{2!} [Y, [Y, X]] + \frac{1}{3!} [Y, [Y, [Y, X]]] + \cdots, \quad (\text{B1})$$

$\chi''_{21}$  is expanded as follows:

$$\begin{aligned} \chi''_{21}(t'' - t', V(t')) = \langle [X_2(t'), X_1^0(t')] \rangle_{\text{eqt}'} + \frac{1}{2!} \left[ \frac{i}{\hbar} t \right]^2 \langle [[H', [H', X_2(t')]], X_1^0(t')] \rangle_{\text{eqt}'} + \cdots \\ + \frac{i}{\hbar} t \langle [[H', X_2(t')], X_1^0(t')] \rangle_{\text{eqt}'} + \frac{1}{3!} \left[ \frac{i}{\hbar} t \right]^3 \langle [[[H', [H', [H', X_2(t')]]], X_1^0(t')] \rangle_{\text{eqt}'} + \cdots, \end{aligned} \quad (\text{B2})$$

where  $H' = H(V(t'), 0)$  and  $t = t'' - t'$ . We have collected the terms of even (odd) powers of  $(t'' - t')$  in the first (second) line on the right-hand side. Operator  $H'$  and  $X_1^0(t')$  consist of  $\phi_n^\dagger$  and  $\phi_n$  with a real coefficient and

$$\langle 0 | \phi(\mathbf{x}_1, t) \cdots \phi(\mathbf{x}_N, t) \left[ i\hbar \frac{\partial}{\partial t} | \Psi \rangle - (H_f - H_t) | \Psi \right] = 0, \quad (\text{A11})$$

which holds for any  $N$ . In this way we arrive at

$$i\hbar \frac{\partial}{\partial t} | \psi \rangle = (H_f - H_t) | \psi \rangle. \quad (\text{A12})$$

The above arguments are easily extended to the interacting Bose system. The final expression is given as follows:

$$i\hbar \frac{\partial}{\partial t} | \Psi \rangle = H(t) | \Psi \rangle, \quad (\text{A13})$$

with  $H(t)$  defined by

$$\begin{aligned} H(t) \equiv \int d\mathbf{x} \phi^\dagger(\mathbf{x}, t) \left[ -\frac{\hbar^2}{2m} \nabla^2 \right] \phi(\mathbf{x}, t) \\ - i\hbar \int d\mathbf{x} \phi^\dagger(\mathbf{x}, t) \frac{\partial}{\partial t} \phi(\mathbf{x}, t) \\ + \frac{g}{2} \int d\mathbf{x} \int d\mathbf{y} \phi^\dagger(\mathbf{x}, t) \phi^\dagger(\mathbf{y}, t) \mathcal{V}(\mathbf{x}, \mathbf{y}) \\ \times \phi(\mathbf{y}, t) \phi(\mathbf{x}, t). \end{aligned} \quad (\text{A14})$$

For the Fermi system, the same formula holds but the commutator in (A1) should be replaced of course by the anticommutator. As noted above, if we use the expansion (A2) with  $\psi_n(\mathbf{x}, t)$  given by (2.4), Eqs. (A13) and (A14) lead to Eqs. (2.17)–(2.22).

## APPENDIX B

We prove several properties of  $\chi''_{11}$  and  $\chi''_{21}$ . Using the relation for any operator  $X$  and  $Y$ ,

$X_2(t')$  with a pure imaginary coefficient. Thus we notice from (6.6) that all the expectation value in the form  $\langle \rangle_{\text{eqt}'}$  appearing on the right-hand side are pure imaginary. Namely, the first (second) line is the imaginary

(real) part of  $\chi''_{21}$ . On the other hand, since  $\Delta E(t)$  is real, we identify  $\chi''_{21}$  contained in (4.13) with the imaginary part of  $\chi''_{21}$ , which is an even function of  $(t''-t')$ . The odd part of  $\chi''_{21}$  vanishes. Therefore,

$$\chi''_{21}(t''-t', V(t')) = \chi''_{21}(-(t''-t'), V(t')) \quad (\text{B3})$$

or

$$\chi_{21}(\omega) = \chi_{21}(-\omega). \quad (\text{B4})$$

A similar argument is true of  $\chi''_{11}$ . In the expression of  $\chi''_{11}$ , like (B2), all the expectation values become real this time. This is because  $\chi''_{11}$  does not contain  $X_2(t')$ . Note that  $X_1^0(t')$  has a real coefficient, in contrast to  $X_2(t')$ . Then the imaginary part of  $\chi''_{11}$  is given by the second line of (B2), which is an odd function of  $(t''-t')$ . Then  $\chi''_{11}$  appearing in (4.13) satisfies

$$\chi''_{11}(t''-t', V(t')) = -\chi''_{11}(-(t''-t'), V(t')) \quad (\text{B5})$$

or

$$\chi_{11}(\omega) = -\chi_{11}(-\omega). \quad (\text{B6})$$

Assuming that the expression (6.11) or (6.12) has a finite value,  $\chi_{11}(\omega)$  is not singular near  $\omega=0$  (see the discussion at the end of Sec. VI). Therefore

$$\chi_{11}(\omega=0) = 0. \quad (\text{B7})$$

Another way of showing the above results (B3)–(B7) goes as follows.

First, let us define the function  $F(\tau)$ .

$$F(\tau) = \langle [e^{\tau H'} X_2(t') e^{-\tau H'}, X_1^0(t')] \rangle_{\text{eq}'} . \quad (\text{B8})$$

We notice that  $F(\tau)$  is pure imaginary for real  $\tau$ . It is clear from the expansion of (B8) like (B2).

Next, we evaluate the trace in a base spanned by eigenstates of both  $H'$  and  $N$ ;

$$\begin{aligned} (H' - \mu' N) |m, i\rangle &= (E_m - \mu' N_m) |m, i\rangle \\ &\equiv K_m |m, i\rangle . \end{aligned} \quad (\text{B9})$$

Here  $i$  denotes the label specifying the degenerate states. Then we get

$$\begin{aligned} F(\tau) &= \sum_m e^{-\beta K_m} \sum_i \langle m, i | [e^{\tau H'} X_2(t') e^{-\tau H'}, X_1^0(t')] |m, i\rangle \\ &= - \sum_m e^{-\beta K_m} \sum_i \langle m, i | [e^{\tau H'} X_2(t') e^{-\tau H'}, X_1^0(t')]^\dagger |m, i\rangle \\ &= \sum_m e^{-\beta K_m} \sum_i \langle m, i | [e^{-\tau H'} X_2(t') e^{\tau H'}, X_1^0(t')] |m, i\rangle \\ &= F(-\tau) , \end{aligned} \quad (\text{B10})$$

where we have used the property  $F(\tau) = -F(\tau)^*$  and the hermiticity of  $X_1^0(t')$ ,  $X_2(t')$ , and  $H'$  in the second and third lines, respectively. Observing that  $F(\tau)$  is analytic as a function of complex variable  $\tau$  [the term such as the step function  $\Theta(\tau)$  or  $\delta(\tau)$  is not involved],  $F(\tau)$  is an even function of complex  $\tau$ . Therefore (B3) and (B4) follow.

Similarly the function  $G(\tau)$  is defined by

$$G(\tau) = \langle [e^{\tau H'} X_1^0(t') e^{-\tau H'}, X_1^0(t')] \rangle_{\text{eq}'} . \quad (\text{B11})$$

Since  $G(\tau)$  is real if  $\tau$  is real, we conclude that  $G(\tau) = -G(-\tau)$ , which gives, using a similar argument as above, (B5)–(B7).

The final task is to show  $\chi_{21}(\omega=0) = 0$ . For this purpose we evaluate the trace in the expression of  $\chi''_{21}(t''-t', V(t'))$  as follows.

$$\begin{aligned} \chi''_{21}(t''-t', V(t')) &= \sum_m e^{-\beta K_m} \sum_i [\langle m, i | \hat{X}_2(t'') \hat{X}_1^0(t') |m, i\rangle - \langle m, i | \hat{X}_1^0(t') \hat{X}_2(t'') |m, i\rangle] \\ &= \sum_{m,n} (e^{-\beta K_m} - e^{-\beta K_n}) e^{-(i/\hbar)(K_n - K_m)(t''-t')} \sum_{i,j} \langle m, i | X_2(t') |n, j\rangle \langle n, j | X_1^0(t') |m, i\rangle . \end{aligned} \quad (\text{B12})$$

Here we have inserted a complete set of eigenstates of  $H'$  and  $N$ . Notice that, since  $X_1^0(t')$  and  $X_2(t')$  commute with  $N$ , we have replaced  $E_n - E_m$  with  $K_n - K_m$  in the second line [8]. Then we get

$$\chi_{21}(\omega) = 2\pi\hbar\omega \left[ \frac{1 - e^{-\beta\hbar\omega}}{\hbar\omega} \right] \sum_{m,n} e^{-\beta K_m} \delta(\omega - (K_n - K_m)/\hbar) \sum_{i,j} \langle m, i | X_2(t') |n, j\rangle \langle n, j | X_1^0(t') |m, i\rangle . \quad (\text{B13})$$

So if  $\sum_{ij} \langle m, i | X_2(t') | n, j \rangle \langle n, j | X_1^0(t') | m, i \rangle$  is not singular, or less singular than  $(K_m - K_n)^{-1}$ , near  $m = n$  then

$$\chi_{21}(\omega=0) = 0. \quad (\text{B14})$$

If it is singular,  $\chi_{21}(\omega=0)$  is expected to be nonzero and real because  $\sum_{ij} \langle m, i | X_2(t') | n, j \rangle \langle n, j | X_1^0(t') | m, i \rangle$  is real (due to the Hermiticity of  $X_1^0$  and  $X_2$  the complex conjugate of this quantity equal to itself as is easily seen). Then by (4.13) and (6.7) such a case contradicts the fact that  $\Delta E$  is real and is safely ruled out. The property (B14) can be confirmed in another way. Indeed, because

of the anti-Hermiticity of the commutator  $[\hat{X}_2(t''), \hat{X}_1^0(t')]$ ,  $\chi_{21}''(t'' - t', V(t'))$  [hence also  $\chi_{21}(\omega=0)$ ] is pure imaginary, which contradicts the fact that  $\chi_{21}(\omega=0)$  is real. This is because, for any anti-Hermite operator  $A$ ,

$$\langle A \rangle_{\text{eq}'} = \sum_m e^{-\beta' K_m} \sum_i \langle m, i | A | m, i \rangle$$

is pure imaginary since  $\sum_i \langle m, i | A | m, i \rangle$  has the same property.

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- [8] Notice that, for any operator  $O$  which commutes with  $N$ , the following relation holds:  $U'(t_1, t_2)^\dagger O U'(t_1, t_2) = U'_{\mu'}(t_1, t_2)^\dagger O U'_{\mu'}(t_1, t_2)$ , where  $U'_{\mu'}(t_1, t_2) = \exp[-(i/\hbar)(t_1 - t_2)(H' - \mu'N)]$ .