体積が変化するときの非平衡熱力学

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I   INTRODUCTION

熱的に孤立した、粒子数一定の平衡系の熱力学では

$$dE = -pdV \qquad (1.1)$$

という公式が知られている。これは、体積 V を無限にゆっくり動かしたときに成立する式である。体積をある有限の速さを持って変化させたときには、補正項が現われ

$$dE = -pdV + Y\dot{V}dV + \cdots \qquad (1.2)$$

あるいは、

$$\Delta E(t) = - \int_{-\infty}^{t} dt' p(t')\dot{V}(t') + \int_{-\infty}^{t} dt' Y(t')\dot{V}(t')^2 \qquad (1.3)$$

という表式が期待される（ドットは時間微分を表す）。最大、最小仕事の原理によれば係数 Y は、正値であるはずである。

　本研究では、(1.3) 式（特に係数 Y）を第一原理（ハミルトニアンとシュレディンガー方程式）から求め、その具体的表式を与えることが目的である。結果として、従来の平衡系の熱力学が再現され、係数 Y の正値性が示される。後者は、最大、最小仕事の原理のミクロな立場からの検証という意味合を持つ。

　この目的のために体積の変化する系を量子力学でどう扱うかが問題となる。ここでは、体積変化を、波動関数に対する境界条件が時間によって変化することとして捉え、多粒子系シュレディンガー方程式の第二量子化を考え直してみる。すると、用意すべきヒルベルトスペース自体は、時間に依存しないものとして導入されることがわかる。

　このようにして得られたハミルトニアンを使いエネルギーの増加の表式を求め、それを体積 V に対する時間微分の階数によって展開（ Adiabatic 展開）を行うことによって (1.3) 式の具体的表式を求める。

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

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

where $\mathcal{T}(\mathbf{x}_k) \equiv -(\hbar^2/2m)\nabla_k^2$ is the kinetic energy and $\mathcal{V}$ 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 kth particle. Spin variables are also easily incorporated. The Schrödinger equation is given by

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

with appropriate boundary conditions [1].

To deal with varying volume $V(t)$ we take a standpoint that the system is enclosed by perfectly rigid walls which move to cause the change in volume. In this case the many-particle Schrödinger equation should be solved with time-dependent boundary conditions [2]. Namely the N-body wave function Ψ satisfies

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

if any one of $\mathbf{x}_k$ is not included in the volume $V(t)$. Since the introduction of mode variables which is time independent is essential in our argument, we reproduce in what follows necessary steps in the pathway to the second quantized form of (2.2),(2.3).

To solve the Schrödinger equation with time dependent boundary conditions, we first expand Ψ in terms of a complete set of function $\psi_E(\mathbf{x}, t)$ at any instant of time that satisfies the boundary condition. Explicitly $\psi_E(\mathbf{x}, t)$ is given by

$$\psi_E(\mathbf{x}, t) = \prod_{j=1}^{3} \sqrt{\frac{2}{L_j(t)}} \sin\left(\frac{n_j \pi x_j}{L_j(t)}\right)$$
$$(j = 1, 2, 3; n_j = 1, 2, \ldots, \infty) \tag{2.4}$$

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

$$\Psi(\mathbf{x}_1 \cdots \mathbf{x}_N, t) = \sum_{E_1' \cdots E_N'} C(E_1' \cdots E_N', t)\psi_{E_1'}(\mathbf{x}_1, t) \cdots \psi_{E_N'}(\mathbf{x}_N, t). \tag{2.5}$$

We call this expansion the *mode expansion* and ψ_E the mode function. The important fact here is that the mode is specified by the time-independent index n_j. We sometimes call E or n_j themselves *the mode (indices)* in what follows.

We put this expression into (2.2), multiply $\psi_{E_1}(\mathbf{x}_1, t) \cdots \psi_{E_N}(\mathbf{x}_N, t)$ 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;

$$i\hbar \frac{\partial C(E_1 \cdots E_N, t)}{\partial t} = \sum_{k=1}^{N} \sum_{W} \langle E_k | \mathcal{T} - i\hbar \frac{\partial}{\partial t} | W \rangle_t C(E_1 \cdots E_{k-1} W E_{k+1} \cdots E_N, t)$$

$$+ \frac{g}{2} \sum_{k \neq l(=1)}^{N} \sum_{W} \sum_{W'} \langle E_k E_l | \mathcal{V} | W W' \rangle_t$$

$$\times \quad C(E_1 \cdots E_{k-1} W E_{k+1} \cdots E_{l-1} W' E_{l+1} \cdots E_N, t), \qquad (2.6)$$

where, using dot for time derivative,

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

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

There are some important differences here compared with the case of time-independent boundary condition. Indeed we notice that the mode function depends on t leading to the appearance of the term $\langle E_k | i\hbar \frac{\partial}{\partial t} | W \rangle_t$. 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 for non-interacting boson, but the similar discussion applies for interacting boson or fermion. The wave function Ψ is symmetric under the interchange of the coordinates. Then the symmetry of C under interchange of mode indices follows, namely,

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

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 $(E_1 \cdots E_N), (E_1' \cdots E_N'), \ldots$, the state 1 occurs n_1 times, the state 2 occurs n_2 times and so on. Then we notice that, even if $(E_1 \cdots E_N), (E_1' \cdots E_N'), \ldots$, are different from each other, coefficient C for all these sets have the same value $C(\underbrace{11 \cdots}_{n_1} \underbrace{22 \cdots}_{n_2} \cdots, t)$ which we call $\overline{C}(n_1 n_2 \cdots n_\infty, t)$.

Introducing the normalized coefficient f

$$f(n_1 n_2 \cdots n_\infty, t) = \left(\frac{N!}{n_1! n_2! \cdots n_\infty!} \right)^{\frac{1}{2}} \overline{C}(n_1 n_2 \cdots n_\infty, t), \qquad (2.10)$$

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

$$i\hbar\frac{\partial f(n_1 n_2 \cdots n_\infty, t)}{\partial t} = \sum_i \langle i|T - i\hbar\frac{\partial}{\partial t}|i\rangle_t n_i f(n_1 n_2 \cdots n_\infty, t)$$

$$+ \sum_{i \neq j} \langle i|T - i\hbar\frac{\partial}{\partial t}|j\rangle_t \sqrt{n_i(n_j+1)} f(n_1 \cdots n_i - 1 \cdots n_j + 1 \cdots n_\infty, t)$$

$$(2.11)$$

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

Let us introduce *time-independent* operators which satisfy

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

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

The eigen-state $|n_j\rangle$ for the number operator $\varphi_j^\dagger \varphi_j$ becomes

$$\varphi_j^\dagger \varphi_j |n_j\rangle = n_j |n_j\rangle \quad (n_j = 0, 1, 2, \ldots, \infty). \tag{2.13}$$

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

$$|n_1 n_2 \cdots n_\infty\rangle = |n_1\rangle|n_2\rangle \cdots |n_\infty\rangle. \tag{2.14}$$

We now rewrite (2.11) as the equation of motion for the state vector $|\Psi(t)\rangle \equiv \sum_{n_1 n_2 \cdots n_\infty} f(n_1 n_2 \cdots n_\infty, t)|n_1 n_2 \cdots n_\infty\rangle$. Noting the relation

$$\sqrt{(n_i'+1)n_j'}|n_1' \cdots n_i' + 1 \cdots n_j' - 1 \cdots n_\infty'\rangle = \varphi_i^\dagger \varphi_j |n_1' n_2' \cdots n_\infty'\rangle, \tag{2.15}$$

we finally arrive at

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

This is the second quantized Schrödinger equation for free boson system with 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.

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

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

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

where $[\cdots, \cdots]_+$ denotes the anticommutator for fermion and $[\cdots, \cdots]_-$ the commutator for 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 $\langle i|\frac{\partial}{\partial t}|j\rangle_t$ 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

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

where

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

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

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 Hermite of course because $f_{\mathbf{n}\mathbf{n}'}$ is an antisymmetric matrix, describes the effect of mixing among different modes brought about by moving wall.

The second quantized Hamiltonian given by (2.20) is our first result 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 non-equilibrium 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,

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

Differentiating the Hamiltonian in Heisenberg picture with t we get

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

This leads us, by integration, to the following formula;

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

Now the expectation value of any operator O is defined as

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

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

$$\rho_I = e^{-\beta H_I} / Tr e^{-\beta H_I} \tag{3.5}$$

$$H_I = H(t_I) - \mu N \tag{3.6}$$

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

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

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

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

where

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

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

The operator X_1 is related to the usual pressure operator while X_2 is a new operator which appears because H depends explicitly on $\dot{V}$. It is one of our main purposes 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. [3] by another approach. The crucial difference from the corresponding expression in Ref. [3] 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.

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

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

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

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

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 Hermite 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. First few terms are given by; V, $\dot{V}$, $(\ddot{V}, (\dot{V})^2)$, $(\dddot{V}, \ddot{V}\dot{V}, (\dot{V})^3) \ldots$, 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 $V(s)$, $\dot{V}(s)$ in $U(t', t_I)$ as follows.

$$V(s) = V(t') + \dot{V}(t')(s - t') + \cdots \quad (4.1)$$
$$\dot{V}(s) = \dot{V}(t') + \cdots \quad (4.2)$$

Of course, we can take other expansion scheme, but later we will see that the above choice turns out to be particularly suited for our purpose.

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

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

$$(4.3)$$

Then $U(t', t_I)$ becomes

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

$$(4.4)$$

where we have discretized the time interval into M steps of size Δt.

Let us introduce

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

$$(4.5)$$

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

$$
\begin{aligned}
U(t', t_I) &= U'(t', t_I) \\
&- \frac{i}{\hbar} \int_{t_I}^{t'} dt'' U'(t', t'') \dot{V}(t') \{(t'' - t') X_1^0(t') + X_2(t')\} U'(t'', t') U'(t', t_I) + \cdots
\end{aligned}
$$

$$(4.6)$$

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 of $\Delta E(t)$ is obtained;

$$
\begin{aligned}
\Delta E(t) &= \int_{t_I}^{t} dt' \dot{V}(t') Tr\{\rho_I U'(t', t_I)^\dagger X_1^0(t') U'(t', t_I)\} \\
&+ \int_{t_I}^{t} dt' \frac{i}{\hbar} \dot{V}(t')^2 \int_{t_I}^{t'} dt''
\end{aligned}
$$

$$\times \quad Tr\{\rho_I U'(t',t_I)^\dagger \left[U'(t',t'')\{(t''-t')X_1^0(t') + X_2(t')\}U'(t',t''), X_1^0(t') \right] U'(t',t_I)\}$$

$$+ \quad \int_{t_I}^t dt'(\ddot{V}(t') - \frac{\dot{V}(t')^2}{V(t')})Tr\{\rho_I U'(t',t_I)^\dagger X_2(t')U'(t',t_I)\} \tag{4.7}$$

Let us discuss the operator $Tr\{\rho_I U'(t',t_I)^\dagger \cdots U'(t',t_I)\}$ 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) to (4.5)). The expectation value in the form $Tr\{\rho_I U'(t',t_I)^\dagger O U'(t',t_I)\} = Tr\{U'(t',t_I)\rho_I U'(t',t_I)^\dagger O\}$ can be interpreted as a thermal *equilibrium* average at time t'; $Tr\{\rho_{eq.}(t')O\}$. The state characterized by $\rho_{eq.}(t')$ is obtained from ρ_I by an adiabatic change effected by U'. Therefore by a standard argument (see for example Ref. [3]) about the adiabatic theorem, $\rho_{eq.}(t')$ represents an equilibrium state characterized by parameters which take different values from that characterizing ρ_I. Here $\rho_{eq.}(t')$ corresponds to the grand canonical distribution of certain temperature $T' = (k\beta')^{-1}$ and chemical potential μ' into which the system has developed through the adiabatic change of the external parameter $V(t)$.

Now employing the notation

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

we rewrite (4.7) as

$$\Delta E(t) = \int_{t_I}^t dt' \dot{V}(t')\langle X_1^0(t')\rangle_{eq.t'}$$

$$+ \int_{t_I}^t dt' \frac{i}{\hbar}\dot{V}(t')^2 \int_{t_I}^{t'} dt''\{(t''-t')\chi_{11}''(t''-t',V(t')) + \chi_{21}''(t''-t',V(t'))\}$$

$$+ \int_{t_I}^t dt'(\ddot{V}(t') - \frac{\dot{V}(t')^2}{V(t')})\langle X_2(t')\rangle_{eq.t'} \tag{4.8}$$

Here we have defined

$$\chi_{11}''(t''-t',V(t')) = \langle [\hat{X}_1^0(t''), \hat{X}_1^0(t')]\rangle_{eq.t'}$$

$$\chi_{21}''(t''-t',V(t')) = \langle [\hat{X}_2(t''), \hat{X}_1^0(t')]\rangle_{eq.t'} \tag{4.9}$$

where

$$\hat{X}(s) = U'(s,t')^\dagger X(t')U'(s,t') \tag{4.10}$$

In (4.8), at every instant t' of the time integration, all the averages are taken by 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), (4.2).

Equation (4.8) is our main result. The first line describes the adiabatic limit, that is, the equilibrium thermodynamics while the second and third lines represent the leading non-equilibrium correction to the equilibrium thermodynamics.

V EQUILIBRIUM THERMODYNAMICS

In this section we examine the first line of (4.8), or

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

where $-p(V(t')) = \langle X_1^0(t') \rangle_{eq.t'}$. 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

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

where Ω is the thermodynamic potential.

Indeed, for non-interacting case, it is easy to show the well-known expression (for example, see Ch. 2 of Ref. [1]),

$$p(t') = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \frac{2}{3} \int_0^\infty d\varepsilon \frac{\varepsilon^{\frac{3}{2}}}{e^{\beta'(\varepsilon-\mu')} - \kappa} \tag{5.3}$$

where $\kappa = 1$ for Bose system while $\kappa = -1$ for Fermi system.

VI NON-EQUILIBRIUM CORRECTION

In this section we discuss the second and the third lines of (4.8). First, it is easy to see that the third line should vanish. To see this, consider the Feynman rule for $\langle X_2(t') \rangle_{eq.t'}$. Let us define the following non-interacting part of our Hamiltonian $H(V(t'), 0) - \mu'N$,

$$H_0 = \sum_n \hbar\omega_n(t')\varphi_n^\dagger\varphi_n - \mu'N \tag{6.1}$$

and corresponding density matrix,

$$\rho_0 = e^{-\beta'H_0}/Tr e^{-\beta'H_0}. \tag{6.2}$$

Then we notice that

$$Tr\{\rho_0 AB \cdots C\} = real \tag{6.3}$$

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

$$\varphi_n^{\dagger\bullet}\varphi_m^\bullet = f_{\beta'}(\omega_n)\delta_{nm}, \quad \varphi_n^\bullet\varphi_m^{\dagger\bullet} = (1 + \kappa f_{\beta'}(\omega_n))\delta_{nm}, \tag{6.4}$$

where

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

Calculating $\langle X_2(t')\rangle_{eq.t'}$ 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 over all factor i coming from the definition of $X_2(t')$ given in (3.15). Therefore $\langle X_2(t')\rangle_{eq.t'}$ is a pure imaginary quantity. This contradicts with the fact that ΔE is real, therefore $\langle X_2(t')\rangle_{eq.t'}$ vanishes. Noting that $f_{nn'}$ is zero if $n = n'$ (see (2.22)) it is a trivial task to confirm $\langle X_2(t')\rangle_{eq.t'} = 0$ for non-interacting system. We have also confirmed this fact by a direct calculation up to first order of $\mathcal{V}$.

Next we go to the last term in the second line of (4.8) and evaluate the expression

$$\int_{t_I}^\infty dt'' \theta(t' - t'')\chi_{21}''(t'' - t', V(t')) = iP \int_{-\infty}^\infty \frac{d\omega}{2\pi} \frac{\chi_{21}(\omega)}{\omega} + \frac{1}{2}\chi_{21}(\omega = 0) \tag{6.6}$$

where

$$\chi_{21}''(t'' - t', V(t')) = \int_{-\infty}^\infty \frac{d\omega}{2\pi}\chi_{21}(\omega, V(t'))e^{-i\omega(t''-t')} \tag{6.7}$$

and P denotes the Cauchy's principal value integral. Here we have considered t_I as $-\infty$. This is natural: in order to get finite energy increase ΔE, the infinite time interval is required because the rate of the change in volume V is very slow. 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 $V(t')$ which is clear from its definition (4.9). We can shoe that χ_{21} has the following properties.

$$\chi_{21}(\omega) = \chi_{21}(-\omega) \tag{6.8}$$

$$\chi_{21}(\omega = 0) = 0. \tag{6.9}$$

Thus the expression (6.6) also vanishes.

The only remaining contribution from the second and third lines of (4.8) is thus

$$\int_{t_I}^\infty dt'' \theta(t'-t'')(t''-t')\chi_{11}''(t''-t', V(t')) = iP \int_{-\infty}^\infty \frac{d\omega}{2\pi}\frac{\chi_{11}(\omega)}{\omega^2} - \frac{i}{2}\frac{d\chi_{11}(\omega)}{d\omega}\bigg|_{\omega=0}. \tag{6.10}$$

Here the definition of $\chi_{11}(\omega)$ is the same as (6.7). Since it is known that $\chi_{11}(\omega) = -\chi_{11}(-\omega)$, the first integral on the right-hand side of (6.10) vanishes. Now the second and third lines of (4.8) of the entire first order correction of non-equilibrium thermodynamics to the equilibrium one becomes

$$\int_{-\infty}^{t} dt' \dot{V}(t')^2 Y(t') \quad \text{with} \quad Y(t') = \frac{1}{2\hbar} \left. \frac{d\chi_{11}(\omega, V(t'))}{d\omega} \right|_{\omega=0}. \quad (6.11)$$

The function $Y(t')$ is proved to be positive as follows. Let us observe a well-known fact [4] that

$$\omega \chi_{11}(\omega) \geq 0, \quad (6.12)$$

then we reach the conclusion that

$$\left. \frac{d\chi_{11}(\omega, V(t'))}{d\omega} \right|_{\omega=0} = \lim_{\omega \to 0} \frac{\chi_{11}(\omega)}{\omega} = \lim_{\omega \to 0} \frac{\omega \chi_{11}(\omega)}{\omega^2} \geq 0 \quad (6.13)$$

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

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 $\chi''(t'' - t', V(t'))$ has a long time tail as $t'' \to +\infty$ 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.

References

[1] In this section, we follow the arguments and notations, with necessary changes about the boundary condition, in Sec. 1 of A. Fetter and Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, Inc. 1971).

[2] For single particle Schrödinger equation ($N = 1$), see, for instance, S. W. Doesher and M. H. Rice, Am. J. Phys. **37**, 1246 (1969); D. N. Pinder, Am. J. Phys. **58**, 54 (1990); A. J. Makowski, J. Phys. A: Math. Gen. **25**, 3419 (1992).

[3] R. Fukuda, Prog. Theor. Phys. **77**, 825 (1987), 845 (1987).

[4] See, for example, Sec. 2.8 of D. Forster, *Hydrodynamics, Broken Symmetry, and Correlation Functions* (W. A. Benjamin, Inc. 1983).