Bernoulli's formula and Poisson's equations for a confined quantum gas: Effects due to a moving piston

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We study a nonequilibrium equation of states of an ideal quantum gas confined in the cavity under a moving piston with a small but finite velocity in the case in which the cavity wall suddenly begins to move at the time origin. Confining ourselves to the thermally isolated process, the quantum nonadiabatic (QNA) contribution to Poisson's adiabatic equations and to Bernoulli's formula which bridges the pressure and internal energy is elucidated. We carry out a statistical mean of the nonadiabatic (time-reversal-symmetric) force operator found in our preceding paper [Nakamura *et al.*, Phys. Rev. E **83**, 041133 (2011)] in both the low-temperature quantum-mechanical and high-temperature quasiclassical regimes. The QNA contribution, which is proportional to the square of the piston's velocity and to the inverse of the longitudinal size of the cavity, has a coefficient that is dependent on the temperature, gas density, and dimensionality of the cavity. The investigation is done for a unidirectionally expanding three-dimensional (3D) rectangular parallelepiped cavity as well as its 1D version. Its relevance in a realistic nanoscale heat engine is discussed.

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I. INTRODUCTION

The equation of states plays an important role in thermodynamics and statistical mechanics. Let us consider Carnot's thermodynamic cycle proposed almost two centuries ago [1]. It is the most efficient cycle for converting a given heat into work. In this cycle, the system is assumed to undergo a series of different thermodynamic states and performs work on its surroundings, thereby acting as a Carnot heat engine. However, such a perfect engine is only a theoretical limit, and practical engines must incorporate the effect of nonzero velocity of the moving piston.

In the Carnot cycle, the pressure (P) and volume (V) of an ideal classical gas (Boltzmann gas) confined in the cavity are assumed to obey the equilibrium equation of states, i.e., Boyle-Charles' law (BCL), and a set of Poisson's adiabatic equations in the isothermal and thermally adiabatic processes, respectively. Poisson's adiabatic equations are derived from the first law of thermodynamics together with BCL. BCL itself is a special limit of the Bernoulli's formula (BF) bridging between the pressure (P) and internal energy (U) for quantum and classical gas in the cavity in d dimensions. BF is available from the relation $PV = -\Omega$ with use of the density of states in calculating the thermodynamic potential Ω for both classical and quantum gas. To be specific, $PV = \frac{2}{3}U$, U, and $2U$ for $d = 3$, 2, and 1, respectively. The last case may be better rewritten as $FL = 2U$ with use of the force (F) and the length (L) of the one-dimensional (1D) cavity. For a classical gas, $U = \frac{3}{2}NkT$, NkT, and $\frac{1}{2}NkT$ for $d = 3$, 2, and 1, respectively, with use of the number of particles N, the Boltzmann constant k, and the temperature T. Then Bernoulli's formula reduces to BCL, $PV = NkT$, irrespective of dimensionality. For a quantum gas, Bernoulli's formula works as well, where $U = E_0[1 + 0.0713(mT/\hbar^2)^2(V/N)^{4/3}]$ with $E_0 = (3/10)(6\pi^2)^{2/3}(\hbar^2/m)(N/V)^{2/3}N$ for $d = 3$ Fermi gas in the low-temperature and high-density regime (see Landau-Lifshitz [2]). In the thermally adiabatic process, a set of Poisson's adiabatic equations also works, which are given by $PV^{(d+2)/d} = \text{const}$, $\frac{P}{T^{(d+2)/2}} = \text{const}$, and $VT^{d/2} = \text{const}$, irrespective of classical and quantal systems [3].

In constructing Bernoulli's formula, the velocity of the wall of a gas container (cylinder, cavity, billiard, etc.) is assumed to be negligibly small. To make the theory of heat engines more realistic, one must evaluate the effect of the nonzero velocity of the piston, i.e., the wall motion of the gas container. Since the kinetic theory of Boltzmann gas tells that a moving piston does not play a role in the equation of states, we shall investigate the nonadiabatic dynamics in the quantum heat engine. While in recent years there appeared papers which treated the quantum engine, they were either concerned with a quantum analog of Carnot's engine [4–7] or with a quantum analog of a nonequilibrium work relation (i.e., a fluctuation theorem) [8,9], and they touched on neither the nonadiabatic pressure due to a moving piston nor the statistical treatment of an ideal quantum gas.

In this paper, confining ourselves to the thermally isolated process, we shall investigate the nonequilibrium equation of states for an ideal quantum gas (Fermi gas) confined into an expanding cavity in the case in which the cavity wall suddenly begins to move at the time origin. Quantum nonadiabatic (QNA) contributions to Bernoulli's formula and to Poisson's adiabatic equations due to the nonzero velocity of the moving piston are elucidated. In Sec. II, with use of the nonadiabatic force operator in our preceding paper [10], the adiabatic and nonadiabatic pressures are defined. In Sec. III, expectation of nonequilibrium pressure is expressed in terms of the density of states, which will enable the calculation of thermodynamic and statistical averages of nonadiabatic

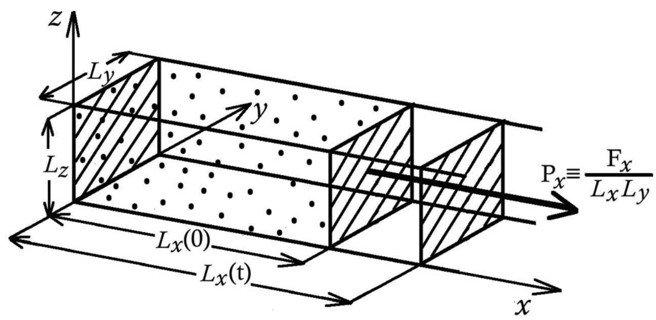

FIG. 1. 3D rectangular parallelepiped cavity confining the quantal gas, with the size $L_x(t) \times L_y \times L_z$. One of its walls is moving in the x direction. $P_x(t)$ and $F_x(t)$ stand for the x components of pressure and force.

pressure. In Secs. IV and V, the unidirectionally expanding cavities in $d = 1$ and 3 dimensions are studied, and explicit forms for QNA contributions to the pressure, internal energy, and equation of states will be given in the low-temperature and high-density regime as well as in the high-temperature and low-density regime. In Sec. VI, the physical implications of QNA contributions will given. Section VII is devoted to a summary and discussions. In Appendixes A and B, using the Fermi-Dirac distribution, we summarize several formulas for thermodynamic averages in the cases of 1D and 3D rectangular cavities. The isothermal process which requires a contact with the heat reservoir is beyond the scope of the paper and will be investigated in due course.

II. ADIABATIC AND NONADIABATIC PRESSURES

Before embarking upon the adiabatic and nonadiabatic pressures, we shall briefly summarize the derivation of the adiabatic and nonadiabatic force operators in our preceding paper [10], but here in the context of the parallel-piped rectangular 3D cavity. Let us consider a Fermi gas (noninteracting Fermi particles) confined in a cavity with a moving wall (i.e., piston). The wall receives the force from the Fermi gas in the cavity. Under the condition that the whole system consisting of Fermi particles and a moving wall maintains the energy conservation, the work done on the wall by the force is supplied by the excess energy due to the energy loss of Fermi particles showing the nonadiabatic transition. In this way, one can conceive both the adiabatic and nonadiabatic forces. In the adiabatic limit, the adiabatic force due to the quantal gas on the cavity wall is proportional to the derivative of the confining energy with respect to the cavity size. What is a characteristic feature of the nonadiabatic force coming from the nonadiabatic transition?

We choose a 3D rectangular parallelepiped cavity with the size $L_x \times L_y \times L_z$, one of whose walls is moving in the x direction (see Fig. 1).

The original Hamiltonian for the cavity with a time-dependent longitudinal size $L_x(t)$ is given by

$$H_{\text{tot}} = H + H_{\perp} \tag{1}$$

with

$$H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \quad H_{\perp} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right). \tag{2}$$

The wave function is a product of the longitudinal and perpendicular parts:

$$\psi_{\text{tot}}(x,y,z,t) = \psi(x,t)\psi_{\perp}(y,z,t), \tag{3}$$

which satisfies the moving and static Dirichlet boundary conditions for ψ and $\psi_{\perp}$, respectively, as

$$\psi(x = 0,t) = \psi(x = L_x(t),t) = 0, \tag{4}$$

$$\psi_{\perp}(y = 0,z,t) = \psi_{\perp}(y = L_y,z,t) = 0, \tag{5}$$

$$\psi_{\perp}(y,z = 0,t) = \psi_{\perp}(y,z = L_z,t) = 0. \tag{6}$$

Throughout the time evolution, the instantaneous (adiabatic) eigenstate is characterized by a set of quantum numbers (n_x,n_y,n_z). The longitudinal perturbation in H commutes with the perpendicular part $H_{\perp}$ in the total Hamiltonian in Eq. (1), and thereby the quantum numbers n_y and n_z are conserved against an expansion along x. Therefore, if a confined particle is initially in a manifold with the fixed n_y and n_z and the cavity expands only in the x direction, there occurs no mixing among manifolds with different n_y and n_z. Consequently, the dynamics of $\psi_{\text{tot}}(x,y,z,t)$ is determined by the time-dependent Schrödinger equation for the longitudinal part $\psi(x,t)$ as

$$i\hbar\frac{\partial}{\partial t}\psi(x,t) = H\psi(x,t). \tag{7}$$

The expectation of the normal component of the force acting on the wall is obtained by

$$\bar{F}_x = -\frac{\partial}{\partial L_x(t)}\langle\psi|H|\psi\rangle = -\langle\psi|\frac{\partial H}{\partial L_x(t)}|\psi\rangle, \tag{8}$$

where, in obtaining the last expression, we used $\frac{\partial}{\partial L_x}|\psi\rangle = \frac{1}{\dot{L}_x}\frac{\partial}{\partial t}|\psi\rangle = \frac{1}{i\hbar\dot{L}_x}H|\psi\rangle$ and its Hermitian conjugate. Hence the force operator is defined by

$$\hat{F}_x = -\frac{\partial H}{\partial L_x(t)}. \tag{9}$$

Since the original Hamiltonian H for the cavity with its time-dependent longitudinal size $L_x(t)$ does not formally include $L_x(t)$ explicitly, however, there is no way to define the force operator directly by using Eq. (9).

To overcome this difficulty, we shall make the time-dependent canonical transformation of H related to the scale transformation of both the coordinate x and amplitude of the wave function ψ. This transformation is defined by [11]

$$\tilde{H} = e^{-iU}\left(H - i\hbar\frac{\partial}{\partial t}\right)e^{iU}, \tag{10}$$

with $U = -\frac{1}{2\hbar}(\hat{x}\hat{p} + \hat{p}\hat{x})\ln L_x(t) = i(x\frac{\partial}{\partial x} + \frac{1}{2})\ln L_x(t)$. This canonical transformation leads to the scaled coordinate $\tilde{x}$ defined by $e^{-iU}xe^{iU} = \tilde{x}L_x(t)$ and the scaled wave function $\tilde{\phi}(\tilde{x},t) = e^{-iU}\psi(x,t) = \sqrt{L_x}\psi(\tilde{x}L_x,t)$. The range of $\tilde{x}$ is $0 \leqslant \tilde{x} \leqslant 1$, which is time-independent. Also the normalization factor of $\tilde{\phi}(\tilde{x},t)$ becomes L_x-independent and satisfies the fixed Dirichlet boundary condition $\tilde{\phi}(0,t) = \tilde{\phi}(1,t) = 0$.

Finally the Schrödinger equation is transformed to

$$i\hbar\frac{\partial\tilde{\phi}}{\partial t} = \tilde{H}\tilde{\phi} \tag{11}$$

with the Hamiltonian

$$\tilde{H} = -\frac{\hbar^2}{2mL_x^2}\frac{\partial^2}{\partial\tilde{x}^2} + i\hbar\frac{\dot{L}_x}{L_x}\tilde{x}\frac{\partial}{\partial\tilde{x}} + \frac{i\hbar}{2}\frac{\dot{L}_x}{L_x}, \tag{12}$$

which is Hermitian. $\tilde{\phi}(x,t)$ now satisfies the fixed Dirichlet boundary condition $\tilde{\phi}(0,t) = \tilde{\phi}(1,t) = 0$.

Taking the L_x derivative of $\tilde{H}$, we can rigorously define the force operator in the transformed space, whose inverse canonical transformation gives the force operator expressed in the original space as

$$\begin{aligned}\hat{F} &= \frac{\hat{p}^2}{mL} - \frac{\dot{L}}{2L^2}(\hat{x}\hat{p} + \hat{p}\hat{x}) \\ &= -\frac{\hbar^2}{m}\frac{1}{L}\partial_x^2 + i\frac{\hbar}{2}\frac{\dot{L}}{L^2}(x\partial_x + \partial_x x),\end{aligned} \tag{13}$$

where we suppressed the suffix x in both the force operator and the longitudinal length. The issue in Eq. (13) is universal, irrespective of the kind of canonical transformations. In fact, one may choose another canonical transformation such as a combination of U in Eqs. (10) and the gauge transformation (see [10]), which also guarantees the wave function to satisfy the fixed Dirichlet boundary condition and the transformed Hamiltonian, say $\tilde{H}'$, to be Hermitian. The derivative of $\tilde{H}'$ with respect to L_x defines the force operator $\hat{F}'$, and the inverse of a combination of the gauge and scale transformations results in the identical expression for $\hat{F}$.

In the final expression of Eq. (13), the first and the second parts define the adiabatic and nonadiabatic forces, respectively. The latter part, which gives an essential contribution when the system is not in the instantaneous eigenstates, is invariant under the time-reversal operation since both $\dot{L}$ and $\hat{p}$ change their signs. The expression in Eq. (13) is the force normal to the wall, and, when divided by an area of the wall, it gives the adiabatic and nonadiabatic pressures ($\hat{P}$) acting on the moving wall of the 3D rectangular parallelepiped cavity:

$$\hat{P} = \frac{\hat{F}}{L_y L_z}. \tag{14}$$

III. EXPECTATION OF NONEQUILIBRIUM PRESSURE IN TERMS OF DENSITY OF STATES

Let us consider the system to be thermally isolated and the wall of the cavity to begin to move at $t = 0$ suddenly (see Fig. 2). The Fermi gas in the cavity is assumed to satisfy the equilibrium Fermi-Dirac distribution until $t = 0$.

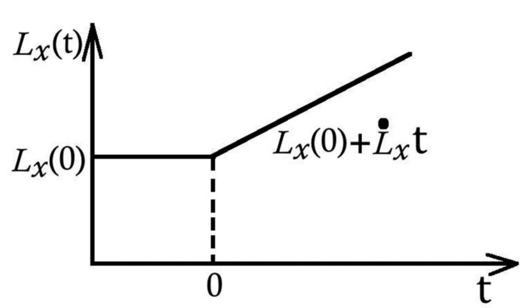

FIG. 2. Time dependence of $L_x(t)$. The wall is assumed to begin to move at the time origin.

The expectation of the force operator is evaluated in terms of the density operator ρ:

$$\bar{F} = \mathrm{Tr}(\rho\hat{\mathrm{F}}). \tag{15}$$

The density operator ρ for a thermally isolated nonequilibrium state of the Fermi gas obeys the von Neumann equation

$$i\hbar\frac{\partial\rho}{\partial t} = [H,\rho], \tag{16}$$

where the original Hamiltonian H and coordinate x are used.

Using adiabatic bases (instantaneous eigenstates) $\{|n\rangle\}$, the matrix elements of ρ satisfy

$$\dot{\rho}_{nm} = \frac{1}{i\hbar}(E_n - E_m)\rho_{nm} - \frac{\dot{L}}{L}\left(\sum_{\ell\neq n}\gamma_{\ell n}\rho_{\ell m} + \sum_{\ell\neq m}\gamma_{\ell m}\rho_{n\ell}\right) \tag{17}$$

with $\gamma_{mn} = (-1)^{m+n+1}\frac{2mn}{m^2-n^2}(1-\delta_{mn})$.

Then $\bar{F}$ becomes

$$\bar{F} = \sum_{m,n}\rho_{nm}F_{mn}, \tag{18}$$

where

$$F_{mn} = \frac{\hbar^2}{m}\frac{(n\pi)^2}{L^3}\delta_{mn} + \frac{i\hbar\dot{L}}{L^2}\gamma_{mn}. \tag{19}$$

To make the problem tractable, we assume $\dot{L} \ll v_F$, that is, the wall velocity $\dot{L}$ is much less than the Fermi velocity v_F, which guarantees a confined particle to collide with the cavity wall many times during the wall displacement of $O(L)$. The above inequality is scaled by L and is written as

$$\frac{\dot{L}}{L} \ll \frac{1}{\tau_F}, \tag{20}$$

where $\tau_F\ (=\frac{L}{v_F})$ is a characteristic time for a particle to travel through the cavity. With use of the smallness parameter $\frac{\dot{L}}{L}$, we substitute the expansion

$$\rho = f(H) + \frac{\dot{L}}{L}g_1 + \left(\frac{\dot{L}}{L}\right)^2 g_2 \tag{21}$$

into the von Neumann equation. Then, for orders of $(\frac{\dot{L}}{L})^0$, $(\frac{\dot{L}}{L})^1$, and $(\frac{\dot{L}}{L})^2$, we have $\dot{f}(H) = 0$, $\dot{g}_{1nm} = \frac{E_n-E_m}{i\hbar}g_{1nm} - (\gamma_{mn}f_m + \gamma_{nm}f_n)$, and $\dot{g}_{2nn} = -\sum_\ell \gamma_{\ell n}(g_{1\ell n} + g_{1n\ell})$, respectively.

The condition Eq. (20) guarantees $\dot{L}t \ll L$ in a wide time range. Then a set of the above equations can be solved as

$$f_{nm} = \frac{1}{e^{\beta(E_n-\mu)}+1}\delta_{nm} \equiv f_n\delta_{nm}, \tag{22}$$

$$g_{1nm} = \frac{i\hbar\gamma_{mn}}{E_n - E_m}(1 - e^{\frac{E_n-E_m}{i\hbar}t})(f_n - f_m), \tag{23}$$

$$\begin{aligned}g_{2nn} = &-2\sum_{\ell\neq n}\gamma_{n\ell}^2(f_n - f_\ell)\left(\frac{\hbar}{E_n - E_\ell}\right)^2 \\ &\times\left[1 - \cos\left(\frac{E_n - E_\ell}{\hbar}t\right)\right].\end{aligned} \tag{24}$$

Equation (22) denotes the initial Fermi-Dirac distribution with inverse temperature $\beta = \frac{1}{kT}$.

Expectation value $\bar{F}$ is given by

$$\bar{F} = \bar{F}_1 + \bar{F}_2 + \bar{F}_3, \tag{25}$$

where

$$\bar{F}_1 = \sum_n f_n F_{nn} = \frac{\hbar^2}{m}\sum_n \frac{(n\pi)^2}{L^3} f_n = \frac{2}{L}\sum_n E_n f_n, \tag{26}$$

$$\begin{aligned}\bar{F}_2 &= \frac{\dot{L}}{L}\sum_{n\neq m} g_{1nm}F_{mn}\\ &= -4\hbar^2\frac{\dot{L}^2}{L^3}\sum_{m\neq n}\frac{E_nE_m}{(E_n-E_m)^2}\frac{f_n-f_m}{E_n-E_m}2\sin^2\left(\frac{E_n-E_m}{2\hbar}t\right)\\ &= -8\pi^2\hbar^2\frac{\dot{L}^2}{L^3}\sum_{m\neq n}E_nE_m\frac{f_n-f_m}{E_n-E_m}\delta(E_n-E_m),\end{aligned} \tag{27}$$

$$\begin{aligned}\bar{F}_3 &= \frac{\hbar^2}{m}\left(\frac{\dot{L}}{L}\right)^2\sum_n g_{2nn}F_{nn}\\ &= -16\frac{\dot{L}^2}{L^3}\sum_{n>m}E_nE_m\frac{f_n-f_m}{E_n-E_m}\\ &\quad\times\left(\frac{\hbar}{E_n-E_m}\right)^2 2\sin^2\left(\frac{E_n-E_m}{2\hbar}t\right)\\ &= -32\pi^2\hbar^2\frac{\dot{L}^2}{L^3}\sum_{n>m}E_nE_m\frac{f_n-f_m}{E_n-E_m}\delta(E_n-E_m).\end{aligned} \tag{28}$$

It should be noted that both $\bar{F}_2$ and $\bar{F}_3$ are quadratic in $\dot{L}$. The absence of $\dot{L}$-linear terms is caused by a subtle cancellation of the linear cross-coupling terms among the matrix elements of the force operator and those of the density matrix both expressed as a series expansion with respect to $\dot{L}$.

In obtaining the final expression for $\bar{F}_1$, $\bar{F}_2$, and $\bar{F}_3$, we used $E_n \equiv \frac{\pi^2\hbar^2n^2}{2mL^2}$ and the asymptotic form

$$\frac{\sin\left(\Delta E\frac{t}{\hbar}\right)}{\Delta E} \approx \pi\delta(\Delta E), \tag{29}$$

which is valid in the time domain much larger than the minimum resolution of time ($t \gg \frac{\hbar}{\Delta E}$). Thanks to Eq. (29), the explicit time dependence of $\bar{F}_2$ and $\bar{F}_3$ is suppressed.

The discrete summations can now be reduced to continuum integrations with use of 1D density of states as

$$\sum_{n=1}^{\infty} = \sum_{k_n(\equiv\frac{\pi n}{L})} = \int_{E_0}^{\infty} D_1(E)dE. \tag{30}$$

Noting $E = \frac{\hbar^2k^2}{2m}$, $D_1(E)$ is given by

$$D_1(E) = \frac{dk/(\pi/L)}{dE} = \frac{\sqrt{m}L}{\sqrt{2}\pi\hbar}E^{-1/2}. \tag{31}$$

Using the above facts, we shall write the final results for $\bar{F}_1$, $\bar{F}_2$, and $\bar{F}_3$:

$$\bar{F}_1 = \frac{2}{L}\int_0^{\infty} ED_1(E)f(E), \tag{32}$$

$$\begin{aligned}\bar{F}_2 = &-8\pi^2\hbar^2\frac{\dot{L}^2}{L^3}\int_0^{\infty}dE\int_0^{\infty}dE'EE'\frac{df}{dE}\bigg|_{E=E'}\\ &\times D_1(E)D_1(E')\delta(E-E'),\end{aligned} \tag{33}$$

$$\begin{aligned}\bar{F}_3 = &-32\pi^2\hbar^2\frac{\dot{L}^2}{L^3}\int_0^{\infty}dE\int_0^{\infty}dE'EE'\frac{df}{dE}\bigg|_{E=E'}\\ &\times D_1(E)D_1(E')\delta(E-E').\end{aligned} \tag{34}$$

The purpose of the present paper is to generalize Bernoulli's formula bridging pressure and internal energy to the case of the expanding cavity. Therefore, one should also provide general formulas for the internal energy in the case of a moving piston. With use of the expansion in Eq. (21) and the matrix elements

$$(\hat{H})_{nm} = \frac{\hbar^2\pi^2n^2}{2mL^2}\delta_{nm} \equiv E_n\delta_{nm}, \tag{35}$$

we have the internal energy $\bar{U}$,

$$\bar{U} = \mathrm{Tr}(\rho\hat{H}) = \bar{U}_1 + \bar{U}_2 + \bar{U}_3. \tag{36}$$

Here

$$\bar{U}_1 = \mathrm{Tr}(f\hat{H}) = \sum_{n=1}^{\infty}E_nf_n = \int_0^{\infty}ED_1(E)f(E)dE \tag{37}$$

and

$$\begin{aligned}\bar{U}_3 &= \left(\frac{\dot{L}}{L}\right)^2\mathrm{Tr}(g_2\hat{H})\\ &= -8\pi^2\hbar^2\left(\frac{\dot{L}}{L}\right)^2\sum_{n>m}\frac{E_nE_m}{E_n-E_m}(f_n-f_m)\\ &= -8\pi^2\hbar^2\left(\frac{\dot{L}}{L}\right)^2\int_0^{\infty}dE\int_0^{E}dE'EE'\frac{df}{dE}\bigg|_{E=E'}\\ &\quad\times D_1(E)D_1(E')\delta(E-E').\end{aligned} \tag{38}$$

Noting the absence of the diagonal elements of g_1,

$$\bar{U}_2 = \frac{\dot{L}}{L}\mathrm{Tr}(g_1\hat{H}) = 0, \tag{39}$$

namely, always vanishing.

IV. CASE OF THE EXPANDING 1D CAVITY

First, concentrating on the expanding 1D cavity, we shall evaluate the final expressions in the previous section in two limiting cases, i.e., in the low-temperature and high-density region for a degenerate quantum gas and in the high-temperature and low-density region for a quasiclassical gas.

A. Low-temperature and high-density region

Having recourse to formulas in Eqs. (A1) and (A2), the expectation of force terms in Eqs. (32)–(34)

becomes

$$\bar{F}_1 = \frac{2\sqrt{m}}{\sqrt{2}\pi\hbar}\int_0^\infty \sqrt{E}f(E)dE$$
$$= \frac{2\sqrt{2m}}{3\pi\hbar}\mu^{3/2}\left[1+\frac{\pi^2}{8}(kT)^2\mu^{-2}+\frac{7\pi^4}{640}(kT)^4\mu^{-4}+\cdots\right], \tag{40}$$

$$\bar{F}_2 = -4m\frac{\dot{L}^2}{L}\int_0^\infty dE\, E\frac{df}{dE} = 4m\frac{\dot{L}^2}{L}\mu, \tag{41}$$

$$\bar{F}_3 = -8m\frac{\dot{L}^2}{L}\int_0^\infty dE\, E\frac{df}{dE} = 8m\frac{\dot{L}^2}{L}\mu, \tag{42}$$

where μ is the chemical potential. Thereby,

$$\bar{F} = \bar{F}_1+\bar{F}_2+\bar{F}_3$$
$$= \frac{2\sqrt{2m}}{3\pi\hbar}\mu^{3/2}\left[1+\frac{\pi^2}{8}(kT)^2\mu^{-2}+\cdots\right]+12m\frac{\dot{L}^2}{L}\mu. \tag{43}$$

Noting the low-temperature and high-density expansion of μ with use of particle number N in Eq. (A4), we have

$$\bar{F} = \frac{\pi^2\hbar^2}{3m}\left(\frac{N}{L}\right)^3\left[1+\frac{1}{\pi^2}\left(\frac{mkT}{\hbar^2}\right)^2\left(\frac{N}{L}\right)^{-4}+\cdots\right]$$
$$+6\pi^2\hbar^2\frac{\dot{L}^2}{L}\left(\frac{N}{L}\right)^2\left[1+\frac{1}{3\pi^2}\left(\frac{mkT}{\hbar^2}\right)^2\left(\frac{N}{L}\right)^{-4}+\cdots\right]. \tag{44}$$

Equation (44) can be rewritten as

$$\bar{F}L^3 - \frac{\pi^2\hbar^2}{3m}N^3\left[1+\frac{\pi^2}{4}\left(\frac{kT}{\mu}\right)^2+\cdots\right]$$
$$= 6\pi^2\hbar^2\dot{L}^2N^2\left[1+\frac{\pi^2}{12}\left(\frac{kT}{\mu}\right)^2+\cdots\right]. \tag{45}$$

Noting $\frac{kT}{\mu}$ = const in the unperturbed adiabatic state, Eq. (45) is merely a generalization of Poisson's adiabatic equation (PAE) in one dimension in the case in which a piston has a small but nonzero velocity. The right-hand side is quadratic in both the velocity of a piston and the particle number, giving a nonadiabatic correction to the equilibrium equation of states.

The internal energy for the expanding 1D cavity is calculated in a similar way: Noting

$$\bar{U}_1 = \frac{\sqrt{2m}L}{3\pi\hbar}\mu^{3/2}\left(1+\frac{\pi^2}{8}(kT)^2\mu^{-2}+\cdots\right) \tag{46}$$

and

$$\bar{U}_3 = 2m\dot{L}^2\mu, \tag{47}$$

we have

$$\bar{U} = \bar{U}_1+\bar{U}_3$$
$$= \frac{\sqrt{2m}L}{3\pi\hbar}\mu^{3/2}\left(1+\frac{\pi^2}{8}(kT)^2\mu^{-2}+\cdots\right)+2m\dot{L}^2\mu. \tag{48}$$

Using the expansion for μ in Eq. (A4), we have

$$\bar{U} = \frac{\pi^2\hbar^2}{6m}\left(\frac{N}{L}\right)^2N\left[1+\frac{1}{\pi^2}\left(\frac{mkT}{\hbar^2}\right)^2\left(\frac{N}{L}\right)^{-4}+\cdots\right]$$
$$+\pi^2\hbar^2\dot{L}^2\left(\frac{N}{L}\right)^2\left[1+\frac{1}{3\pi^2}\left(\frac{mkT}{\hbar^2}\right)^2\left(\frac{N}{L}\right)^{-4}+\cdots\right]. \tag{49}$$

The first term corresponds to the 1D version of the existing result (Landau-Lifshitz [2]), and the second one is a nonequilibrium correction. Combining Eqs. (44) and (49), we have

$$\bar{F}L - 2\bar{U} = 4\pi^2\hbar^2\dot{L}^2\left(\frac{N}{L}\right)^2$$
$$\times\left[1+\frac{1}{3\pi^2}\left(\frac{mkT}{\hbar^2}\right)^2\left(\frac{N}{L}\right)^{-4}+\cdots\right], \tag{50}$$

which generalize Bernoulli's formula in one dimension. The right-hand side gives a nonadiabatic contribution. This equation stands for the nonequilibrium equation of states for a quantal gas confined in the expanding cavity with the finite velocity ($\dot{L}$) of a piston.

B. High-temperature and low-density region

In this subsection, we shall investigate the opposite limit, i.e., the high-temperature and low-density quasiclassical regime. Here we shall have recourse to a high-temperature expansion of a Fermi-Dirac distribution expansion with a negative value μ,

$$f(E) \equiv \frac{1}{e^{\beta(E-\mu)}+1} = \sum_{n=1}^{\infty}(-1)^{n-1}e^{-n\beta(E-\mu)}. \tag{51}$$

Substituting Eq. (51) into the middle terms in each of Eqs. (40)–(42), one can evaluate the force:

$$\bar{F}_1 = \frac{2\sqrt{m}}{\sqrt{2}\pi\hbar}\sum_{n=1}^{\infty}(-1)^{n-1}\int_0^\infty E^{1/2}e^{-n\beta(E-\mu)}dE$$
$$= \left(\sqrt{\frac{m}{2\pi\hbar^2}}\right)(kT)^{3/2}e^{\beta\mu}\left(1-\frac{e^{\beta\mu}}{2\sqrt{2}}+O(e^{2\beta\mu})\right), \tag{52}$$

$$\bar{F}_2+\bar{F}_3 = -12m\frac{\dot{L}^2}{L}\sum_{n=1}^{\infty}(-1)^n n\beta\int_0^\infty dE\, Ee^{-n\beta(E-\mu)}$$
$$= 12m\frac{\dot{L}^2}{L}kTe^{\beta\mu}\left(1-\frac{1}{2}e^{\beta\mu}+O(e^{2\beta\mu})\right). \tag{53}$$

Therefore,

$$\bar{F} = \bar{F}_1+\bar{F}_2+\bar{F}_3$$
$$= \left(\sqrt{\frac{m}{2\pi\hbar^2}}\right)(kT)^{3/2}e^{\beta\mu}\left(1-\frac{e^{\beta\mu}}{2\sqrt{2}}+O(e^{2\beta\mu})\right)$$
$$+12m\frac{\dot{L}^2}{L}kTe^{\beta\mu}\left(1-\frac{1}{2}e^{\beta\mu}+O(e^{2\beta\mu})\right). \tag{54}$$

Equation (54) can be rewritten as

$$\frac{\bar{F}}{(kT)^{3/2}} - \left(\sqrt{\frac{m}{2\pi\hbar^2}}\right)e^{\beta\mu}(1-\cdots) = 12m\frac{\dot{L}^2}{L}(kT)^{-1/2}e^{\beta\mu}(1-\cdots). \quad (55)$$

Since $\beta\mu = \text{const}$ in the unperturbed adiabatic state (see Landau-Lifshitz [2]), Eq. (55) is a generalization of the Poisson equation in one dimension expressed in terms of pressure and temperature.

Using in Eq. (54) a high-temperature and low-density expansion of $e^{\beta\mu}$ in Eq. (B3), we have

$$\bar{F} = \frac{N}{L}kT\left[1 - \frac{3\sqrt{\pi}}{2}\frac{\frac{N}{L}\hbar}{\sqrt{mkT}} + O\left(\frac{\left(\frac{N}{L}\hbar\right)^2}{mkT}\right)\right] + 12\sqrt{2\pi}\hbar\frac{\dot{L}^2}{L}\frac{N}{L}\sqrt{mkT}\left[1 - \left(1+\frac{1}{\sqrt{2}}\right)\sqrt{\pi}\frac{\frac{N}{L}\hbar}{\sqrt{mkT}}\right]. \quad (56)$$

Similarly, the internal energy is now given by

$$\bar{U} = \bar{U}_1 + \bar{U}_3 = \frac{N}{2}kT\left[1 - \frac{3\sqrt{\pi}}{2}\frac{\frac{N}{L}\hbar}{\sqrt{mkT}} + O\left(\frac{\left(\frac{N}{L}\hbar\right)^2}{mkT}\right)\right] + 2\sqrt{2\pi}\hbar\dot{L}^2\frac{N}{L}\sqrt{mkT}\left[1 - \left(1+\frac{1}{\sqrt{2}}\right)\sqrt{\pi}\frac{\frac{N}{L}\hbar}{\sqrt{mkT}}\right]. \quad (57)$$

Therefore, a generalized Bernoulli's formula in the quasi-classical region is given by

$$\bar{F}L - 2\bar{U} = 8\sqrt{2\pi}\hbar\dot{L}^2\frac{N}{L}\sqrt{mkT} \times \left[1 - \left(1+\frac{1}{\sqrt{2}}\right)\sqrt{\pi}\frac{\frac{N}{L}\hbar}{\sqrt{mkT}}\right]. \quad (58)$$

The right-hand side is a nonequilibrium contribution due to the finite velocity of a piston. We find that a deviation from Bernoulli's formula appears only when the quantum effect will be incorporated. In fact, in the limit $\hbar \to 0$, we see $\bar{U} = \frac{N}{2}kT$ and Eq. (58) becomes the 1D version of Boyle-Charles' law, $\bar{F}L = NkT$, which includes no contribution due to the kinematics of the piston.

V. CASE OF A 3D RECTANGULAR PARALLELEPIPED CAVITY SHOWING A UNIDIRECTIONAL EXPANSION

The realistic heat engine is composed of a 3D cavity with a piston moving in a fixed (x) direction. The force $\bar{F}$ in the previous sections is taken as x component of the force vector for the case of 1D motion of the piston in the 3D rectangular parallelepiped cavity with size $L_x \times L_y \times L_z$ under the fixed perpendicular (or transverse) modes (n_y,n_z).

We shall denote $\bar{F}_x$ as the x component of the force vector averaged over both longitudinal and perpendicular modes. Noting Eq. (14), the expectation of pressure on the wall of a piston is given by

$$\bar{P} = \frac{\bar{F}_x}{L_yL_z}, \quad (59)$$

where L_yL_z is an area of the wall.

$\bar{F}_x$ can be evaluated in a similar way as $\bar{F}$, but Fermi-Dirac distribution should include a contribution of the energy due to the perpendicular modes. Namely, the eigenenergy of a particle is now

$$E(n_x,n_y,n_z) = E_\parallel(n_x) + E_\perp(n_y,n_z) \quad (60)$$

with

$$E_\parallel(n_x) = \frac{\hbar^2}{2m}\left(\frac{n_x\pi}{L_x}\right)^2, \quad (61)$$

$$E_\perp(n_y,n_z) = \frac{\hbar^2}{2m}\left[\left(\frac{n_y\pi}{L_y}\right)^2 + \left(\frac{n_z\pi}{L_z}\right)^2\right], \quad (62)$$

and the Fermi-Dirac distribution is given by

$$f(E) = \frac{1}{e^{\beta[(E_\parallel+E_\perp)-\mu]}+1}. \quad (63)$$

The statistical average is the one over the longitudinal mode (n_x), followed by another one over the perpendicular modes (n_y,n_z). The expectation value $\bar{F}_x$ is given by

$$\bar{F}_x = \bar{F}_{x1} + \bar{F}_{x2} + \bar{F}_{x3}. \quad (64)$$

In the low-temperature and high-density regime, we have the following results:

$$\bar{F}_{x1} = \frac{2}{L_x}\int_0^\infty dE\int_0^E dE_\parallel E_\parallel D_1(E_\parallel)D_2(E-E_\parallel)f(E) = \frac{8\sqrt{2}}{15\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2}L_yL_z\mu^{5/2}\left(1+\frac{5\pi^2}{8}(kT)^2\mu^{-2}\right) \quad (65)$$

and

$$\bar{F}_{x2} = -8\pi^2\hbar^2\frac{\dot{L}_x^2}{L_x^3}\int_0^\infty dE\int_0^E dE_\parallel \times \int_0^E dE'_\parallel E_\parallel E'_\parallel \frac{df}{dE}\bigg|_{E=E'_\parallel+E_\perp} \times D_1(E_\parallel)D_1(E'_\parallel)D_2(E-E_\parallel)\delta(E'_\parallel-E_\parallel) = \frac{4\hbar^2}{\pi}\left(\frac{m}{\hbar^2}\right)^2\frac{\dot{L}_x^2}{L_x}L_yL_z\mu^2\left(1+\frac{\pi^2}{3}(kT)^2\mu^{-2}\right), \quad (66)$$

where we employed the 2D density of states,

$$D_2(E) = \frac{2L_yL_z}{\pi}\frac{m}{\hbar^2}, \quad (67)$$

together with $D_1(E)$ in Eq. (31). $\bar{F}_{x3}$ can be obtained in a similar way, but $8\pi^2\hbar^2\int_0^E dE'_\parallel$ in the integral of $\bar{F}_{x2}$ is to be replaced by $32\pi^2\hbar^2\int_0^{E_\parallel} dE'_\parallel$, which eventually leads to $\bar{F}_{x3} = 2\bar{F}_{x2}$.

Then the pressure on the wall is

$$\bar{P} = \frac{\bar{F}_{x1} + \bar{F}_{x2} + \bar{F}_{x3}}{L_y L_z} = \frac{8\sqrt{2}}{15\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2}\mu^{5/2}\left(1 + \frac{5\pi^2}{8}(kT)^2\mu^{-2}\right) + \frac{12\hbar^2}{\pi}\left(\frac{m}{\hbar^2}\right)^2\frac{\dot{L}_x^2}{L_x}\mu^2\left(1 + \frac{\pi^2}{3}(kT)^2\mu^{-2}\right). \quad (68)$$

With use of the low-temperature expansion of μ in Eq. (A6), Eq. (68) can be written as

$$\bar{P}V^{5/3} - \frac{3^{2/3}\pi^{4/3}}{5\times 2^{2/3}}\frac{\hbar^2}{m}N^{5/3}\left[1 + \frac{5\pi^2}{12}\left(\frac{kT}{\mu}\right)^2\right] = \frac{3^{7/3}\pi^{5/3}\hbar^2}{2^{4/3}}N^{4/3}V^{1/3}\frac{\dot{L}_x^2}{L_x}\left[1 + \frac{\pi^2}{6}\left(\frac{kT}{\mu}\right)^2\right]. \quad (69)$$

This is a 3D version of Poisson's adiabatic equation which now incorporates the nonadiabatic contribution. As in the case of the 1D cavity, the nonadiabatic contribution is proportional to the square of the wall velocity and to inverse of the longitudinal size of the cavity, but the coefficient shows a different dependence on particle number.

The internal energy for the 3D rectangular cavity with a moving piston is straightforward:

$$\bar{U}^{3\mathrm{D}} = \bar{U}_1^{3\mathrm{D}} + \bar{U}_3^{3\mathrm{D}} \quad (70)$$

with

$$\bar{U}_1^{3\mathrm{D}} = \int_0^\infty dE \int_0^E dE_\parallel E D_1(E_\parallel)D_2(E - E_\parallel)f(E), \quad (71)$$

$$\bar{U}_3^{3\mathrm{D}} = -8\pi^2\hbar^2\left(\frac{\dot{L}_x}{L_x}\right)^2\int_0^\infty dE \times \int_0^E dE_\parallel \int_0^{E_\parallel} dE'_\parallel E_\parallel E'_\parallel \frac{df}{dE}\bigg|_{E=E'_\parallel+E_\perp} \times D_1(E_\parallel)D_1(E'_\parallel)D_2(E - E_\parallel)\delta(E'_\parallel - E_\parallel). \quad (72)$$

It should be noted that, in the calculation of $\bar{U}_1^{3\mathrm{D}}$, the bulk energy $E\,(=E_\parallel + E_\perp)$ is averaged, which is a 3D generalization of the 1D energy. The final result for the internal energy is

$$\bar{U}^{3\mathrm{D}} = \frac{4\sqrt{2}}{5\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2}L_xL_yL_z\mu^{5/2}\left(1 + \frac{5\pi^2}{8}(kT)^2\mu^{-2}\right) + \frac{2\hbar^2}{\pi}\left(\frac{m}{\hbar^2}\right)^2\frac{\dot{L}_x^2}{L_x}L_xL_yL_z\mu^2\left(1 + \frac{\pi^2}{3}(kT)^2\mu^{-2}\right). \quad (73)$$

[With use of the expansion for μ in Eq. (A6), the first term on the right-hand side of Eq. (73) proves to agree with the result by Landau-Lifshitz reproduced in the Introduction. The minor discrepancy of a numerical prefactor of $O(1)$ is due to our choice of anisotropic density of states in Eq. (71) for the 3D rectangular parallelepiped cavity.]

Bernoulli's formula in the present case becomes:

$$\bar{P}V - \frac{2}{3}\bar{U}^{3\mathrm{D}} = \frac{32\hbar^2}{3\pi}\left(\frac{m}{\hbar^2}\right)^2\frac{\dot{L}_x^2}{L_x}V\mu^2\left(1 + \frac{\pi^2}{3}(kT)^2\mu^{-2}\right) \quad (74)$$

with $V = L_xL_yL_z$. With use of the low-temperature expansion of μ in Eq. (A6), Eq. (74) can be rewritten as

$$\bar{P}V - \frac{2}{3}\bar{U}^{3\mathrm{D}} = c_0\hbar^2\left(\frac{N}{V}\right)^{4/3}\frac{\dot{L}_x^2}{L_x}V\left[1 + c_1\left(\frac{V}{N}\right)^{4/3}\left(\frac{mkT}{\hbar^2}\right)^2\right] \quad (75)$$

with $c_0 = \frac{2(3\sqrt{2})^{4/3}\pi^{5/3}}{3}$ and $c_1 = \frac{4}{3(3\sqrt{2})^{4/3}\pi^{2/3}}$. The right-hand side is a nonadiabatic contribution to the equilibrium equation of states in three dimensions due to a moving piston. In the quantum adiabatic limit, $\dot{L}_x = 0$, the above equation reduces to the standard Bernoulli's formula for the 3D quantum gas.

We shall proceed to the high-temperature and low-density regime. The values of $\bar{F}_{x1}$, $\bar{F}_{x2}$, $\bar{F}_{x3}$, $\bar{U}_1^{3\mathrm{D}}$, and $\bar{U}_3^{3\mathrm{D}}$ for the 3D cavity are evaluated by substituting into the second expressions in each of Eqs. (65), (66), (71), and (72) the expansion of Fermi-Dirac distribution in Eq. (51). The results are

$$\bar{F}_{x1} = \sqrt{2}\pi^{-3/2}\left(\frac{m}{\hbar^2}\right)^{3/2}(kT)^{5/2}L_yL_ze^{\beta\mu}(1 - 2^{-5/2}e^{\beta\mu}), \quad (76)$$

$$\bar{F}_{x2} + \bar{F}_{x3} = \frac{24\hbar^2}{\pi}\frac{\dot{L}_x^2}{L_x}\left(\frac{m}{\hbar^2}\right)^2(kT)^2L_yL_ze^{\beta\mu}\left(1 - \frac{1}{4}e^{\beta\mu}\right). \quad (77)$$

Then the pressure defined by

$$\bar{P} = \frac{\bar{F}_{x1} + \bar{F}_{x2} + \bar{F}_{x3}}{L_yL_z} \quad (78)$$

satisfies

$$\frac{\bar{P}}{T^{5/2}} - \sqrt{2}\pi^{-3/2}\left(\frac{m}{\hbar^2}\right)^{3/2}e^{\beta\mu}(1 - 2^{-5/2}e^{\beta\mu}) = \frac{24\hbar^2}{\pi}\frac{\dot{L}_x^2}{L_x}\left(\frac{m}{\hbar^2}\right)^2\frac{1}{\sqrt{kT}}e^{\beta\mu}\left(1 - \frac{1}{4}e^{\beta\mu}\right). \quad (79)$$

Similarly, we see

$$\bar{U}_1^{3\mathrm{D}} = \frac{3\sqrt{2}}{2}\pi^{-3/2}\left(\frac{m}{\hbar^2}\right)^{3/2}(kT)^{5/2}Ve^{\beta\mu}(1 - 2^{-5/2}e^{\beta\mu}), \quad (80)$$

$$\bar{U}_3^{3\mathrm{D}} = \frac{4\hbar^2}{\pi}\frac{\dot{L}_x^2}{L_x}\left(\frac{m}{\hbar^2}\right)^2(kT)^2Ve^{\beta\mu}\left(1 - \frac{1}{4}e^{\beta\mu}\right) \quad (81)$$

leading to the internal energy, $\bar{U}^{3\mathrm{D}} = \bar{U}_1^{3\mathrm{D}} + \bar{U}_3^{3\mathrm{D}}$. Bernoulli's formula is now given by

$$\bar{P}V - \frac{2}{3}\bar{U}^{3\mathrm{D}} = \frac{64\hbar^2}{3\pi}\frac{\dot{L}_x^2}{L_x}\left(\frac{mkT}{\hbar^2}\right)^2Ve^{\beta\mu}\left(1 - \frac{1}{4}e^{\beta\mu}\right). \quad (82)$$

TABLE I. Nonadiabatic contributions to the equation of states in the thermally isolated process in three dimensions.

Equation of states	Low-temperature quantal region	High-temperature quasiclassical region
Poisson's adiabatic equations	$\bar{P}V^{5/3} - \frac{3^{2/3}\pi^{4/3}}{5\times 2^{2/3}}\frac{\hbar^2}{m}N^{5/3}[1+\frac{5\pi^2}{12}(\frac{kT}{\mu})^2+\cdots]$	$\frac{\bar{P}}{T^{5/2}} - \sqrt{2}\pi^{-3/2}(\frac{m}{\hbar^2})^{3/2}e^{\beta\mu}(1-2^{-5/2}e^{\beta\mu})$
	$= \frac{3^{7/3}\pi^{5/3}\hbar^2}{2^{4/3}}N^{4/3}V^{1/3}\frac{\dot{L}_x^2}{L_x}[1+\frac{\pi^2}{6}(\frac{kT}{\mu})^2+\cdots]$	$= \frac{24\hbar^2}{\pi}\frac{\dot{L}_x^2}{L_x}(\frac{m}{\hbar^2})^2\frac{1}{\sqrt{kT}}e^{\beta\mu}(1-\frac{1}{4}e^{\beta\mu}+\cdots)$
Bernoulli's formula	$\bar{P}V - \frac{2}{3}\bar{U}^{3\mathrm{D}}$	$\bar{P}V - \frac{2}{3}\bar{U}^{3\mathrm{D}}$
	$= 2^{5/3}3^{1/3}\pi^{5/3}\hbar^2(\frac{N}{V})^{4/3}\frac{\dot{L}_x^2}{L_x}V$	$= \frac{32\sqrt{2\pi}\hbar^2}{3\pi}\frac{\dot{L}_x^2}{L_x}(\frac{mkT}{\hbar^2})^{1/2}N$
	$\times[1+\frac{2^{4/3}}{3^{7/3}\pi^{2/3}}(\frac{V}{N})^{4/3}(\frac{mkT}{\hbar^2})^2+\cdots]$	$\times[1+\frac{\sqrt{2}-1}{4\sqrt{2}}\pi^{3/2}\frac{N}{V}(\frac{\hbar^2}{mkT})^{3/2}+\cdots]$

Noting the high-temperature and low-density expansion of $e^{\beta\mu}$ in Eq. (B5), we see

$$\bar{P}V - \frac{2}{3}\bar{U}^{3\mathrm{D}} = \frac{32\sqrt{2\pi}\hbar^2}{3\pi}\frac{\dot{L}_x^2}{L_x}\left(\frac{mkT}{\hbar^2}\right)^{1/2}N \times\left[1+\frac{\sqrt{2}-1}{4\sqrt{2}}\pi^{3/2}\frac{N}{V}\left(\frac{\hbar^2}{mkT}\right)^{3/2}\right]. \quad (83)$$

We can confirm that the nonadiabatic contribution (NC) appears as a quantum effect and plays a role with decreasing the system's size (L_x). In other words, NC vanishes in the classical limit ($\hbar \to 0$), which is consistent with the kinetic theory of Boltzmann gas which incorporates the effect of moving piston. The essential results obtained in this section are summarized in Table I.

VI. PHYSICAL IMPLICATIONS OF QUANTUM NONADIABATIC CONTRIBUTIONS

So far we have obtained the completely analytical nonadiabatic contribution to the nonequilibrium equation of states in the cases of 3D rectangular parallelepiped cavity and its 1D version separately. To physically interpret the obtained results, however, it is more convenient to see the nonequilibrium equations of states for the general d-dimensional hyper-rectangular cavity which has the volume $V = L^{d-1}L_x$ and the moving wall (surface) with area $S = L^{d-1}$. Such general derivation is also possible by using the *density of states in d dimensions*. After tedious and lengthy calculation (to be published elsewhere), Bernoulli's formulas for the d-dimensional cavity are given by

$$\bar{P}V - \frac{2}{d}U \sim \hbar^2 V\left(\frac{N}{V}\right)^{1+\frac{1}{d}}\frac{\dot{L}_x^2}{L_x} \quad (84)$$

and

$$\bar{P}V - \frac{2}{d}U \sim \hbar(mkT)^{\frac{1}{2}}\left(\frac{N}{V}\right)V\frac{\dot{L}_x^2}{L_x}, \quad (85)$$

respectively, for the low-temperature high-density and high-temperature low-density regions. In a similar way, the corresponding Poisson's adiabatic equations are

$$\frac{\bar{P}V^{\frac{d+2}{d}}}{\mathrm{const}} - 1 \sim m\left(\frac{N}{V}\right)^{-\frac{1}{d}}\frac{\dot{L}_x^2}{L_x} \quad (86)$$

and

$$\frac{\bar{P}/(kT)^{\frac{d+2}{2}}}{\mathrm{const}} - 1 \sim \hbar\left(\frac{m}{kT}\right)^{\frac{1}{2}}\frac{\dot{L}_x^2}{L_x}, \quad (87)$$

respectively, for the low-temperature high-density and high-temperature low-density regions. The apparently extra dimensionality of energy ([ML^2 T^{-2}]) on the right-hand sides in all of the four equations above is traced back to our simplified replacement in Eq. (29) and therefore can be suppressed. Equations (84)–(87) recover all the results for $d = 1$ and 3 cavities in the previous sections. We find the following important features:

(i) Quantum nonadiabatic (QNA) contributions are quadratic in the wall velocity and therefore time-reversal symmetric, in marked contrast to the conventional belief [12] that the nonadiabatic force is linear in the wall velocity and breaks the time-reversal symmetry.

(ii) QNA contributions are positive, which means that the moving wall gives rise to the apparently repulsive interaction among noninteracting Fermi particles, irrespective of the direction of the wall motion, namely for both expansion and contraction of the cavity.

(iii) QNA contributions are inversely proportional to the longitudinal size of the cavity and become more and more important when the cavity size is decreased. In particular, they will play a nontrivial role in nanoscale heat engines based on quantum dots.

(iv) QNA contributions play an essential role in Bernoulli's formula rather than in Poisson's equation. In fact, the coefficients prior to $\frac{\dot{L}_x^2}{L_x}$ are increased in Eq. (84) and decreased in Eq. (86) as particle density $\frac{N}{V}$ is increased. Similarly, the coefficients are increased in Eq. (85) and decreased in Eq. (87) as temperature is increased.

The above four issues constitute the most important finding of the present paper. Poisson's adiabatic equation and Bernoulli's formula, both of which are the basic laws of thermodynamics, are now generalized so as to include the QNA contributions.

VII. SUMMARY AND DISCUSSIONS

Confining ourselves to the thermally isolated process, we study a nonequilibrium equation of states of an ideal quantum gas confined to the cavity under a moving piston with a small but finite velocity. The cavity wall is assumed to begin to move suddenly at the time origin. The quantum nonadiabatic (QNA) contribution to Bernoulli's formula which bridges the pressure and internal energy is elucidated. The statistical means of the nonadiabatic (time-reversal symmetric) force and pressure operator [10] are carried out in both the low-temperature quantum-mechanical and high-temperature quasiclassical regimes. QNA contributions are quadratic in the piston's velocity and therefore time-reversal symmetric, in marked contrast to conventional belief [12], and they are positive, which means that the moving piston gives rise to the apparently repulsive interaction among noninteracting Fermi particles, for both expansion and contraction of the cavity. QNA contributions are inversely proportional to the longitudinal size of the cavity, and thereby play a nontrivial role in nanoscale heat engines based on quantum dots. The investigation is done for an expanding 3D rectangular parallelepiped cavity as well as its 1D version. The nonequilibrium contributions to Poisson's adiabatic equation are also elucidated.

In the context of a classical gas, Curzon and Ahlborn [13] and others [14–16] investigated a *finite-time* Carnot heat engine and obtained an interesting efficiency. However, they did not consider a quantum gas, nor did they show a nonequilibrium equation of states due to a moving piston. Therefore, one of the directions to extend our work may be to proceed to the same analyses as given here of the isothermal process which requires a contact of a nanoscale engine with a heat reservoir. Another direction may be the fast-forwarding of the adiabatic expansion of a cavity [17,18] in the framework of the von Neumann equation to see an accelerated quantum Carnot heat engine. These subjects will be investigated in due course.

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APPENDIX A: THERMODYNAMIC AVERAGES IN THE LOW-TEMPERATURE REGION AT $T \ll T_0$ (DEGENERATE TEMPERATURE)

With use of the Fermi-Dirac distribution $f(E) = \frac{1}{e^{\beta(E-\mu)}+1}$, we summarize several formulas for thermodynamic averages (see Landau-Lifshitz [2]) in the cases of 1D and 3D rectangular cavities.

In the low-temperature region at $T \ll T_0$ (degenerate temperature), we see

$$\int_{E_0}^{\infty} g(E)f(E)dE = \int_{E_0}^{\mu} g(E)dE + \frac{\pi^2(kT)^2}{6}g'(\mu) + O[(kT)^4], \quad \text{(A1)}$$

$$-\int_{E_0}^{\infty} \varphi(E)\frac{df}{dE}dE = \varphi(\mu) + \frac{\pi^2(kT)^2}{6}\varphi''(\mu) + O[(kT)^4], \quad \text{(A2)}$$

where $g(E_0) = \varphi(E_0) = 0$ is assumed.

Choosing the 1D density of states $D_1(E)$ as $g(E)$, we have

$$N = \int_0^{\infty} D_1(E)f(E)dE = \frac{\sqrt{2m}L}{\pi\hbar}\mu^{1/2}\left(1 - \frac{\pi^2}{24}(kT)^2\mu^{-2} + \cdots\right), \quad \text{(A3)}$$

from which the chemical potential is obtained as

$$\mu = \frac{\pi^2\hbar^2}{2m}\left(\frac{N}{L}\right)^2\left[1 + \frac{1}{3\pi^2}\left(\frac{mkT}{\hbar^2}\right)^2\left(\frac{N}{L}\right)^{-4} + \cdots\right]. \quad \text{(A4)}$$

This expansion is justified in the low-temperature and high-density regime.

In the case of the 3D rectangular cavity,

$$N = \int_0^{\infty}\int_0^{E} dE_{\parallel} D_1(E_{\parallel})D_2(E - E_{\parallel})f(E) = \frac{8}{3\sqrt{2}\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2} V\mu^{3/2}\left(1 + \frac{\pi^2(kT)^2}{8}\mu^{-2}\right), \quad \text{(A5)}$$

which leads to the low-temperature expansion of μ as

$$\mu = \frac{(3\sqrt{2})^{2/3}}{4}\pi^{4/3}\frac{\hbar^2}{m}\left(\frac{N}{V}\right)^{2/3} \times \left[1 - \frac{4}{3}(3\sqrt{2})^{-4/3}\pi^{-2/3}\left(\frac{mkT}{\hbar^2}\right)^2\left(\frac{V}{N}\right)^{4/3} + \cdots\right]. \quad \text{(A6)}$$

APPENDIX B: THERMODYNAMIC AVERAGES AT THE HIGH-TEMPERATURE REGION AT $T \gg T_0$

In the case of a high-temperature region at $T \gg T_0$, we shall use a high-temperature expansion of the Fermi-Dirac distribution with a negative value μ as given in Eq. (51). Then we see

$$\int_{E_0}^{\infty} g(E)f(E)dE = \sum_{n=1}^{\infty}(-1)^{n-1}\int_{E_0}^{\infty} g(E)e^{-n\beta(E-\mu)}dE. \quad \text{(B1)}$$

Choosing the 1D density of states $D_1(E)$ as $g(E)$, we have

$$N = \frac{L}{\sqrt{2\pi}}\sqrt{\frac{mkT}{\hbar^2}}e^{\beta\mu}\left(1 - \frac{1}{\sqrt{2}}e^{\beta\mu}\right), \quad \text{(B2)}$$

from which μ is determined by

$$e^{\beta\mu} = \sqrt{2\pi}\frac{N}{L}\frac{\hbar}{\sqrt{mkT}}\left(1 - \sqrt{\pi}\frac{\frac{N}{L}\hbar}{\sqrt{mkT}} + \cdots\right). \quad \text{(B3)}$$

This expansion is justified in the high-temperature and low-density regime.

In the case of a 3D cavity, the particle number is

$$N = \frac{2\sqrt{2}}{\pi^2}\left(\frac{m}{\hbar^2}\right)^{3/2} V \sum_{n=1}^{\infty}(-1)^{n-1}e^{n\beta\mu}\int_0^\infty dE\, E^{1/2}e^{-n\beta E}$$
$$= \sqrt{2}\pi^{-3/2}\left(\frac{mkT}{\hbar^2}\right)^{3/2} V e^{\beta\mu}(1-2^{-3/2}e^{\beta\mu}), \tag{B4}$$

and the chemical potential is expanded as

$$e^{\beta\mu} = \frac{\pi^{3/2}}{\sqrt{2}}\frac{N}{V}\left(\frac{\hbar^2}{mkT}\right)^{3/2} \times \left[1 + \frac{\pi^{3/2}}{4}\frac{N}{V}\left(\frac{\hbar^2}{mkT}\right)^{\frac{3}{2}} + \cdots\right]. \tag{B5}$$

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