Theory of Applying Heat Flow from Thermostatted Boundary Walls: Dissipative and Local-Equilibrium Responses and Fluctuation Theorems

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We construct a microscopic theory of applying a heat flow from thermostatted boundary walls in the film geometry. We treat a classical one-component fluid, but our method is applicable to any fluids and solids. We express linear response of any variable $B$ in terms of the time-correlation functions between $B$ and the heat flows $J_K$ from the thermostats to the particles. Furthermore, the surface variables $J_K$ can be written in the form of space integrals of bulk quantities from the equations of motion. Owing to this surface-to-bulk relation, the steady-state response functions consist of dissipative and local-equilibrium parts, where the former gives rise to Fourier’s law with Green’s expression for the thermal conductivity. In the nonlinear regime, we derive the steady-state distribution in the phase space in the McLennan-Zubarev form from the first principles. Some fluctuation theorems are also presented.

I. INTRODUCTION

In the linear response theory in statistical mechanics, response of any physical quantity to a small perturbation is expressed in terms of appropriate time-correlation functions. For thermal disturbances, Green expressed the transport coefficients such as the viscosities and the thermal conductivity in terms of the time-correlation functions of the stress and the heat flux, respectively. These expressions also followed from the relaxations of the time-correlation functions of the hydrodynamic variables. These gross variables obey the fluctuating hydrodynamic equations with random stress and heat current slightly away from equilibrium, where the latter satisfy the fluctuation-dissipation relations. Some attempts were also made to develop nonlinear theories of thermal disturbances. On the other hand, for externally applied fields (such as magnetic field), Kubo developed a linear response theory, where the Hamiltonian consists of the unperturbed one $H$ and a small time-dependent perturbation as $H' = H - \gamma_{ex}(t)A$. Here, $\gamma_{ex}(t)$ is an applied field and $A$ is its conjugate variable.

Thermal disturbances are usually induced from boundaries, while the early theories started with nearly homogeneous velocity and temperature gradients in the cell interior and are not directly applicable to heterogeneous systems. Hence, we should develop a theory treating perturbations applied at boundaries. With this objective, we recently applied shear strains to particle systems by slightly moving boundary walls. We set up a Hamiltonian in Kubo’s form, where the applied field $\gamma_{ex}(t)$ is the mean shear strain in a film and the conjugate variable $A$ is expressed in terms of the tangential forces from the bottom and top walls to the particles. Then, linear response of any variable $B$ is expressed in terms of the time-correlation function of $B$ and $A$. As a key relation, we further set $A = \int dr [\Pi_{xz} - z \partial J_z / \partial t]$, where $\Pi_{xz}$ is the shear stress (xz component), and $J_z$ is the momentum density (z component) in the bulk. This surface-to-bulk relation reveals how the surface forces induce bulk response, leading to Green’s expression for the shear viscosity $\eta$. It is worth noting that Petrovich and Harrowell expressed $\eta$ in terms of the surface-force time-correlation.

The thermal conductivity $\lambda$ (as well as $\eta$) can be calculated from the Green-Kubo formula via equilibrium molecular dynamics simulation. However, to study nonequilibrium steady states, we need at least two thermostats at different temperatures. There have been a number of such nonequilibrium simulations. In particular, a heat flow was applied across solid-liquid interfaces, in near-critical fluids, and in one-dimensional lattice gases. We also mention the theories on fluctuation theorems. In their application to heat-conducting steady states, relevant are the heat flows $J_K$ from the thermostats to the particles, where $K$ represents the top or bottom thermostat in the film geometry. Then, in the linear regime, $\lambda$ can be expressed in terms of the surface variables $J_K$. However, Green’s expression for $\lambda$ is written in terms of the heat flux in the bulk, so it has not been derived from the fluctuation theorems. On the other hand, the Green-Kubo formula readily follows from the fluctuation theorems for a perturbation applied in the bulk region.

In this paper, we use Nosé-Hoover thermostats in top and bottom boundary layers in contact with a classical fluid. We induce heat conduction by changing the boundary temperatures by $\delta T_K(t)$ for $t > 0$. In the linear regime, we obtain response relations of any variable $B$ in terms of the time-correlation functions $\langle B(t) J_K(0) \rangle$, in equilibrium. As in the case of boundary-driven strains, we further express $J_K$ as a sum of bulk terms, where one term yields local-equilibrium response and another one dissipative response. Remarkably, the latter is proportional to the heat flux integral $\int dr J^K_z(r, t)$, giving rise to Green’s expression for $\lambda$. We then calculate the relaxations of the hydrodynamic variables after a boundary...
temperature change, where we account for the adiabatic (piston) effect at a fixed cell volume. These average deviations are related to \( \langle B(t)J_K(0) \rangle \). We also calculate the Evans-Searles dissipation function analytically in transient states in the linear regime, which is related to the entropy production and the logarithm of the distribution function of the hydrodynamic variables.

In this paper, we also study nonlinear dynamics in the phase space on the basis of the research on fluctuation theorems, where the boundary temperature changes \( \delta T \) need not be small. It enables us to understand the local-equilibrium response. In the latter finding, we obtain the steady-state distribution in the classical form of McLennan and Zubarev from the first principles. Here, using the surface-to-bulk relationship, we can introduce the local-equilibrium distribution with a space-dependent temperature, from which relaxation to a steady state occurs in a microscopic time.

The organization of this paper is as follows. In Sec. II, we will present the theoretical background of our thermostatted system. In Sec. III, the linear response will be discussed using the Liouville equation. In Sec. IV, a nonlinear theory will be presented. We will also calculate the relaxation behaviors of the hydrodynamic variables in Appendix A and the dissipation function in Appendix B after a boundary temperature change. A theory of long-range correlations in the canonical ensemble will be presented in Appendix C, which is crucial in calculating the local-equilibrium response.

II. THEORETICAL BACKGROUND

We treat a classical one-component fluid with particle number \( N \) in a film cell. We write the particle positions as \( r_i = (x_i, y_i, z_i) \), the velocities as \( v_i = v_i = (v_i^x, v_i^y, v_i^z) \), and the momenta as \( p_i = mv_i = (p_i^x, p_i^y, p_i^z) \) with \( m \) being the particle mass. Hereafter, the upper dot denotes taking the time derivative \( \partial / \partial t \). The space dimensionality \( d \) can also be one or two. We write the cell thickness as \( H \) and the lateral dimension as \( L \) in the \( xy \) plane. The surface area of each boundary layer is \( A = L^{d-1} \) and the cell volume is \( V = HA \). We can impose the periodic boundary condition along the \( x \) and \( y \) axes. These lengths are much longer than the particle diameters. The fluid is in a liquid or supercritical one-phase state with high density \( n = N/V \).

A. Heat variable and heat inputs

We introduce thermostatted boundary layers, which are in the regions \( -\ell_w < z < 0 \) at the bottom and \( 0 < z - H < \ell_w \) at the top. To each layer, \( M \) particles are bound by spring potentials \( \psi(|r_k - R_k|) \), where \( r_k \) are the positions of the bound particles and \( R_k \) are the pinning centers fixed to the layers at a high density. We assume \( \ell_w \ll H \) and \( M \ll N \) for simplicity. In our previous papers, we used the harmonic form \( \psi(r) = s_0 r^2 /2 \), where impenetrable walls were realized for large \( s_0 \). In one-dimensional model solids, only the end particles were thermostatted (where \( M = 1 \)).

Particle pairs \( i \) and \( j \) interact via short-range potentials \( \phi_{ab}(r_{ij}) \) with \( r_{ij} = |r_i - r_j| \), where \( i \in a \) and \( j \in b \) with \( a \) and \( b \) denoting either of unbound or bound particles. We write \( \phi_{ij} = \phi_{ab}(r_{ij}) \) and \( \psi_k = \psi(|r_k - R_k|) \). The total energy of the particles is written as

\[
\mathcal{H} = \sum_i \frac{1}{2m_i} |p_i|^2 + \frac{1}{2} \sum_{i,j} \phi_{ij} + \sum_{k>N} \psi_k \tag{1}
\]

where we sum over all the particles. The mass of the bound particles can differ from that of the unbound ones.

We define the number density and the energy density of the unbound particles microscopically as

\[
\hat{n}(r, t) = \sum_{i \leq N} \delta(r - r_i), \tag{2}
\]

\[
\hat{e}(r, t) = \sum_{i \leq N} e_i \delta(r - r_i), \tag{3}
\]

where \( e_i = m|v_i|^2 /2 + \sum_{j \leq N} \phi_{ij}/2 \) is the energy supported by particle \( i \). Hereafter, the variables with an upper caret symbol are microscopically defined space-dependent variables. Following the literature, we introduce the heat variable \( \hat{q}(r, t) \) by

\[
\hat{q}(r, t) = \hat{e}(r, t) - \hat{n}(r, t). \tag{4}
\]

Here, \( h = (e + p)/n \) is the enthalpy per particle, where \( e \), \( p \), and \( n \) are the thermodynamic energy density, pressure, and number density, respectively. Then, the equilibrium average of \( \hat{q} \) is equal to \(-p \) and the entropy per particle \( s \) satisfies the thermodynamic differential relation \( nTds = ds - hdn \), so we can treat \( \delta \hat{q} = \hat{q} + p \) as the deviation of the fluctuating entropy variable multiplied by \( nT \). See the last paragraph of this subsection for more discussions on the flux of \( \hat{q} \).

The unbound particles \( i \leq N \) obey Newton’s equations \( m\dot{v}_i = f_i \) with \( f_i = -\partial \mathcal{H} / \partial r_i \) being the force on particle \( i \). Then, \( \hat{q} \) evolves in time as

\[
\frac{\partial}{\partial t} \hat{q} + \nabla \cdot \mathbf{J}_h = \sum_{i \leq N} \mathbf{v}_i \cdot (f_i^{\text{top}} + f_i^{\text{bot}}) \delta(r - r_i). \tag{5}
\]

where \( \mathbf{J}_h(r, t) \) is the heat flux in the cell and the right hand side represents the heat-input density from the walls. We write the forces on unbound particle \( i \leq N \) from the top and bottom bound particles \( k > N \) as

\[
f_i^{\text{top}} = -\sum_{k \in \text{top}} \nabla_i \phi_{ik}, \quad f_i^{\text{bot}} = -\sum_{k \in \text{bot}} \nabla_i \phi_{ik}. \tag{6}
\]
where $\nabla_i = \partial_i \mathbf{r}_i = (\nabla_i^x, \nabla_i^y, \nabla_i^z)$. The $\alpha$ component of $J^\alpha_k$ ($\alpha = x, y, z$) is microscopically expressed as

$$J^\alpha_k = \sum_{i \leq N} (e_i - h) r^\alpha_i \delta(\mathbf{r} - \mathbf{r}_i)$$
$$- \sum_{i,j \leq N} \frac{1}{2} \phi'_{ij} x^\alpha_{ij} (r_{ij} \cdot \mathbf{v}_j) \delta(\mathbf{r} - \mathbf{r}_i, \mathbf{r}_j),$$

(7)

where $\phi'_{ij} = d\phi_{ij}/dr_{ij}$ and $x^\alpha_{ij}$ is the $\alpha$ component of $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. We use the Irving-Kirkwood-delta function \( \delta(\mathbf{r}, \mathbf{r}_i, \mathbf{r}_j) = \int_0^1 \mathrm{d}l \delta(\mathbf{r} - \lambda \mathbf{r}_i - (1-\lambda) \mathbf{r}_j) \), which is nonvanishing on the line segment connecting $\mathbf{r}_i$ and $\mathbf{r}_j$. The microscopic expression for the pressure is then

$$\hat{p} = \sum_{i \leq N} \frac{|p_i|^2}{dm} \delta(\mathbf{r} - \mathbf{r}_i) - \sum_{i,j \leq N} \frac{r_{ij}}{2d} \phi'_{ij} \delta(\mathbf{r} - \mathbf{r}_i, \mathbf{r}_j).$$

(8)

where the equilibrium average $p(T) = \langle \hat{p} \rangle_e$ in the bulk region is the thermodynamic pressure.

It is convenient to define the total internal energy of the unbound particles as

$$\mathcal{H}_{\text{in}} = \sum_{i \leq N} e_i = \sum_{i \leq N} \frac{1}{2m} |p_i|^2 + \sum_{i \leq N,j \geq N} \phi_{ij}.$$

(9)

At fixed volume $V$ and $N$, $\mathcal{H}_{\text{in}}$ changes in time as

$$\dot{\mathcal{H}}_{\text{in}} = \frac{d}{dt} \int \mathrm{d}r \hat{q} = \dot{\mathcal{I}}_{\text{top}} + \dot{\mathcal{I}}_{\text{bot}},$$

(10)

where we use $\int \mathrm{d}r \hat{\mathbf{n}} = N$ and the space integral $\int \mathrm{d}r \cdot \cdots$ is taken in a region containing all the unbound particles. The $\mathcal{I}_K$ is the heat flow from the bound particles in the layer $K$ to the unbound particles defined as

$$\mathcal{I}_K = \sum_{i \leq N} \mathbf{v}_i \cdot \mathbf{f}_i^K.$$

(11)

Hereafter, the subscript $K$ represents top or bottom.

Using Eq. (5) we also integrate the product $z \partial \hat{\mathbf{q}} / \partial t$ as

$$\frac{d}{dt} \int \mathrm{d}r z \hat{\mathbf{q}} = \int \mathrm{d}r J^z_k = \sum_{k \leq K} \sum_{i \leq N} z_i \mathbf{v}_i \cdot \mathbf{f}_i^K$$
$$= \frac{H \mathcal{I}_{\text{top}}}{H}.$$  

(12)

In the first line, the left hand side is written in terms of the degrees of freedom of the unbound particles, while the right hand side involves the bound ones. In the second line, we retain the contribution at the top replacing $z_i$ by $\mathcal{I}$ from $|z_i - H| < \ell_w \ll H$. We thus find

$$\mathcal{I}_{\text{top}} = \int \mathrm{d}r \frac{z}{H} \frac{\partial \hat{\mathbf{q}}}{\partial t} = \frac{1}{H} \mathcal{G}, \quad \mathcal{I}_{\text{bot}} = \mathcal{H}_{\text{in}} - \mathcal{I}_{\text{top}},$$

(13)

where we define the integrated heat flux along the $z$ axis,

$$\mathcal{G}(t) = \int \mathrm{d}r J^z_k(\mathbf{r}, t).$$

(14)

In the periodic boundary condition, the surface terms are nonexistent in Eq. (12). Then, the space-time integral of the heat flux $\int_0^t \mathrm{d}s \mathcal{G}(s)$ is equal to

$$G_\lambda(t) = \sum_i z_i(t) (e_i(t) - (e_i)e).$$

(15)

This yields Helfand’s formula \( \mathcal{G} = \lim_{t \to \infty} \langle (G_\lambda(t) - G_\lambda(0))^2 \rangle_{e}/2t \mathcal{V} k_B T^2 \rangle \), which is equivalent to Green’s one in Eq. (15).\( ^{51,52} \)

Between the heat flux $J^\alpha_k$ and the momentum density $J^\alpha(\mathbf{r}) = \sum\sum\sum p_i^{\alpha} \delta(\mathbf{r} - \mathbf{r}_i)$, we can consider their equal-time correlation $G_{\alpha\beta}(\mathbf{r} - \mathbf{r}', t) = \langle J^\alpha_k(\mathbf{r}) J^\beta(\mathbf{r}') \rangle_e$. It is a short-ranged function of $\mathbf{r} - \mathbf{r}'$ and its space integral vanishes. Namely, we have $\int \mathrm{d}r G_{\alpha\beta}(\mathbf{r}) = 0$. This means that $J^\alpha_k(\mathbf{r})$ is orthogonal to the long-wavelength hydrodynamic variables, which is crucial in the projection operator formalism of irreversibility.\( ^{9,10,15} \)

B. Nosé-Hoover thermostats in boundary layers

We attach Nosé-Hoover thermostats to the bound particles at the top and the bottom separately.\( ^{3,4,2,42,43} \) Their equations of motion are deterministic and are written as

$$\dot{p}_k = f_k - \zeta_k p_k \quad (k > N),$$

(16)

where $p_k = m_k v_k$ and $f_k = - \partial \mathcal{H} / \partial \mathbf{r}_k$ with $m_k$ being the mass of bound particle $k$. The coefficients $\zeta_k(t)$ are fluctuating friction constants obeying

$$\tau_k^2 \zeta_k = 2 \beta E_K / dM - 1,$$

(17)

where $\tau_k$ is the characteristic time common to the two thermostats. In this section, we fix $\beta = 1/k_BT$. We assume that $\tau_k$ is a short time independent of $t$ (see arguments around Eqs. (34) and (48)). We write the kinetic energy of the bound particles in the layer $K$ as

$$E_K = \sum_{k \leq K} \frac{1}{2m_k} |p_k|^2.$$

(18)

From Eq. (16) $E_K$ depends on $t$ as

$$\dot{E}_K = \sum_{k \leq K} \mathbf{v}_k \cdot f_k - 2 \zeta_k E_K.$$

(19)

It is convenient to introduce the total energy of the bound particles in the layer $K$ as

$$\mathcal{H}_K = E_K + \sum_{j \leq K} \left[ \frac{1}{2} \sum_{k \leq K} \phi_{jk} + \sum_{i \leq N} \phi_{sk} + \psi_k \right].$$

(20)

The total energy of the particles in Eq. (2) is the sum,

$$\mathcal{H} = \mathcal{H}_{\text{in}} + \mathcal{H}_{\text{top}} + \mathcal{H}_{\text{bot}}.$$  

(21)

From Eqs. (11), (19), and (20) we find

$$\dot{\mathcal{H}}_K = - \mathcal{I}_K - 2 \zeta_k E_K.$$  

(22)
Therefore, the heat flow from the thermostat $K$ to the particles (consisting of the bound ones in the layer $K$ and the unbound ones) is written as

$$\mathcal{J}_K = \mathcal{H}_K + I_K = -2\zeta_K E_K. \quad (23)$$

From Eqs.(10) and (23) $\mathcal{H}$ changes in time as

$$\mathcal{H} = \mathcal{J}_{\text{top}} + \mathcal{J}_{\text{bot}}. \quad (24)$$

From Eqs.(13), (23), and (24) we now find

$$\mathcal{J}_{\text{top}} = \frac{d}{dt} \left[ \int dr \frac{z}{H} \dot{q} + \mathcal{H}_{\text{top}} \right] - \frac{1}{H} G,$$

$$\mathcal{J}_{\text{bot}} = \frac{d}{dt} \left[ \int dr (1 - \frac{z}{H}) \dot{q} + \mathcal{H}_{\text{bot}} \right] + \frac{1}{H} G, \quad (25)$$

which are our desired surface-to-bulk relations.

C. Liouville equation and equilibrium distribution

We denote all the degrees of freedom in our system by the symbol $\Gamma = (r_i, p_i, \zeta_K)$ for the $N + 2M$ particles and the two thermostats. We also introduce the sign reversal of the momenta and the friction constants,

$$\Gamma = (r_i, p_i, \zeta_K) \rightarrow \Gamma^* = (r_i, -p_i, -\zeta_K). \quad (26)$$

In our system the time-reversal symmetry holds. As a result, for each phase-space trajectory segment $\Gamma_t$ ($0 < t < t_0$), we can conceive its time-reversed conjugate $\Gamma_t^* = (\Gamma_{t_0-t})^*$, where $t_0$ is a fixed time.

The phase-space distribution $P(\Gamma, t)$ is governed by the Liouville equation $\dot{P} + LP = 0$ in the Euler description in the phase space $\mathbb{R}^{2N}$, where

$$\mathcal{L} = \frac{\partial}{\partial t} \Gamma = \sum_i \left[ \frac{\partial}{\partial r_i} \cdot \mathbf{v}_i + \frac{\partial}{\partial \mathbf{p}_i} \cdot \mathbf{v}_i \right] + \sum_K \frac{\partial}{\partial \zeta_K} \zeta_K, \quad (27)$$

For any initial distribution $P(\Gamma, 0)$, we obtain

$$P(\Gamma, t) = \int d\Gamma_0 \delta(\Gamma - \Gamma_t) P(\Gamma_0, 0), \quad (28)$$

using trajectories $\Gamma_t$ starting from $\Gamma_0$ at $t = 0$.

When the phase-space velocity $\dot{\Gamma}(t)$ depends only on the instantaneous position $\Gamma_t$ autonomously in stationary environment, $\mathcal{L}$ is independent of $t$ leading to the convenient expression $P(\Gamma, t) = \exp[-\mathcal{L}t]P(\Gamma, 0)$. Also phase-space trajectories are written as $\Gamma_t = \exp(-t\mathcal{L}^T)\Gamma$ with the starting point being $\Gamma$, where $\mathcal{L}^T = -\mathcal{L}/\partial \mathcal{L}$ is the transpose operator of $\mathcal{L}$. For any phase-space function $B(\Gamma)$, we have $B(\Gamma_t) = \exp(-t\mathcal{L}^T)B(\Gamma)$. Hereafter, this $B(\Gamma_t)$ will be written simply as $B(t)$. The time derivative of $B$ is written as $\dot{B} = -\mathcal{L}^T B$.

For stationary and homogeneous $T$, we assume that the system tends to the following equilibrium distribution,

$$P_e(\Gamma) = \gamma \exp \left[ \beta F(T) - \beta \mathcal{H}(\Gamma) - \sum_K \gamma \frac{\zeta_K^2}{2} \right], \quad (29)$$

where $F(T)$ is the Helmholtz free energy for all the particles. The stationarity condition $\mathcal{L}P_e = 0$ holds for

$$\gamma = dM \tau_0^2. \quad (30)$$

where the factor $dM$ appears because a single thermostat is attached to $M$ particle in each boundary layer. Hereafter, $\langle \cdots \rangle_c = \int d\Gamma (\cdots) P_c(\Gamma)$ denotes the equilibrium average. Then, $\langle \zeta_K \zeta_K' \rangle_c = \delta_{KK'}/\gamma$ and $\langle \zeta_K \zeta' \rangle_c = 2\delta_{KK'}/\gamma^2$. The stationality in equilibrium gives

$$\langle B(t + t_0) C(t_0) \rangle_c = \langle B(t) C(t_0) \rangle_c = \langle B(0) C(-t) \rangle_c, \quad (31)$$

Equal-time correlation functions $\langle B(0) C(t) \rangle_c$ will simply be written as $\langle BC \rangle_c$, which have no time-dependence.

From Eqs.(23) and (29) we have $\langle \mathcal{J}_K \rangle_c = 0$ and

$$\langle \mathcal{J}_K \mathcal{J}_K' \rangle_c = \delta_{KK'} \langle k_B T \rangle^2 (dM + 2)/\tau_0^2. \quad (32)$$

For $K = K'$, the right hand side is large for large $M/\tau_0^2$. In contrast, we find $\langle \langle I_K \rangle_e \rangle_c \propto k_B T n A$ from Eq.(11), which is different from Eq.(32). If $B(\{r, p\})$ is a variable determined by the particle positions and momenta and not by $\zeta_K$, we have $\langle B \mathcal{J}_K \rangle_c = 0$. For example, we obtain

$$\langle \dot{q} \mathcal{J}_K \rangle_c = \langle \mathcal{H} \mathcal{J}_K \rangle_c = \langle \mathcal{H} \mathcal{J}_K \rangle_c = \langle \mathcal{J}_K \mathcal{J}_K \rangle_c = 0. \quad (33)$$

However, the time-correlation functions $\langle B(t) \mathcal{J}_K(0) \rangle_c$ are nonvanishing for $t \gg \tau_0$ (from Eqs. (41) and (42) below) and should be nearly equal to $\langle B(t) I_K(0) \rangle_c$.

In the Nosé-Hoover thermostating, the time $\tau_0$ in Eq.(17) determines the thermalization speed within the boundary layers. We assume that $\tau_0$ is shorter than the typical microscopic time $\tau_m$ in the bulk. Then, the temperature fluctuations of the thermostats ($\approx 2E_K/dMk_B - T$) decay to zero quickly. We also assume a large spring constant ($= d^2\psi/dr^2$) to rigidly pin the bound particles on the wall. Then, the potential part of $\mathcal{H}_K$ in Eq.(20) should also relax rapidly (see the second paragraph at the beginning of Sec.II). Under these conditions, Eqs.(19) and (23) indicate

$$\zeta_K \equiv -I_K/2E_K, \quad (34)$$

This should hold even when the boundary temperatures $T_K(t)$ vary in time. Thus, slow time-evolution of $\zeta_K(t)$ arises from that of $I_K(t)$. Such thermostat layers can serve as isothermal boundaries in the hydrodynamic description. In their simulation on shear flow, Hoover et al. assumed the friction of the form

$$\zeta = \sum_i \mathbf{p}_i \cdot \mathbf{f}_i/\sum_i |\mathbf{p}_i|^2 \text{ for a single thermostat coupled to all the particles as } \mathbf{p}_i = \mathbf{f}_i - \mathbf{c}_p. \text{ In this method, } \sum_i |\mathbf{p}_i|^2 \text{ is exactly fixed at a constant.}\phantom{\quad (34)}$$

III. LINEAR RESPONSE

Next, starting with the equilibrium distribution $P_e(\Gamma)$ in Eq.(29) at $t = 0$, we slightly change the top and bottom temperatures in Eq.(17) from $T$ to $T + \delta T(t)$ for $t > 0$. We calculate linear response to $\delta T(t)$.
A. Small boundary temperature changes

We define the mean temperature deviation \( \delta T_m \) and the mean temperature gradient \( \mathcal{T} \) by
\[
\delta T_m = (\delta T_{\text{top}} + \delta T_{\text{bot}})/2, \\
\mathcal{T} = (\delta T_{\text{top}} - \delta T_{\text{bot}})/H.
\]
which can depend on \( t (>0) \). We fix the thermostat time \( \tau_h \) and \( \gamma \) (see discussions around Eq.(48)).

To linear order, \( \mathcal{L} \) in Eq.(27) is changed by
\[
\delta \mathcal{L}(t) = -\frac{2}{\gamma} \sum_K \delta \beta_K(t) E_K \frac{\partial}{\partial \beta_K} \delta \beta_K(t). 
\]
where \( \delta \beta_K(t) \approx -\delta T_K(t)/k_B T^2 \). The deviation \( \delta P(t) = P(t) - P_c \) obeys the linearized equation,
\[
\frac{\partial}{\partial t} \delta P(t) + L \delta P(t) = -\delta \mathcal{L}(t) P_c. 
\]
From \( \partial P_c/\partial \beta_K = -\gamma \beta_K P_c \), we thus obtain
\[
\delta P(\Gamma, t) = -\int_0^t ds \sum_K \mathcal{K}_K(-s) \delta \beta_K(t - s) P_c(\Gamma), 
\]
with the aid of \( e^{-sL} \delta \mathcal{K}_K P_c = \mathcal{K}_K(-s) P_c \) (see Eq.(31)).

Here, we use backward trajectories \( \Gamma_{-s} \) \( (0 < s < t) \) with \( \Gamma_0 = \Gamma \in \mathcal{J}_K(-s) \). Note that the variables \( \mathcal{J}_K \) have already appeared in Eqs.(23)-(25). From the time-reversal symmetry in Eq.(26), we change \( \Gamma_{-s} \) to \( (\Gamma_s)^* \) and \( \mathcal{J}_K(-s) \) to \( -\mathcal{J}_K(s) \) in Eq.(39). Then, we obtain
\[
\delta P(\Gamma^*, t) = \int_0^t ds \sum_K \mathcal{K}_K(s) \delta \beta_K(t - s) P_c(\Gamma), 
\]
using forward trajectories \( \Gamma_{s} \) \( (0 < s < t) \) with \( \Gamma_0 = \Gamma \). Now, for any phase-space variable \( \mathcal{B}(\Gamma) \), we consider its deviation \( \delta \mathcal{B} = \mathcal{B} - \langle \mathcal{B} \rangle \).

From Eq.(39), its nonequilibrium average is written to linear order as
\[
\delta \mathcal{B}(t) = -\int_0^t ds \sum_K \chi_{BK}(s) \delta \beta_K(t - s). 
\]
We use the time-correlation functions,
\[
\chi_{BK}(t) = \langle \mathcal{B}(t) \mathcal{J}_K(0) \rangle \langle \mathcal{B}(0) \mathcal{J}_K(-t) \rangle, 
\]
which should be nearly equal to \( \langle \mathcal{B}(t) \mathcal{J}_K(0) \rangle \) for \( t \gg \tau_h \). For \( \mathcal{B} = \mathcal{H} \), Eq.(41) gives the average energy change \( \delta \mathcal{H}(t) \), where with the aid of Eq.(24) we have
\[
\delta \mathcal{H}(t) = \langle \mathcal{H}(t) \mathcal{J}_K(0) \rangle = \int_0^t ds \sum_K \chi_{HK}(s). 
\]
For the heat flows \( \mathcal{J}_K \), we define their time correlations,
\[
\chi_{KK'}(t) = \langle \mathcal{J}_K(t) \mathcal{J}_{K'}(0) \rangle, 
\]
which are nearly equal to \( \langle \mathcal{I}_K(t) \mathcal{I}_{K'}(0) \rangle \) for \( t \gg \tau_h \). Let us consider the average heat flux \( \langle \mathcal{J}_K \rangle = -\lambda \mathcal{H} \) in the steady states with constant \( \delta T_K \) for small boundary resistance. The coefficient \( \lambda \) is the thermal conductivity,
\[
\lambda = \frac{H}{2k_B T^2} \int_0^\infty dt \langle \mathcal{J}_K(r, t) | \mathcal{J}_{\text{bot}}(0) - \mathcal{J}_{\text{top}}(0) \rangle_c 
= \frac{1}{V k_B T^2} \int_0^\infty dt \int d\mathbf{r} \langle \mathcal{J}_K(r, t) \mathcal{J}_{K}^*(\mathbf{r}', 0) \rangle_c. 
\]
The first line follows from Eq.(41), where the integrand depends on \( t \) and \( z \) but its time integral is independent of \( z \). In the second line, we obtain Green’s expression using Eq.(25) and the relation \( \int_0^\infty dt \langle \mathcal{J}_K(r, t) \mathcal{C}(0) \rangle_c = 0 \).

When \( \mathcal{B} = \hat{a}(r, t) \) is a space-dependent variable such as \( \hat{a}(r, t) \) and \( \mathcal{J}_K(\mathbf{r}, t) \) in Eq.(41), its nonequilibrium average \( \delta \hat{a}(z, t) \) and the correlation functions \( \chi_{ak}(z, t) = \langle \hat{a}(r, t) \mathcal{J}_K(0) \rangle_c \) obey the hydrodynamic equations and depend on \( z \) and \( t \) in the film geometry. Here, as will be shown in Appendix A, there are two timescales and by Lepri et al.
\[
t_a = H/c, \quad t_D = H^2/AD, 
\]
where \( c \) is the sound speed and \( D = \lambda/C_p \) is the thermal diffusion constant with \( C_p = nT (\partial s/\partial T)_p \) being the isobaric specific heat per unit volume. For realistic \( H \) we have \( t_D/t_a \sim Hc/D \gg 1 \). Then, as a causality effect, there should be no response in the interior before arrival of sounds emitted from the boundaries. We thus predict
\[
\chi_{ak}(z, t) = 0 \quad (0 < ct < z \text{ and } H - z). 
\]
Recently, similar causality was confirmed numerically in a low-\( T \) glass for propagation of transverse sounds.

We are assuming that the thermostat time \( \tau_h \) in Eq.(17) is independent of \( T \). The boundary heat flows \( \mathcal{J}_K \) in Eq.(23) then appear in the response functions in Eq.(42). This was also assumed in our simulation on glasses and by Lepri et al. in their simulation of heat conduction in one dimension. More generally, when \( \tau_h \) depends on \( T \), \( \mathcal{J}_K \) in Eqs.(39)-(42) is replaced by
\[
\mathcal{J}_K = \mathcal{J}_K - dM k_B T^2 \left( \frac{\partial}{\partial T} \tau_h^2 \right) \mathcal{K} \mathcal{K}, 
\]
where the second correction term \( \propto d\tau_h/\partial T \) is small for \( t \gg \tau_h \) from Eq.(34). It disappears in the time integral \( \int_0^\infty dt \langle \mathcal{B}(t) \mathcal{J}_K(0) \rangle_c \) for \( \langle \delta \mathcal{B} \mathcal{K} \rangle_c = 0 \).

B. Dissipation function in linear regime

We can rewrite the linear response relation (41) as
\[
\delta \mathcal{B}(t) = \langle \mathcal{B}(t) \mathcal{O}(t) \rangle_c, 
\]
where $\Omega(t)$ is given by

$$\Omega(t) = -\int_0^t ds \sum_K J_K(s) \delta \beta_K(s). \quad (50)$$

We here calculate this function in the linear regime with details in Appendix B. It is one example of the Evans and Searles dissipation function in their nonlinear theory.\textsuperscript{27,36} In Sec.IVA, it will be derived in the nonlinear regime.

From Eqs.(41) and (42), we notice that the average $\bar{\Omega}(t)$ and the variance of $\Omega(t)$ are related as

$$\bar{\Omega}(t) = \frac{1}{2} (\Omega(t)^2)_e \quad (t > 0). \quad (51)$$

Since $\Omega(t)$ fluctuates, we can define its distribution,

$$f(\omega, t) = \int d\Gamma_0 P(\Gamma_0) \delta(\Omega(t) - \omega). \quad (52)$$

For $\bar{\Omega}(t) \gg 1$, $\Omega(t)$ arises from many microscopic events, so $f(\omega, t)$ asymptotically tends to be Gaussian as

$$f(\omega, t) \propto \exp[\omega^2/2 - \omega^2/4\bar{\Omega}(t)]. \quad (53)$$

The magnitude of $\bar{\Omega}(t)$ increases with increasing the system size and/or the duration time $t$.

We can also obtain a bulk form of $\Omega(t)$ from Eq.(25). Using $G(t)$ in Eq.(14), we write its time derivative as

$$\dot{\Omega}(t) = -\int d\Gamma \delta \beta(\Gamma) \frac{\partial \tilde{q}(r,t)}{\partial t} - \sum_K \delta \beta_K(\Gamma) \tilde{H}_K(t) - G(t)[\beta(t) - \beta_0(t)]/H. \quad (54)$$

Here, we set $\delta \beta(z,t) = \delta \beta_0(t) z/H + \delta \beta_0(t)(1 - z/H)$, which is equal to $-\delta \tilde{T}(z,t)/k_BT^2$ to linear order with

$$\delta \tilde{T}(z,t) = \delta T(t) + T(t)z. \quad (55)$$

The second law of thermodynamics suggests the following (not rigorously). In the first two terms in Eq.(54), $\dot{q}(r,t)$ and $\tilde{H}_K(t)$ should tend to increase locally upon heating (decrease upon cooling). Here, $\delta \tilde{T}(z,t)$ represents the temperature deviation correctly near the walls and approximately far from them even in transient states. In the third term, the integrated heat flux $G(t)$ should tend to be negative (positive) when $\delta T_{0w}$ is larger (smaller) than $\delta T_{0t}$. Therefore, it is very probable that $\Omega(t)$ is positive for most initial states in the canonical ensemble, especially for large systems and/or at long times.

After the typical microscopic time $t_m$, we can calculate the nonequilibrium average $\bar{\Omega}(t)$ from the hydrodynamics (see Appendix B). Using the hydrodynamic deviation of the temperature $\delta T(r,t)$, that of the density $\delta n(r,t)$, and that of the velocity field $v(r,t)$, we can express $\bar{\Omega}(t)$ as

$$\bar{\Omega}(t) = \int dr \left[ \frac{\rho |v|^2}{2k_BT} - \frac{(\Delta S)_2}{k_B} + \int_0^t dt \left( \dot{\epsilon}_{th} + \dot{\epsilon}_v \right) \right] > 0. \quad (56)$$

Here, $\rho |v|^2/2$ is the hydrodynamic kinetic energy density with $\rho = mn$ and $(\Delta S)_2$ is the negative, second-order entropy deviation written as\textsuperscript{4,54,55}

$$\Delta S_2 = -\frac{1}{2T^2}C_v(\delta T)^2 - \frac{1}{2n^2k_BT^2}(\delta n)^2 < 0, \quad (57)$$

where $C_v = \langle \partial e/\partial T \rangle_n$ is the isochoic specific heat per unit volume and $\kappa_T = \langle \partial n/\partial T \rangle_T/n$ is the isothermal compressibility. In the last term in Eq.(56), $\dot{\epsilon}_{th}$ is the heat production rate per unit volume due to $\lambda$ and $\dot{\epsilon}_v$ is that due to the viscousities.$^2$

$$\dot{\epsilon}_{th} = \lambda |\nabla \delta T|^2/T, \quad \dot{\epsilon}_v = \eta \sum_{ij}(\nabla_i v_j + \nabla_j v_i - \frac{1}{D} \delta_{ij} \nabla \cdot \mathbf{v})^2 + \eta_b |\nabla \cdot \mathbf{v}|^2, \quad (58)$$

where $\nabla_i v_j = \partial v_j/\partial x_i$ $(i,j = x,y,z)$, $\eta$ is the shear viscosity, and $\eta_b$ is the bulk viscosity.

The physical meaning of $(\Delta S)_2$ is as follows. We treat the thermodynamic entropy $S = ns$ per unit volume as a function of the energy density $e$ and the number density $n$. Then we superimpose small deviations $\delta e$ and $\delta n$ on $e$ and $n$. Up to second order we find\textsuperscript{4,54,55}

$$(\Delta S)_2 = S(e + \delta e, n + \delta n) - S(e, n) - (\delta e - \mu \delta n)/T = \left[ \delta e \delta(1/T) - \delta n \delta(e/\mu/T) \right]/2, \quad (59)$$

where $\mu$ is the reference chemical potential and the second line leads to Eq.(57). Here, $\delta e$ and $\delta n$ are coarse-grained variables varying smoothly in space. We can also treat $\delta e$, $\delta n$, and $\mathbf{v}$ as local thermal fluctuations. For small deviations, their distribution is given by\textsuperscript{4,54,55}

$$P_{hyd} = \mathcal{N} \exp \left[ \int dr \left( \frac{\Delta S_2}{k_B} - \frac{\rho |v|^2}{2k_BT} \right) \right], \quad (60)$$

where $\mathcal{N}$ is the normalization factor. The temperature fluctuation is defined by $\delta T \equiv C_v^{-1}[\delta e - (\delta e/\delta n)n]T_{\delta n}$ with $\langle \delta T(r)\delta T(r') \rangle_e = k_B T^2 C_v^{-1} \delta(t - t')$. From Eqs.(56) and (60), $\bar{\Omega}(t)$ is rewritten as

$$\bar{\Omega}(t) = -\ln(P_{hyd}/\mathcal{N}) + \int_0^t dt \int dr \delta \beta(\dot{\epsilon}_{th} + \dot{\epsilon}_v). \quad (61)$$

In Eqs.(56), (57), and (61) time-dependence of $\delta T_K(t)$ can be arbitrary.

To explicitly calculate $\bar{\Omega}(t)$, we assume $\delta T_K(t) = \theta(t)\delta T_k$, where $\theta(t)$ is the Heaviside step function. In the initial stage $0 < t < t_a$, the disturbances are localized near the walls and $\bar{\Omega}(t)$ grows algebraically and $\bar{\Omega}(t) \propto A$ (see Eq.(B3)). For $t > t_a$, we calculate $\bar{\Omega}(t)$ as

$$\bar{\Omega}(t) = \frac{\psi_1(t)C_v}{k_BT^2} \left( t + t_D \psi_2(t) \right) \frac{\lambda T^2}{k_BT^2}, \quad (62)$$

where $\bar{\Omega}(t) \propto V = AH$. The $\psi_1(t)$ and $\psi_2(t)$ are monotonically increasing, positive functions of the scaled time $t = t/t_D = 4Dt/H^2$ with $\psi_1(0) = \psi_2(0) = 0$.\textsuperscript{4,53,54}
\(\psi_1(\infty) = 1\), and \(\psi_2(\infty) = 1/3\). As a unique effect, \(\psi_1(\tau)\) tends to 1 quickly on the piston time \((\sim t_D / \gamma_s^2)\) for \(\gamma_s = C_p / C_v \gg 1\) near the criticality. At long times \((t_D)\), we have \(\Omega(t) \approx (\epsilon_k / k_B T) V t\).

In Kubo’s theory, the dissipation function is given by
\[\Omega(t) = \beta \int_0^t ds A(s) \frac{\gamma_{ex}(s)}{\gamma_{th}(s)} = \beta (H(t) - H(0))\]
for the total Hamiltonian \(H' = H - \gamma_{ex}(t) A\) without thermostats, where \(\gamma_{ex}(t)\) is applied for \(t > 0\). Then, Eq. (51) holds in the linear regime, while Eqs. (94)-(96) hold in the nonlinear regime (if the perturbation \(H' - H\) remains unchanged). Thus, we generally have \(\Omega(t) = \beta \delta H(t) > 0\).

**C. Time-correlations with \(\mathcal{J}_K\)**

In the early hydrodynamic stage \(t_m < t < t_s\), Eq. (A4) and (A5) indicate that the time-correlation functions \(\chi_K(t)\) and \(\chi_K(t)\) in Eqs. (43) and (44) behave as
\[
\chi_K(t) \approx - \int_0^t ds \chi_K(s) \sim k_B T^2 A \lambda / \sqrt{D t}.
\]
which increases as \(t^{-1/2}\) as \(t \downarrow t_m\). Thus, \(\chi_K(t)\) assume large positive values for \(0 < t \leq t_m\) as in Eq. (32), but they are negative for \(t > t_m\). For \(K a\), we have \(\chi_K(t) = 0\) in the time range \(0 < t < t_s\) for \(H \gg D / c\) from Eq. (47). For \(t > t_s\), Eq. (A13) leads to
\[
\int_0^t ds \chi_K(s) A k_B T^2 = \lambda \psi_1^2 / H \tau_s + (2 \psi_2 + 1) \left(1 + \psi_2^2\right) \lambda / H.
\]
where \(\psi_1 = d\psi_1(\tau) / d\tau\) and \(\psi_2 = d\psi_2(\tau) / d\tau\) (see Appendices A and B). The first term in Eq. (64) behaves as \(\lambda (1 - \gamma_s^{-1}) / \sqrt{4\pi D t} \tau_s\) for \(t_s < t < t_D / \gamma_s - 1\) from Eq. (B7) and is continuously connected to Eq. (63).

In the limit \(t \to \infty\), Eq. (64) becomes
\[
\int_0^\infty dt \chi_K(t) = (2\delta \lambda^2 - 1) k_B T^2 A \lambda / H.
\]

**D. Steady-state relations using surface heat flows**

In the steady state at constants \(\delta T_K\), the expression for the average follows from Eqs. (23) and (41) as
\[
\delta \mathcal{B} = - \sum_K \langle \delta B(U_{K \infty} + \delta H_K) \rangle e \delta \beta_K.
\]
Using backward trajectories \(\Gamma_{-s}\) with \(\Gamma_0 = \Gamma\), we define
\[
U_{K \infty} = \int_s^\infty dse^{-\epsilon s} \mathcal{I}_K(-s),
\]
where \(\epsilon\) is a positive small number ensuring convergence of the time integral. Up to linear order, the steady-state distribution \(P_{st}(\Gamma)\) is expressed as
\[
P_{st}(\Gamma) / P_e(\Gamma) = 1 - \sum_K \langle U_{K \infty} + \delta H_K \rangle e \delta \beta_K.
\]
In particular, if \(\delta \beta_{top} = \delta \beta_{bot} = - \delta T / k_B T^2\), \(P_{st}(\Gamma)\) is the new equilibrium distribution with the shifted temperature \(T + \delta T\), since Eq. (10) gives \(\sum_K U_{K \infty} = \mathcal{H}_{in} - \langle \mathcal{H}_{in} \rangle e\). From the time reversal symmetry, we also obtain
\[
P_{st}(\Gamma^*) / P_e(\Gamma) = 1 - \sum_K \langle U_{K \infty} + \delta H_K \rangle e \delta \beta_K,
\]
where forward trajectories appear as in Eq. (40) with
\[
U_{K \infty} = - \int_s^\infty dse^{-\epsilon s} \mathcal{I}_K(s).
\]
We also consider the steady-state averages \(\mathcal{J}_K, \bar{\mathcal{I}}_K,\) and \(\bar{\mathcal{J}}_K\). From Eq. (5) we find
\[
\frac{d}{dz} \bar{\mathcal{J}}_K(z) = \left\langle \sum_{i \leq N} \psi_i \cdot \left\langle f_{i \top} + f_{i \bot} \right\rangle \delta(z - z_i) \right\rangle_s \frac{1}{A}.
\]
where we set \(\delta(r - r_i) \to \delta(z - z_i) / A\) and \(\left\langle \cdot \cdot \cdot \right\rangle_s\) denotes the steady-state average. Thus, \(\bar{\mathcal{J}}_K\) is a constant in the interior but depends on \(z\) near the boundaries decaying to zero in the walls. Integrating Eq. (72) across the boundaries and using Eqs. (13) and (25), we obtain
\[
\bar{\mathcal{J}}_{top} = \bar{\mathcal{I}}_{top} = - A \bar{\mathcal{J}}_h, \quad \bar{\mathcal{I}}_{bot} = \bar{\mathcal{I}}_{bot} = A \bar{\mathcal{J}}_h.
\]
where \(\bar{\mathcal{J}}_h = - \lambda T\) for negligible boundary resistance.

**E. Steady-state bulk relations**

Using Eq. (25), we obtain the bulk expression for the steady-state average,
\[
\delta \mathcal{B} = \int dr' \gamma_B(r') \delta T(r') + \sum_K \gamma_{BK} \delta T_K - \chi_B T.
\]
where $\delta \bar{T}(z)$ is the temperature profile in Eq.(54). The first two terms are local-equilibrium parts written in terms of equal-time correlations as

$$\gamma_B(r) = \langle \delta B \delta \hat{g}(r) \rangle_c/k_BT^2, \quad (75)$$

$$\gamma_{BK} = \langle \delta B \delta \mathcal{H}_K \rangle_c/k_BT^2. \quad (76)$$

which vanish if $B$ is odd with respect to the time reversal.

The third term in Eq.(74) is dissipative. In terms of $\mathcal{G}(t)$ in Eq.(14), $\chi_B^\beta$ is given by

$$\chi_B^\beta = \int_0^\infty dt \langle \delta B(t) \mathcal{G}(0) \rangle_c/k_BT^2, \quad (77)$$

which yields Green’s expression (45) for $B = \mathcal{G}$. If $B(t)$ is a long-wavelength hydrodynamic variable, it evolves slowly in time remaining nearly orthogonal to $J_0^n(0)$. For this case, we can neglect the dissipative term in Eq.(74) at long wavelengths.

We further examine the first term in Eq.(74) when $B = \hat{a}(r)$ is a space-dependent variable having the even-time-reversal symmetry. In this case, we should replace $\gamma_B(r')$ by the two-point equal-time correlation function,

$$\gamma_a(r, r') = \langle \delta \hat{a}(r) \delta \hat{g}(r') \rangle_c/k_BT^2, \quad (78)$$

while the second term $(\propto \delta \hat{a}(r) \delta \mathcal{H}_K)_c$ in Eq.(74) vanishes far from the boundaries. We treat the equilibrium average $a \equiv \langle \hat{a} \rangle_c$ as a thermodynamic quantity depending on $T$ and $p$. In Appendix C, we will find the behavior,

$$\gamma_a(r, r') = g_a(r - r') + \left( \frac{\partial \hat{a}}{\partial p} \right) \left( \frac{\partial p}{\partial T} \right)_T \frac{1}{V}. \quad (79)$$

where $r$ and $r'$ are far from the boundaries. The function $g_a(r)$ is short-ranged satisfying

$$\int dr g_a(r) = \left( \frac{\partial \hat{a}}{\partial T} \right)_p. \quad (80)$$

The second term in Eq.(79) is proportional to $V^{-1}$. Thus,

$$\int dr \gamma_a(r, r') = \left( \frac{\partial \hat{a}}{\partial T} \right)_n. \quad (81)$$

We assume that the correlation length of $g_a(r)$ is much shorter than $H$. The long-range behavior $(\propto V^{-1})$ in the density correlation functions has been studied in the canonical ensemble. In Appendix C, we will examine it for general correlation functions $(\delta \hat{a}(r) \delta \hat{b}(r'))_c$.

We now substitute Eq.(79) into the first term in Eq.(74). Using Eq.(80) we obtain the local-equilibrium part of the steady-state average far from the boundaries,

$$\delta \bar{a}_{loc}(z) = \left( \frac{\partial \hat{a}}{\partial T} \right)_p \delta \bar{T}(z) + \left( \frac{\partial \hat{a}}{\partial p} \right) \delta \bar{p}, \quad (82)$$

where $\delta \bar{T}(z')$ is replaced by $\delta \bar{T}(z)$ in $\int dr' g_a(r - r') \delta \bar{T}(z')$ and $\delta \bar{p}$ is the homogeneous pressure deviation,

$$\delta \bar{p} = \left( \frac{\partial p}{\partial T} \right)_n \delta T_m. \quad (83)$$

If $\delta \bar{a}$ is equal to $\delta \bar{p}$ in Eq.(8), its average deviation is equal to the above $\delta \bar{p}$. For $\delta \bar{a} = \delta \bar{n}$ and $\delta \bar{q}$, we obtain

$$\delta \bar{n}(z) = \langle \partial n/\partial T \rangle_p (\delta \bar{T}(z) - \delta T_m), \quad (84)$$

$$n \delta \bar{q}(z) = C_p (\delta \bar{T}(z) - \delta T_m) + C_V \delta T_m. \quad (85)$$

Thus, the space average of $\delta \bar{n}$ is zero and that of $n \delta \bar{q}$ is $C_V \delta T_m$. We confirm that $\delta \bar{T}(z)$ introduced in Eq.(55) is the local temperature deviation in steady states.

As another application of Eq.(77), we can set $B(t) = \hat{a}(r, t) \hat{b}(r', t)$, where $\hat{a}$ and $\hat{b}$ are hydrodynamic variables. Then, we obtain the steady-state pair correlation $g_{ab}(r, r') = \langle \hat{a}(r, t) \hat{b}(r', t) \rangle_s$. To linear order in $T$, it depends only on $r = |r - r'|$ far from the boundaries and its deviation is long-ranged as $T r^{-1}$ for $d = 3$ and as $\ln r$ for $d = 2$ due to the mode-coupling effect.

IV. NONLINEAR THEORY

We finally study nonlinear dynamics, where $\delta T_K(t)$ are time-dependent and need not small.

A. Phase-space distribution

The trajectory equation is non-autonomous as

$$\dot{\Gamma}_t = \mathcal{V}(\Gamma_t, t), \quad (86)$$

where $\mathcal{V}(\Gamma, t)$ is the phase-space velocity in the Euler description. It depends on $t$ in addition to $\Gamma$, since the equations for $\zeta_K(t)$ are changed from Eq.(17) to

$$\tau_n^2 \zeta_K(t) = 2 \beta_K(t) E_K(t)/dM - 1, \quad (87)$$

where $\beta_K(t) = 1/k_BT + \delta T_K(t)$ and $\tau_n$ is a constant.

The phase-space distribution $P(\Gamma, t)$ obeys the Liouville equation and is still expressed in the form of Eq.(28) in terms of the initial distribution $P(\Gamma, 0)$. Using trajectories starting from $\Gamma_0$ and reaching $\Gamma_t$, we find

$$P(\Gamma_t, t) = e^{-\Xi(t)} P(\Gamma_0, 0). \quad (88)$$

Here, $e^{-\Xi(t)}$ is equal to the Jacobian $d\Gamma_t/d\Gamma_0$, where the phase-space volume element moves from $d\Gamma_0$ to $d\Gamma_t$. We can then rewrite Eq.(88) as

$$d\Gamma_t P(\Gamma_t, t) = d\Gamma_0 P(\Gamma_0, 0). \quad (89)$$

Generally, $\Xi(t)$ is equal to the time integral of the phase-space expansion factor $\Lambda(t)$ as

$$\Xi(t) = \int_0^t ds \Lambda(s). \quad (90)$$

where $\Lambda(t) = \Lambda(\Gamma_t, t)$ with $\Lambda(\Gamma, t) = (\partial \mathcal{V}/\partial \Gamma)_t$. For the Nosé-Hoover thermostating, Eq.(16) gives

$$\Lambda(t) = -dM \sum_K \zeta_K(t). \quad (91)$$
For any initial distribution $P(\Gamma, 0)$, Evans and Searles defined the dissipation function $\Omega(t)$ by [27,36]

$$\ln[P(\Gamma_0, 0)/P(\Gamma_t, 0)] = \Xi(t) + \Omega(t).$$

Let $P(\Gamma, 0)$ be equal to the equilibrium distribution $P_e(\Gamma)$ in Eq.(29). Then, time derivative of Eq.(92) gives

$$\dot{\Omega}(t) = \frac{d}{dt}[\beta H(t) + \sum_k \gamma k^2/(2\kappa k^2)] - \Lambda(t)$$

$$= -\sum_k \delta \beta_k(t) J_k(t),$$

where $H(t) = H(\Gamma_t)$. This agrees with Eq.(50). We find

$$d\Gamma_t P_e(\Gamma_t) = d\Gamma_0 P_e(\Gamma_0) \exp[-\Omega(t)].$$

Phase-space integration of Eq.(94) gives

$$\langle e^{-\Omega(t)} \rangle_e = \int d\Gamma_0 P_e(\Gamma_0) e^{-\Omega(t)} = 1.$$  

Here, if $e^{-\Omega(t)}$ is expanded with respect to $\Omega(t)$, we obtain $\langle \Omega(t) \rangle_e = \langle \Omega(t)^2 \rangle_e/2 + \cdots$, which coincides with Eq.(51) in second order. We also find $\dot{\Omega}(t) > 0$ since $e^{-x} + x \geq 1$ holds for any $x$. From Eqs.(89) and (94) we also obtain

$$P(\Gamma, t) = P_e(\Gamma) \exp[\Omega(t)],$$

where the trajectories $\Gamma_s (0 < s < t)$ in $\Omega(t)$ end at $\Gamma_t = \Gamma(t)$ with the initial points $\Gamma_0$ being a function of $\Gamma$. Note that $\Omega(t)$ satisfies Eqs.(94)-(96) for any $P(\Gamma, 0)$. See another choice of $P(\Gamma, 0)$ in Sec.IVE.

Evans and Searles [27,36,38] obtained a different form of $\Omega(t)$, where $J_k(t) = -2E_k(t)\zeta_k(t)$ in our $\Omega(t)$ is replaced by $-dMk_BT_k(t)\zeta_k(t)$. Thus, there is no essential difference between our $\Omega(t)$ and theirs on long timescales ($\gg \tau_0$) from Eq.(34). In our scheme, their result exactly follows for $\tau_0 \propto T^{-1}$. In Appendix D, we will derive $\Omega(t)$ generally including $T$-dependence of $\tau_h$.

**B. Transition between equilibrium states**

Let the two boundary walls have the same temperature $T(t) = T + \delta T(t)$ with $\delta T(0) = 0$, which tends to the final one $T_f = T + \delta T_f$ for $t \gg t_{ex}$. We set $\delta \beta(t) = \delta \beta_{top}(t) = \delta \beta_{bot}(t)$ and use Eq.(24) to find the simple form,

$$\Omega(t) = -\int_0^t ds \dot{H}(s) \delta \beta(s).$$  

It is convenient to define the following excess function,

$$\Omega_{ex}(t) = \Omega(t) + H(t) \delta \beta(t) = \int_0^t ds \dot{H}(s) \delta \beta(s),$$

where $\dot{\beta}(t) = d\beta(t)/dt$ and $\Omega_{ex} = H(0)\delta \beta$ for the stepwise change. If $\dot{\beta}(t) = 0$ for $t > t_{ex}$, $\Omega_{ex}(t)$ is independent of $t$ for $t > t_{ex}$ for each $\Gamma_0$. We rewrite Eq.(94) as

$$d\Gamma_t P_e(\Gamma_t) e^{-\dot{H}(t) \delta \beta(t)} = d\Gamma_0 P_e(\Gamma_0) e^{-\Omega_{ex}(t)}.$$  

The left hand side is proportional to the canonical distribution at the temperature $T(t)$, which is expressed as

$$P_e(\Gamma; T(t)) = P_e(\Gamma) \exp[\mathcal{F}(t) - \mathcal{H}(\Gamma)\delta \beta(t)].$$

Here, the factor $\exp[\mathcal{F}(t)]$ arises from the normalization condition. Phase-space integration of Eq.(99) gives

$$\mathcal{F}(t) = \beta(t) F(T(t)) - \beta F(T)$$

$$= -\ln \left[ e^{-\Omega_{ex}(t)} \right],$$

where $F(T)$ is the Helmholtz free energy for all the particles. More generally, for any variable $\mathcal{B}(\Gamma)$, we consider its equilibrium average at the temperature $T(t)$, written as $b(T(t)) = \int d\Gamma \mathcal{B}(\Gamma) P_e(\Gamma; T(t))$, which changes from $b(T)$ at the initial temperature $T$ to $b(T_f)$ at the final one $T_f$ as $t$ increases. We multiply Eq.(99) by $\mathcal{B}(t) = \mathcal{B}(\Gamma_t)$ and perform its phase-space integration to obtain

$$b(T(t)) = e^{\mathcal{F}(t)}(\mathcal{B}(t)) e^{-\Omega_{ex}(t)}$$

$$= b(T) + e^{\mathcal{F}(t)} \langle \mathcal{B}(t) e^{-\Omega_{ex}(t)} \rangle_e,$$

where $\delta \mathcal{B}(t) = \mathcal{B}(t) - b(T)$. In Eqs.(101) and (102), the average is over $P_e(\Gamma_0)$ with trajectories starting from $\Gamma_0$. We can confirm Eq.(102) to linear order using $\langle \delta \mathcal{B}(t) \rangle_e \equiv \langle \delta \mathcal{B}(t) \rangle_{ex} + \langle \delta \mathcal{B}(t) \delta \beta(t) \rangle_e$, $\langle \delta \mathcal{B}(t) \rangle_e = k_B T^2(\partial \mathcal{B}/\partial T)_n$, and $e^{-\Omega_{ex}} \equiv 1 - \Omega_{ex}$.

Previously, Williams et al. [38] obtained some general relations and one of them is equivalent to Eq.(101). We note that Eq.(101) resembles Jarzynski’s equality [29] for isothermal transitions between two equilibrium states.

**C. Time reversal**

For each trajectory segment $\Gamma_s (0 < s < t)$, we can conceive its time-reversed conjugate: $\Gamma_s' = \Gamma_s^* (t)$ and $\Gamma_{s'} = \Gamma_{s}^* (t)$ at fixed $t$ (see Eq.(26)). In the present non-stationary (non-autonomous) situation, the time-reversed friction variables, written as $\zeta_k(s)$, obey

$$\tau_k \frac{d}{ds} \zeta_k(s) = 2\beta_k(t - s) E_k'(s)/dM - 1.$$  

Here, $\beta_k(t - s)$ appear. Then, the time-reversed dissipation function $\Omega'(t)$ is just equal to $-\Omega(t)$, where $\Omega(t)$ is the original one. Assuming the equilibrium distribution $P_e(\Gamma_0)'(= P_e(\Gamma_t))$ for the initial points $\Gamma_0'$, we define

$$f_r(\omega, t) = \int d\Gamma_0' P_e(\Gamma_0') \delta(\Omega'(t) - \omega).$$

Here, $d\Gamma_0' P_e(\Gamma_0') = d\Gamma_t P_e(\Gamma_t) = d\Gamma_0 P_e(\Gamma_0) e^{-\Omega(t)}$ from Eq.(94) and $\delta(\Omega'(t) - \omega) = \delta(\Omega(t) + \omega)$ from $\Omega'(t) = -\Omega(t)$. Then, $f_r(\omega, t)$ is related to $f(\omega, t)$ in Eq.(52) as

$$f_r(\omega, t) = e^{\omega} f(-\omega, t),$$

which is a well-known result [30,31,39].
Furthermore, we find $f_\omega(\omega, t) = f(\omega, t)$ when
\[ \delta \bar{\beta}_K(s) = \delta \bar{\beta}_K(t - s) \quad (0 < s < t). \tag{106} \]
This holds for stepwise changes. Under Eq.(106), we have
\[ f(\omega, t) = e^{\omega} f(-\omega, t). \tag{107} \]
This is the transient fluctuation theorem by Evans and Searles\cite{33,34,35}, which is exact for stepwise changes of external parameters. It was checked in simulations of small systems\cite{33,34,35}. We can also realize Eq.(106) for periodic $\delta T_K(t)$, where Eq.(107) holds for particular $t$. In the nonlinear regime, $f(\omega, t)$ can significantly deviate from the Gaussian form in Eq.(53) at small $t$ due to events with large $|\Omega(t)|^{33,35,41}$.

When the Gaussian form is nearly realized with $\Omega(t) \gg 1$, we have $e^{\omega} f(\omega, t) \propto \exp[-(\omega + \Omega)^2/4\Omega^2]$, so the equality (95) holds due to rare events with largely negative $\Omega(t)(\geq -\Omega(t))$.

Furthermore, under Eq.(106), Eqs.(28) and (95) give
\[ P(\Gamma^*, t) = P_e(\Gamma) e^{-\Omega(t)}, \tag{108} \]
where we use forward trajectories $\Gamma'_s$ starting from $\Gamma_0 = \Gamma$ in $\Omega(t)$. For example, from Eq.(108), the average of the heat flow $\bar{J}_h^e(z, t)$ in Eq.(7) is written as
\[ \bar{J}_h^e(z, t) = -\langle \bar{J}_h^e(r, 0) e^{-\Omega(t)} \rangle_c, \tag{109} \]
which obeys the hydrodynamics and satisfies Eq.(47).

### D. Local-equilibrium distribution

For the stepwise boundary-temperature change, we have obtained Eqs.(107)-(109). We can further perform time-integration of Eq.(54). Some calculations give
\[ \Omega(t) = \Psi(\Gamma_0) - \Psi(\Gamma_t) + D(t). \tag{110} \]
Using $\mathcal{G}(t)$ in Eq.(14) we introduce
\[ \Psi(\Gamma) = \int d\delta \bar{\beta}(z) \dot{q}(r; \Gamma) + \sum_k \delta \bar{\beta}_K(\Gamma), \tag{111} \]
\[ D(t) = -\gamma_a \int_0^t ds \mathcal{G}(s). \tag{112} \]
Here, we write $\dot{q}(r; \Gamma_t) = \dot{q}(r, t)$ to avoid confusion and the coefficients $\delta \bar{\beta}(z)$ and $\gamma_a$ are defined by
\[ \delta \bar{\beta}(z) = \delta \bar{\beta}_{bot} - \gamma_a z, \quad \gamma_a = (\delta \bar{\beta}_{bot} - \delta \bar{\beta}_{top})/H, \tag{113} \]
where $\delta \bar{\beta}(z) \approx -\delta T(z)/k_B T^2$ and $\gamma_a \approx T/k_B T^2$ in linear order with $\delta T(z)$ being given by Eq.(55). The $D(t)$ represents the entropy production in the bulk region.

Using $\Psi(\Gamma)$ in Eq.(111) we can define the local-equilibrium distribution at fixed $N$ and $V$ in the form
\[ P_{lc}(\Gamma) = C_{lc} P_e(\Gamma) \exp[-\Psi(\Gamma)], \tag{114} \]
where the local inverse temperature is given by $\beta + \delta \bar{\beta}(z)$ and $C_{lc}$ is the normalization constant determined by
\[ C_{lc} = \langle e^{-\Psi(\Gamma)} \rangle_c^{-1} = \langle e^{\Psi(\Gamma)} \rangle_{lc}. \tag{115} \]
Hereafter, $\langle \cdots \rangle_{lc}$ denotes the average over $P_{lc}(\Gamma)$. Then, using Eqs.(111) and (114), we rewrite Eq.(94) as
\[ d\Gamma_t P_{lc}(\Gamma_t) = d\Gamma_0 P_{lc}(\Gamma_0) \exp[-D(t)], \tag{116} \]
As in Eq.(95), phase-space integration of Eq.(116) yields
\[ \langle e^{-D(t)} \rangle_{lc} = \int d\Gamma_0 P_{lc}(\Gamma_0) e^{-D(t)} = 1, \tag{117} \]
which yields $D(t) = \int d\omega f_{lc}(\omega, t) > 0$, supporting the second law of thermodynamics in the bulk region.

### E. Steady-state distribution in nonlinear regime

To seek the steady-state distribution $P_{st}(\Gamma)$, we start with the local-equilibrium one $P_{st}(\Gamma) = 1$ at $t = 0$ assuming a stepwise boundary-temperature change. The relaxation $P_{lc} \to P_{st}$ should take place as microscopic events in a microscopic time in the preexisting temperature gradient, as was discussed by Mori\cite{32}. On the other hand, the relaxation from $P_e$ occurs slowly on the time scale of $t_D$. Here, for the choice $P(\Gamma, 0) = P_{lc}(\Gamma)$, the dissipation function is given by $D(t)$ in Eq.(112). In fact, from Eqs.(110)-(112), time derivative of Eq.(92) becomes
\[ \frac{d}{dt} \left[ \beta H(t) + \Psi(t) + \sum_k \frac{\gamma_k}{2} \xi_k(t)^2 \right] = \Delta(t) + D(t), \tag{118} \]
where $\Psi(t) = \Psi(\Gamma(t))$. This again leads to Eq.(116). Here, use is made of the approximation in the second line of Eq.(12), which is valid for large $H$.

The counterparts of Eqs.(96) and (108) are given by
\[ P(\Gamma, t) = P_{lc}(\Gamma) \exp[D(t)], \tag{119} \]
\[ P(\Gamma^*, t) = P_{lc}(\Gamma) \exp[-D(t)]. \tag{120} \]
As the counterpart of Eq.(109), Eq.(120) yields
\[ \bar{J}_h^e(z, t) = -\langle \bar{J}_h^e(r, 0) e^{-D(t)} \rangle_{ls}, \tag{121} \]
which tends to $-\lambda T$ homogeneously in a short time in contrast to $\bar{J}_h^e(z, t)$ in Eq.(109). Thus, we find
\[ P_{st}(\Gamma) = P_{st}(\Gamma) \exp[D(t_{lc})], \tag{122} \]
\[ P_{st}(\Gamma^*) = P_{st}(\Gamma) \exp[-D(t_{lc})], \tag{123} \]
where $t_{lc}$ is taken to be longer than the relaxation time of $P_{lc} \to P_{st}$. In Eqs.(119) and (121) we use backward trajectories $\Gamma_{-s}$ ($0 < s < t$) with $\Gamma_{-0} = \Gamma$ and
\[ D(t) = -\gamma_a \int_0^t ds \mathcal{G}(-s), \tag{124} \]
where we change $G(s)$ in Eq.(112) to $G(t-s)$ and shift the time origin by $-t$. In Eqs.(120) and (123), we use forward trajectories $\Gamma_s$ ($0 < s < t$) with $\Gamma_0 = \Gamma$.

We can also assume that $P_{st}(\Gamma)$ is given by the time average of $P(\Gamma, t)$ in a time interval with width longer than $t_{lc}$. Then, the Laplace transformation $\int_0^\infty dt e^{-st} P(\Gamma, t)$ tends to $P_{st}(\Gamma)/e$ for $0 < e < t_{lc}^{-1}$. With the aid of $e^{-st} = -d(e^{-s})/dt$, we obtain

$$P_{st}(\Gamma) = P_{lc}(\Gamma) \left[ 1 - \int_0^\infty dt e^{-st} \mathcal{G}(t) \gamma_a e^{\mathcal{D}(t)} \right],$$

(125)

$$P_{st}(\Gamma^*) = P_{lc}(\Gamma) \left[ 1 + \int_0^\infty dt e^{-st} \mathcal{G}(t) \gamma_a e^{\mathcal{D}(t)} \right],$$

(126)

which readily give the linear forms (69) and (70).

In the early literature, the steady-state distribution was expressed in the form of Eq.(122) for simple fluids, where $t_{lc}$ was pushed to $\infty$. In particular, Kawasaki and Gunton, studied sheared steady states with $P_{st}/P_{lc} = \exp[-\beta \int_0^\infty dt \int d\mathbf{r} \Pi_{xx}(\mathbf{r}, -t) \gamma_s]$, where $\Pi_{xx}$ is the shear stress and $\gamma_s$ is the shear rate. They calculated the nonlinear shear viscosity due to the mode-coupling effect, where the life times of the shear modes are cut off by applied shear at long wavelengths.

V. SUMMARY AND REMARKS

We have presented a microscopic theory of applying a heat flow from thermostatted boundary walls and have derived Green’s expression for the thermal conductivity $\lambda$ in the bulk. Our theory is based on the surface-to-bulk connecting relationship in Eqs.(13) and (25). We give only the boundary temperatures and do not assume a constant temperature gradient in the interior, so our method is applicable to any inhomogeneous systems. We summarize our main results as follows.

(i) In Sec.II, we have explained our system composed of unbound particles in the cell, those bound to the boundary layers, and thermostats attached to the layers. We have introduced the heat flows $I_K$ from the bound particles to the unbound ones in Eq.(11) and those $J_K$ from the thermostats to the particles in Eq.(23). They have bulk expressions in Eqs.(13) and (25) as key relations.

(ii) In Sec.III, we have derived linear response relations to small boundary temperature changes $\delta T_K(t)$ from the Liouville equation. Their surface expressions have been given in Eqs.(41) and (42) in terms of the time-correlation functions $\langle B(t) J_K(0) \rangle$. Using Eq.(25), we have also obtained the bulk response expressions composed of local-equilibrium and dissipative parts. We have also calculated the nonequilibrium average of the Evans-Searles dissipation function $\Omega(t)$ generally in terms of the hydrodynamic variables in Eqs.(56) and (61) and explicitly for a stepwise temperature change in Eq.(62).

(iii) In Sec.IV, we have examined the phase-space distribution $P(\Gamma, t)$ in the nonlinear regime. First, we have summarized salient results when the initial distribution $P(\Gamma, 0)$ is the equilibrium one. In particular, for $\delta T_{op}(t) = \delta T_{tot}(t)$, we have obtained simple results including Eqs.(101) and (102). Furthermore, using Eq.(25), we have introduced the local-equilibrium distribution $P_{lc}(\Gamma)$ in Eq.(114). In the case $P(\Gamma, 0) = P_{lc}(\Gamma)$, we have obtained the steady-state one $P_{st}(\Gamma)$ in the McLenann-Zubarev form in Eqs.(122) and (123).

(iv) We have examined the linear relaxations of the hydrodynamic variables in Appendix A and the dissipation function in in Appendix B after a boundary temperature change. These results enable us to calculate the time-correlation functions $\langle B(t) J_K(0) \rangle$. We have presented a theory of the long-range correlation in the canonical ensemble in Appendix C, which leads to the local-equilibrium response in steady states. In Appendix D, we have calculated $\Omega(t)$ including $T$-dependence of $\gamma_s$.

We make some remarks as follows. (1) Though we have used Nosé-Hoover thermostats, our results should be independent of the thermostating method on long-time scales ($\gg \tau_\eta$). (2) We should examine the thermal boundary resistance at a solid-fluid interface in more detail. Its Green-Kubo type formula has not yet been firmly established from our viewpoint. (3) It is of great interest to generalize our results to multi-component fluids, where the thermo-diffusion effect is crucial. (4) Our scheme is applicable to systems in the presence of two-phase interfaces and to mesoscopically heterogeneous systems such as glasses and polycrystals. (5) In our previous paper on shear strains, we examined only the linear response. We should further examine sheared states in the presence of thermostats. (6) Numerical study of the relaxation $P_{lc} \rightarrow P_{st}$ should be informative, which is easy particularly for one-dimensional systems.

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Appendix A: Thermal relaxation after a boundary temperature change at a fixed volume

To examine slow dynamics in the film region $0 < z < H$, we treat averaged smooth quantities obeying the linearized hydrodynamic equations on timescales much longer than the typical molecular time $t_m$. We start with the heat conduction equation

$$nT \frac{\partial}{\partial t} \delta s = \lambda \nabla^2 \delta T,$$

(A1)

without significant Kapitza resistance. Here, $\delta s$ is the deviation of the entropy per particle related to that of the temperature $\delta T$ and that of the pressure $\delta p$ by

$$n T \delta s = C_p [\delta T - (\partial T/\partial p)_s \delta p].$$

(A2)

Here, $n T \delta s$ is the average deviation of $\dot{q}$ in Eq.(4) and $\delta p$ is that of $\dot{p}$ in Eq.(8) slightly away from equilibrium.
They are related to $\chi_{nK}(z,t) = \langle \hat{a}(r,t) \hat{J}_K(0) \rangle_e$ for $\hat{a} = \hat{q}$ and $\hat{p}$ (see Sec.IIIA). In the linear order, the temperature deviation $\delta T$ is defined by Eq.(A2). The average boundary heat fluxes $I_K(t) (= J_K(t))$ are written as

$$I_{\text{top}}(t) = A\lambda \delta T'(H,t), \quad I_{\text{bot}}(t) = -A\lambda \delta T'(0,t),$$

where $A$ is the surface area and $\delta T'(z,t) = \partial T/\partial z$.

Let the boundary temperatures be changed by constant $\delta T_k$ in a time range $[0, t_{\text{ex}}]$ with $t_{\text{ex}} < t_a = H/c$. For example, we can assume the linear increase: $\delta T_k(t)/\delta T_k = t/t_{\text{ex}}$ for $0 < t < t_{\text{ex}}$.

**Intermediate stage.** For $t_m \ll t < t_a$, we treat the thermal diffusion near the walls. Along the $z$ axis, $\delta T(z,t)$ decreases from $\delta T_k(t)$ at the boundaries and decays to 0 far from them on the diffusion length $\sqrt{D t}$. Thus, for $0 < t < t_a$, $I_K(t)$ and $\delta H(t)$ increase as

$$I_K(t) \sim A\lambda \delta T_k(t)/\sqrt{D t},$$

$$\delta H(t) \sim \sum_K A\lambda \delta T_k(t)/\sqrt{t/D}.$$  

See Eq.(63) for the corresponding response functions. **Intermediate and final stages.** For $t \gg t_a$, $\delta p$ is known to be homogenized after repeated sound traversals in the cell (the piston effect), where $\delta p$ is equal to the space average of $(\partial p/\partial T)_n\delta T + (\partial p/\partial n)_T \delta n$. Thus,

$$\delta p(t) = (\partial p/\partial T)_n \delta T_{\text{sp}}(t),$$

where $\langle \delta T_{\text{sp}} \rangle = \int_0^H dz \delta T(z,t)/\bar{H}$. As a result, the temperature increases by $(\partial T/\partial p)_n \delta p$ adiabatically throughout the cell. This effect is amplified near the criticality, where the ratio $(\partial T/\partial p)_n/(\partial T/\partial p)_s = 1 - \gamma_s^{-1}$ is close to 1 with $\gamma_s = C_p/C_V \gg 1$. The inhomogeneous part of $\delta T$ near the walls is governed by the thermal diffusion.

For $t \gg t_a$, we can use Eq.(A6) to calculate the Laplace transformation (LT) of $\delta T(z,t)$ defined by

$$F_T(z,\omega) = \int_0^\infty dt e^{-\omega t} \delta T(z,t),$$

which is valid for $\omega \ll t_a^{-1}$. Some calculations give

$$F_T = \left[ 1 + \frac{\cosh v - \cosh u}{\varphi(u)} \right] \frac{\delta T_m}{\omega} + \frac{H \sinh v}{2 \sinh u} \frac{T}{\omega},$$

where $\delta T_m$ and $T$ are given in Eqs.(35) and (36) and

$$u = H(\omega/4D)^{1/2} = (t_D\omega)^{1/2},$$

$$v = u(2s/H - 1),$$

$$\varphi(u) = \cosh u + (\gamma_s - 1)u^{-1} \sinh u.$$  

Here, $F_T(z,\omega)$ depends on $z$ through $v$ with $v = \pm u$ at $z = 0$ and $H$. From Eq.(A8) its space average is given by

$$\langle F_T \rangle_{\text{sp}} = \left( \frac{\partial T}{\partial p} \right)_n F_p = \frac{\gamma_s \sinh u}{u \varphi(u)} \cdot \frac{\delta T_m}{\omega},$$

where $F_p(\omega)$ is the LT of $\delta p(t)$ in Eq.(A6). The LTs: $F_K(\omega) = \int_0^\infty dt e^{-\omega t} I_K(t)$ are also given by

$$F_K(\omega) = A\lambda D \left[ \frac{2 \sinh u}{H u \varphi(u)} \delta T_m + \frac{T}{u \tanh u} \right],$$

where $+$ is for $K = \text{top}$ and $-$ is for $K = \text{bot}$. For $\gamma_s \gg 1$, we have near-critical behavior $\varphi \cong (\gamma_s - 1)/u \gg 1$ for $1 \ll u \ll \gamma_s$ (see Eqs.(B7) and (B8)).

We remark the following. (i) We find $F_T(z,\omega) = \delta T(z)/\omega$ as $\omega \rightarrow 0$ and $\delta T(z,t) = \delta T(z)$ as $t \rightarrow \infty$, where $\delta T(z)$ is given in Eq.(54) in the steady state. (ii) For $u \gg 1$, we have $\omega(F_T)_{\text{sp}} \cong \delta T_m \gamma_s/(u + (\gamma_s - 1))$. Thus, for $\gamma_s \gg 1$, we have $\langle \delta T_{\text{sp}} \rangle(t) \cong \delta T_m$ for $t \gg t_1$, where

$$t_1 = (\gamma_s - 1)^{-2} H^2/4D \ll t_D.$$  

in particular, for $T = 0$, Thus, thermalization occurs at $t \sim t_1$. We assume $t_1 \gg t_a$, which holds for $H \gg \gamma_s D/c$, while Eq.(A8) holds even in the reverse case $t_1 \ll t_a$. (iii) The second term in Eq.(A8) gives rise to the temperature relaxation approaching the linear profile $T(z - H/2)$ diffusively on the timescale of $t_D$.

**Appendix B: Dissipation function in hydrodynamic regime**

In this appendix, we first derive Eq.(56). From Eqs.(A1)-(A3) the hydrodynamic average of the dissipation function in Eq.(50) is written as

$$\frac{\bar{\Omega}(t)}{A} = \frac{\lambda}{k_B T^2} \int_0^t dt \left[ (\delta T \delta T')_{z=H} - (\delta T \delta T')_{z=0} \right]$$

$$= \frac{1}{k_B T} \int_0^t dt \int_0^H dz \left[ \frac{\partial \delta s}{\partial t} \delta T + \frac{\lambda}{T} (\delta T')^2 \right].$$  

To derive the second line, we change the integrand in the first line to $\int_0^H dz \delta T \delta T'' + (\delta T')^2$ and use Eq.(A1). We also calculate the time derivative of $(\Delta S)_2$ in Eq.(57) as

$$\frac{d}{dt} \int d\omega (\Delta S)_2 = - \int d\omega \left[ \frac{n \sinh \varphi}{T} \delta T + \frac{\delta n}{\delta \varphi} \delta p - \frac{n \tanh \varphi}{T} \delta T' \right],$$

where $(\Delta S)_2 = nT \delta s + T \langle \partial p/\partial T \rangle_n \delta n/n$. Here, the space integral of $(\partial \delta n/\partial T) \delta p/n$ is changed to that of $u \cdot \nabla \delta p = \varphi \cdot [ -\delta p + \varphi \cdot \delta \varphi]%$ from $\partial (\delta n)/\partial t = -n \nabla \cdot \delta T$ and $\delta \varphi$ is the viscous stress tensor. Thus, we are led to Eq.(56).

Second, we explicitly calculate $\bar{\Omega}(t)$. In the initial stage $0 < t < t_a$, the bottom and top disturbed regions are separated, so Eq.(A4) yields

$$\bar{\Omega}(t)/A \sim \lambda \sqrt{t/D} \sum_K \langle \delta T_K(t) \rangle^2/k_B T^2.$$  

For $t \gg t_a$, Eq.(A8) gives the LT of $\bar{\Omega}(t)$ in the form,

$$F_{\bar{\Omega}}(\omega) = \frac{V\lambda T^2}{k_B T^2 K^2} \left[ \frac{4 \sinh u}{H u \varphi(u)} \cdot \frac{(\delta T_m)^2}{H^2} + \frac{T^2}{u \tanh u} \right].$$  

(B4)
whose inverse LT yields Eq.(62). Using \( \tau = t/t_D \) we have

\[
\psi_1(\tau) = \sum_{\ell \geq 1} \frac{2\gamma_\ell}{\ell^2} \left[ 1 - \exp(-\pi^2 \ell^2 \tau) \right], \tag{B5}\]

\[
\psi_2(\tau) = \sum_{\ell \geq 1} \frac{2}{\ell^2 \pi^2} \left[ 1 - \exp(-\pi^2 \ell^2 \tau) \right]. \tag{B6}\]

In Eq.(B5), \( \alpha_\ell \) (\( \ell \geq 1 \)) are the solutions of \( \tan \alpha_\ell = \alpha_\ell / (\gamma_\ell - 1) \) with \( \ell - 1 < \alpha_\ell / \pi < \ell \). The inverse LTs of \( t_p \gamma_\ell \sinh u/\varphi(u) \) and \( t_p / (u \tanh u) - 1/\omega \) are \( \psi'_1 = \partial_v / \partial \tau' \) and \( \psi'_2 = \partial_v / \partial \tau' \), respectively, which indicate \( \psi_1(\infty) = 1 \) and \( \psi_2(\infty) = 1/3 \). For \( \gamma_\ell \gg 1 \), \( \psi_1 \) depends on \( \gamma_\ell \) in a singular manner as

\[
\psi_1(\tau) \cong 2(\gamma_\ell - 1)(\tau/\pi)^{1/2} \quad (t < t_1) \tag{B7}
\]

\[
\cong 1 - (\gamma_\ell - 1)^{-1}(\tau/\pi)^{1/2} \quad (t_1 < t < t_D). \tag{B8}\]

Thus, \( \psi_1 \) approaches to 1 for \( t \sim t_1 \) (the piston effect).

**Appendix C: Long-range correlation in finite systems in canonical ensemble**

We examine the long-range correlations in a finite system in the \( T-N-V \) canonical ensemble\(^{37,46,48} \), which are absent in the \( T-\mu-V \) grand canonical ensemble. We treat macroscopic one-component fluids, but extension to multi-component fluids\(^{49} \) is straightforward. The average \( \langle \cdot \rangle_\psi \) is taken at fixed \( V, T, N \), and \( N = nV \).

In the canonical ensemble, the density correlation function \( g(r, r') = \langle \delta n(r) \delta n(r') \rangle_\psi \) in the bulk is of the form,

\[
g(r, r') = n\delta(r-r') + n^2g(|r-r'|) - k_BTn^2\kappa_T/V \tag{C1}\]

where \( g(r) \) is the pair correlation function and \( \kappa_T \) is the isothermal compressibility. Space integration of Eq.(C1) in the cell vanishes from \( 1+n \int dr g(r) = k_BTn\kappa_T \).

For any density variables \( \hat{a}(r) \) and \( \hat{b}(r) \), we consider their deviations \( \delta \hat{a}(r) = \hat{a}(r) - \hat{a} \) and \( \delta \hat{b}(r) = \hat{b}(r) - \hat{b} \), where the averages \( \langle \cdot \rangle_\psi \) are thermodynamic quantities. In the canonical ensemble, we have

\[
\langle \delta \hat{a}(r) \delta \hat{b}(r') \rangle_\psi = g_{ab}(r-r') - k_BTn^2\kappa_TD_{ab}/V \tag{C2}\]

where \( g_{ab}(r-r') \) is a short-ranged function and

\[
D_{ab} = \left( \frac{\partial a}{\partial n} \right)_T \left( \frac{\partial b}{\partial n} \right)_T = \frac{1}{n\kappa_T} \left( \frac{\partial a}{\partial p} \right)_T \left( \frac{\partial b}{\partial n} \right)_T. \tag{C3}\]

Here, if \( \hat{b} = \hat{q} \), Eq.(79) follows from \( n^2 \langle \delta b / \delta n \rangle_T = -(\partial p / \partial T)_n \). If \( \hat{b} = \hat{p} \), the second term of Eq.(C2) is \( -nk_BT(\partial a / \partial n)_T/V \). If \( \hat{b} \) is the temperature fluctuation \( \delta T \equiv C_V^{-1}\delta q + (\partial T/\partial n)_n \delta n \), we have \( D_{ab} = 0 \).

A general theory of Lebowitz et al.\(^{27,49} \) can yield Eq.(C2), but we here present its simple derivation. We divide the cell into regions \( A \) and \( B \) with volumes \( V_A \) and \( V_B = V - V_A \), where \( r \) is in \( A \) and \( r' \) is in \( B \) far from the boundaries. We examine the fluctuation of the particle number \( N_A \) in \( A \) around \( N_A = nV_A \). Then, for each \( N_A \), the conditional average of \( \hat{a}(r) \) is \( a(T, N_A/V_A) \), so

\[
\delta \hat{a}(r) = a(T, N_A/V_A) - a(T, n) \cong \left( \frac{\partial a}{\partial n} \right)_T \frac{\delta N_A}{V_A}, \tag{C4}\]

where \( |\delta N_A| \ll \bar{N}_A \). In B, we have \( N_B = \bar{N}_B - \delta N_A \) with \( \bar{N}_B = nV_B \) so that \( \delta b(r') = -(\partial b/\partial n)_T \delta N_A/V_B \). Thus,

\[
\langle \delta \hat{a}(r) \delta \hat{b}(r') \rangle_\psi = -D_{ab} \sum_{\delta N_A} P(N_A)(\delta N_A)^2/V_A V_B. \tag{C5}\]

where \( P(N_A) \) is the distribution of \( N_A \) proportional to \( \exp[-F(T, N_A)/k_BT - F(T, N - N_A)/k_BT] \), where \( F \) is the Helmholtz free energy. Up to second order, we find

\[
P(N_A) \propto \exp[-(V/2k_BT\kappa_T \bar{N}_A N_B)(\delta N_A)^2]. \tag{C6}\]

Using this Gaussian distribution we sum over \( \delta N_A \) in Eq.(C5) to obtain the second term in Eq.(C2).

Finally, we write the space integral of the first term in Eq.(C2) as \( \langle \hat{a} \hat{b} \rangle = \int d^3r g_{ab}(r) \) in the grand canonical ensemble. Then, we have \( \langle \hat{a} \hat{b} \rangle = n_kBT(\partial a / \partial p)_T \) and \( \langle \hat{a} \hat{q} \rangle = k_BT^2(\partial a / \partial T)_p \). We can now rewrite the second term in Eq.(C2) as \( -\langle \hat{a} \hat{b} \rangle / (V\langle \hat{n} \rangle) \).

**Appendix D: Dissipation function including temperature-dependence of \( \gamma_h \)**

We here derive the dissipation function \( \Omega(t) \) for \( T \)-dependent \( \gamma_h \) in the nonlinear theory, where \( \gamma_h = \gamma_h(T_k(t)) \) depends on \( t \) and \( K \). From Eq.(17), we have

\[
\dot{\gamma}_h(t) = |2E_K(t) - dm_kBT_k(t)|/Q_K(t), \tag{D1}\]

where \( Q_K(t) = [\gamma_h((T_k(t))^2]dm_kBT_k(t) \). Evans and Searles\(^{27,36,38} \) treated \( Q_K(t) \) as a constant \( Q \).

For \( P(T, 0) = P_c(T) \), the first line of Eq.(93) gives

\[
\Omega(t) = 2 \sum_K \beta_K(t)E_K(t)\gamma_h(t) - \sum_K \left[ \beta_K(t)Q_K(t) - \beta Q_K(0) \right] \gamma_h(t) \gamma_h(t). \tag{D2}\]

The first term yields Eq.(50) from Eq.(23), while the second term arises from \( T \)-dependence of \( \gamma_h \) from \( \beta_K(t)Q_K(t) = dm\gamma_h(T_k(t))^2 \). In particular, if \( Q_K(t) = Q_K(0) \) or if \( \gamma_h^2 \propto T^{-1} \), Eqs.(D1) and (D2) yield

\[
\Omega(t) = -dm \sum_K \gamma_h(t) \gamma_h(t)/T, \tag{D3}\]

whose time-integration gives the Evans-Searles \( \Omega(T) \) for heat conduction\(^{27,36,38} \). However, for any \( T \)-dependence of \( \gamma_h \), the difference between our \( \Omega(T) \) and theirs is negligible for \( t \gg \gamma_h \), since the second term in Eq.(D2) is proportional to \( \delta \gamma_h(t)^2/2t^2 \). In the linear regime, Eq.(D2) gives Eq.(48) from \( \gamma_h(T_k) - \gamma_h(T) \cong (\partial \gamma_h / \partial T)T \). In particular, we have \( \gamma_h(T_k) = -dmkBT\gamma_h(t) \) for \( \gamma_h^2 \propto T^{-1} \).
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