Steady shear flow thermodynamics based on a canonical distribution approach

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A nonequilibrium steady-state thermodynamics to describe shear flow is developed using a canonical distribution approach. We construct a canonical distribution for shear flow based on the energy in the moving frame using the Lagrangian formalism of the classical mechanics. From this distribution, we derive the Evans-Hanley shear flow thermodynamics, which is characterized by the first law of thermodynamics $d\mathcal{E}=Td\mathcal{S}-\mathcal{Q}d\gamma$ relating infinitesimal changes in energy $\mathcal{E}$, entropy $\mathcal{S}$, and shear rate γ with kinetic temperature T. Our central result is that the coefficient $\mathcal{Q}$ is given by Helfand's moment for viscosity. This approach leads to thermodynamic stability conditions for shear flow, one of which is equivalent to the positivity of the correlation function for $\mathcal{Q}$. We show the consistency of this approach with the Kawasaki distribution function for shear flow, from which a response formula for viscosity is derived in the form of a correlation function for the time-derivative of $\mathcal{Q}$. We emphasize the role of the external work required to sustain the steady shear flow in this approach, and show theoretically that the ensemble average of its power $\dot{W}$ must be non-negative. A nonequilibrium entropy, increasing in time, is introduced, so that the amount of heat based on this entropy is equal to the average of $\dot{W}$. Numerical results from nonequilibrium molecular-dynamics simulation of two-dimensional many-particle systems with soft-core interactions are presented which support our interpretation.

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I. INTRODUCTION

The great success of thermodynamics as a physical theory to describe various equilibrium phenomena has stimulated attempts to generalize it to a theory applicable to macroscopic time-dependent phenomena, namely to a nonequilibrium thermodynamics. Many efforts have been devoted to this subject, and led to some proposals for nonequilibrium thermodynamics, for example, the classical irreversible thermodynamics [1], the rational thermodynamics [2,3], and the extended irreversible thermodynamics [4]. Recently, a nonequilibrium thermodynamics, which tries to give more rigorous predictions by restricting its applied field into nonequilibrium steady states, is also discussed [5–7].

Shear flow is a typical example of nonequilibrium steady phenomena. For a constant velocity gradient, it has a steady current (the shear stress), and has many applications in the investigation of rheological properties of materials [8,9]. Such models have been widely used to calculate the shear viscosity, whose shear rate dependence is still actively discussed [10–13]. The apparent existence of a critical phenomenon, appearing as a transition from a uniform bulk phase to an organized stringlike phase, is shown at high shear rate [14–16]. The phenomenon of shear banding has also been discussed recently [17–19]. The nonequilibrium molecular dynamics of shear flow with thermostatting is widely used as a method of calculating the shear viscosity [20], and the nonequilibrium properties of such systems exhibit the conjugate pairing rule of the Lyapunov spectrum [21–24] and satisfy the fluctuation theorem [25,26]. Shear flow has also been described by the Bhatnagar-Gross-Krook kinetic equation, which is a simplification of the Boltzmann equation, and using this equation, transport coefficients and hydrodynamic modes were calculated [27–29]. Steady shear flow is a spatially homogeneous and time-independent phenomenon, so a simple description can be expected. However, no convincing thermodynamic description of shear flow has been given.

Evans and Hanley [30–33] have proposed nonequilibrium steady-state thermodynamics to describe shear flow. It expresses the first law of thermodynamics for the shear flow by adding the term $\xi d\gamma$ expressing the response to a shear rate γ, namely

$$d\mathcal{E} = Td\mathcal{S} + \xi d\gamma \tag{1}$$

as the relation among infinitesimal quasistatic changes of internal energy $\mathcal{E}$, entropy $\mathcal{S}$, the shear rate γ at temperature T, and the coefficient ξ defined by $\xi \equiv \partial\mathcal{E}/\partial\gamma|_{\mathcal{S}}$ [34]. As a conceptual feature, the Evans-Hanley thermodynamics is characterized by the fact that the shear rate is an external parameter chosen as an additional variable to describe nonequilibrium effects. This is analogous to the choice of variables in equilibrium thermodynamics where the variables are chosen as parameters manipulated externally, for example the temperature and volume, etc. This choice of thermodynamic variables has the advantage that observables are rather easy to access by experiments and computer simulations. This feature also distinguishes the Evans-Hanley thermodynamics from some other nonequilibrium thermodynamics, in which local quantities related to conserved quantities, such as the local momentum density, are chosen as additional variables to describe nonequilibrium effects, because they change slowly with time and are consistent with the phenomenological equations of hydrodynamics. Compared with such general formalisms for nonequilibrium thermodynamics, the Evans-Hanley thermodynamics gives a much simpler description, as its applied field is restricted to a steady shear rate. On the other hand, one of the problems in the Evans-Hanley shear flow thermodynamics was that a clear physical meaning for the coefficient ξ, especially its microscopic expression, was not known, so that one has not had clear experimental or numerical evidence to support this thermodynamics. On this point, Ref. [35] tried to calculate numerically a value of ξ by introducing a nonequilibrium entropy in a low-density system. Also recently, Ref. [36] discussed a phenomenological expression for ξ in a linear viscoelastic fluid.

Another important aspect of nonequilibrium thermodynamics is its construction from a solid statistical mechanical foundation. Some attempts in this direction have been discussed using the nonequilibrium canonical distribution approach [37–42], the projection operator approach [43–48], and so on. As one such approach, the nonequilibrium canonical distribution approach justifies a response formula for thermodynamic perturbations, which is different from the mechanical perturbation expressed as a change in an external parameter appearing explicitly in the Hamiltonian [49]. It uses, in principle, the distribution $f(\boldsymbol{\Gamma})$ of canonical type,

$$f(\boldsymbol{\Gamma}) = \Xi^{-1} \exp\left\{ -\beta\left[H(\boldsymbol{\Gamma}) + \sum_{\alpha=1}^{\tilde{n}} \mu_\alpha(\boldsymbol{\Gamma}) A_\alpha(\boldsymbol{\Gamma}) \right]\right\}, \quad (2)$$

where Ξ is a normalization constant, β is the inverse temperature, $H(\boldsymbol{\Gamma})$ is the Hamiltonian as a function of the phase-space vector $\boldsymbol{\Gamma}$, and $\mu_\alpha(\boldsymbol{\Gamma})$ and $A_\alpha(\boldsymbol{\Gamma})$ are pairs of conjugate variables whose forms depend on the nonequilibrium phenomena under consideration. In many cases, the distribution $f(\boldsymbol{\Gamma})$, and therefore the functions $\mu_\alpha(\boldsymbol{\Gamma})$ and $A_\alpha(\boldsymbol{\Gamma})$, $\alpha = 1,2,\ldots,\tilde{n}$, are introduced based on the "local equilibrium assumption" [42], although it is not always necessary. Using the distribution $f(\boldsymbol{\Gamma})$ and the Liouville operator $\hat{\mathcal{L}}$, we calculate average quantities as the ensemble average under time evolution of the distribution function,

$$\tilde{f}(\boldsymbol{\Gamma},t) \equiv \exp\{-i\hat{\mathcal{L}}(t-t_0)\} f(\boldsymbol{\Gamma}), \quad (3)$$

which may be regarded as the distribution function at time t evolved from the initial canonical distribution function $f(\boldsymbol{\Gamma})$ at time t_0. In this way, we can derive the thermal response formula for viscosity, thermal conductivity, and so on [39–42]. This approach was generalized to non-Hamiltonian systems such as the Sllod equation for shear flow systems with isokinetic thermostat [50–52], and was used to calculate some thermal quantities, such as the specific heat of nonequilibrium steady states [53,54]. However, it is still an open problem to construct the Evans-Hanley shear flow thermodynamics from this nonequilibrium canonical distribution approach based on distributions of this type (2). Usually, the thermodynamic relation for the first law of thermodynamics in the canonical distribution approach is introduced based upon the local equilibrium assumption, but the form (1) for shear flow cannot be justified by this assumption, because the term $\xi d\gamma$ cannot be attributed to an equilibrium thermodynamical relation even if we consider a very small portion of the system.

The principal aim of this paper is to derive the Evans-Hanley shear flow thermodynamics based on the canonical distribution approach to nonequilibrium steady states. First we show that the canonical distribution for shear flow is represented by the distribution (2) in the case where $\tilde{n}=1$, $\mu_\alpha(\boldsymbol{\Gamma})=\gamma$ and $A_\alpha(\boldsymbol{\Gamma})=-Q(\boldsymbol{\Gamma})$. Here $Q(\boldsymbol{\Gamma})$ is the Helfand moment of viscosity and its time derivative is connected with the off-diagonal component of the pressure tensor. The canonical distribution given here is different from the canonical distribution based on the local equilibrium assumption, because the "nonequilibrium term" $-\gamma Q(\boldsymbol{\Gamma})$ in the distribution $f(\boldsymbol{\Gamma})$ cannot be neglected regardless of the system size. To derive the canonical distribution for shear flow, we introduce the Hamiltonian for the moving frame which follows the steady global current, then using the Lagrangian techniques of classical mechanics, and the fact that the quantity $H(\boldsymbol{\Gamma}) + \sum_{\alpha=1}^{\tilde{n}} \mu_\alpha(\boldsymbol{\Gamma}) A_\alpha(\boldsymbol{\Gamma})$ in the distribution (2) should correspond to this moving frame Hamiltonian. This procedure gives a systematic way to choose the function $\sum_{\alpha=1}^{\tilde{n}} \mu_\alpha(\boldsymbol{\Gamma}) A_\alpha(\boldsymbol{\Gamma})$ for the canonical distribution approach to nonequilibrium steady states.

Second, we show that our approach is consistent with the so-called Kawasaki distribution [20,40]. This implies that with the ensemble average of the shear stress using the distribution (3), the linear-response formula for viscosity is derived in the form of a correlation function of the time-derivative of the Helfand moment for viscosity Q. We also emphasize the role of the work required to sustain the steady shear flow in our justification of the first law of the shear flow thermodynamics. We introduce a nonequilibrium entropy, which increases in time, and show that the heat based on this entropy has the same magnitude as the power needed to sustain the shear flow.

Third, we derive the form (1) of the first law of thermodynamics for shear flow from our canonical distribution approach, and show that the quantity ξ in the form (1) is given by $\xi=-\overline{Q}$, with $\overline{Q}$ being the ensemble average of the Helfand moment for viscosity $Q(\boldsymbol{\Gamma})$. We also discuss the thermodynamic stability condition for shear flow, which leads to the positivity of the correlation function of $Q(\boldsymbol{\Gamma})$ as well as the positivity of the specific heat.

Finally, we present some numerical calculations of many-particle systems with soft-core interactions to support our thermodynamic interpretation of steady shear flow. Here, we use the Sllod equations with an isokinetic thermostat and Lee-Edwards boundary condition [55]. In these simulations, we show the shear rate dependence of the average of Helfand's moment of viscosity, its correlation function, and the work needed to sustain the shear flow.

II. CANONICAL DISTRIBUTION FOR STEADY FLOWS

A. Moving frame and energy

Systems discussed here are steady flows, with the global velocity distribution of the flow given by a time-independent function $\mathbf{V}(\mathbf{r})$ at the position $\mathbf{r}$ in the inertial frame $\mathcal{F}^{(ine)}$. The system consists of N particles with equal mass m and is described by classical mechanics (without magnetic fields).

We use the Lagrangian formalism of classical mechanics to compare quantities in different frames. The Lagrangian formalism is a direct consequence of the frame-independent principle of least action $\delta\int_{t_1}^{t_2} dt L=0$ for fixed values of positions at times t_1 and t_2, where L is the Lagrangian.

In the inertial frame $\mathcal{F}^{(ine)}$, the Lagrangian $L^{(ine)}=L^{(ine)}(\mathbf{v}^{(ine)},\mathbf{q})$ is given by

$$L^{(ine)}(\mathbf{v}^{(ine)},\mathbf{q}) = \frac{1}{2}m[\mathbf{v}^{(ine)}]^2 - U(\mathbf{q}) \tag{4}$$

as a function of $\mathbf{v}^{(ine)} \equiv (\mathbf{v}_1^{(ine)},\mathbf{v}_2^{(ine)},\ldots,\mathbf{v}_N^{(ine)})$ and $\mathbf{q} \equiv (\mathbf{q}_1,\mathbf{q}_2,\ldots,\mathbf{q}_N)$, where $\mathbf{v}_j^{(ine)}$ and $\mathbf{q}_j$ are the velocity and the spatial position of the jth particle, respectively, and $U(\mathbf{q})$ is the potential function. Using the definitions $\mathbf{p}^{(ine)} \equiv \partial L^{(ine)}/\partial \mathbf{v}^{(ine)}$ and $H^{(ine)}(\mathbf{p}^{(ine)},\mathbf{q}) \equiv \mathbf{p}^{(ine)}\cdot\mathbf{v}^{(ine)} - L^{(ine)}$, the Lagrangian (4) leads to expressions for the momentum $\mathbf{p}^{(ine)}=m\mathbf{v}_j^{(ine)}$ and the Hamiltonian $H^{(ine)}(\mathbf{p}^{(ine)},\mathbf{q}) = [\mathbf{p}^{(ine)}]^2/(2m)+U(\mathbf{q})$. Here we note that the Hamiltonian $H^{(ine)}$ is a function of $\mathbf{p}^{(ine)}$ and $\mathbf{q}$.

We introduce the velocity $\mathbf{v}_j^{(mov)}$ of the jth particle in the moving frame $\mathcal{F}^{(mov)}$, which is connected to the velocity $\mathbf{v}_j^{(ine)}$ in the inertial frame $\mathcal{F}^{(ine)}$ by $\mathbf{v}_j^{(mov)} \equiv \mathbf{v}_j^{(ine)} - \mathbf{V}(\mathbf{q}_j)$. The quantity $\mathbf{v}_j^{(mov)}$ is often referred to as the thermal velocity of particle j. The position $\mathbf{q}$ is invariant under this frame change $\mathcal{F}^{(ine)} \to \mathcal{F}^{(mov)}$ [40,57]. Inserting the velocity $\mathbf{v}_j^{(ine)}=\mathbf{v}_j^{(mov)}+\mathbf{V}(\mathbf{q}_j)$ into Eq. (4), the Lagrangian $L^{(mov)}=L^{(mov)}(\mathbf{v}^{(mov)},\mathbf{q})$ of the system in the moving frame $\mathcal{F}^{(mov)}$ is given by

$$L^{(mov)}(\mathbf{v}^{(mov)},\mathbf{q}) = L^{(ine)} = \frac{1}{2}m\sum_{j=1}^{N}[\mathbf{v}_j^{(mov)} + \mathbf{V}(\mathbf{q}_j)]^2 - U(\mathbf{q}) \tag{5}$$

as a function of $\mathbf{v}^{(mov)} \equiv (\mathbf{v}_1^{(mov)},\mathbf{v}_2^{(mov)},\ldots,\mathbf{v}_N^{(mov)})$ and $\mathbf{q}$. Equation (5) leads to the momentum $\mathbf{p}^{(mov)} \equiv \partial L^{(mov)}/\partial \mathbf{v}^{(mov)}$ as

$$\mathbf{p}_j^{(mov)} = m[\mathbf{v}_j^{(mov)} + \mathbf{V}(\mathbf{q}_j)] = m\mathbf{v}_j^{(ine)} = \mathbf{p}_j^{(ine)}. \tag{6}$$

Therefore, the momentum is independent of the choice of the frames $\mathcal{F}^{(mov)}$ and $\mathcal{F}^{(ine)}$, and hereafter we use the notation $\mathbf{p} \equiv (\mathbf{p}_1,\mathbf{p}_2\ldots,\mathbf{p}_N) \equiv \mathbf{p}^{(mov)} = \mathbf{p}^{(ine)}$ for the momentum, and also use the notation $\mathbf{\Gamma} \equiv (\mathbf{p},\mathbf{q})$ for the phase-space vector. On the other hand, the Hamiltonian $H^{(mov)}=H^{(mov)}(\mathbf{\Gamma})$ in the moving frame $\mathcal{F}^{(mov)}$ is given by

$$H^{(mov)}(\mathbf{\Gamma}) = H^{(ine)}(\mathbf{\Gamma}) - \sum_{j=1}^{N}\mathbf{p}_j \cdot \mathbf{V}(\mathbf{q}_j). \tag{7}$$

using the definition $H^{(mov)}(\mathbf{\Gamma}) \equiv \mathbf{p}\cdot\mathbf{v}^{(mov)} - L^{(mov)}$. It is essential to note that although the momenta $\mathbf{p}^{(mov)}$ and $\mathbf{p}^{(ine)}$ are equal, the Hamiltonian $H^{(mov)}(\mathbf{\Gamma})$ in the moving frame $F^{(mov)}$ is different from the Hamiltonian $H^{(ine)}(\mathbf{\Gamma})$ in the inertial frame $\mathcal{F}^{(ine)}$ and their difference is proportional to the global current distribution $\mathbf{V}(\mathbf{q}_j)$. The transformation from the inertial frame to the noninertial frame of reference, namely the moving frame, is well known in classical analytical mechanics [57].

We must distinguish the dynamics generated by the inertial frame Hamiltonian $H^{(ine)}(\mathbf{\Gamma})$ from those generated by the moving frame Hamiltonian $H^{(mov)}(\mathbf{\Gamma})$. To discuss these dynamics, we introduce the Liouville operator defined by

$$i\hat{\mathcal{L}}^{(\varpi)}X \equiv \frac{\partial H^{(\varpi)}(\mathbf{\Gamma})}{\partial \mathbf{p}}\cdot\frac{\partial X}{\partial \mathbf{q}} - \frac{\partial H^{(\varpi)}(\mathbf{\Gamma})}{\partial \mathbf{q}}\cdot\frac{\partial X}{\partial \mathbf{p}} \tag{8}$$

for any quantity $X(\mathbf{\Gamma})$, where $\varpi = ine$ for the frame $F^{(ine)}$ and $\varpi = mov$ for the frame $\mathcal{F}^{(mov)}$. Using the Liouville operator $\hat{\mathcal{L}}^{(ine)}$ $(\hat{\mathcal{L}}^{(mov)})$, the distribution $\varrho(\mathbf{\Gamma},t)$ of $\mathbf{\Gamma}$ at time t is given by $\exp\{-i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}\varrho(\mathbf{\Gamma},t_0)$ $[\exp\{-i\hat{\mathcal{L}}^{(mov)}(t-t_0)\}\varrho(\mathbf{\Gamma},t_0)]$ using the distribution $\varrho(\mathbf{\Gamma},t_0)$ at the initial time t_0 in the frame $F^{(ine)}$ $(F^{(mov)})$.

B. Canonical distribution

The central assumption of this paper is that in the moving frame $F^{(mov)}$ defined by the global velocity distribution $\mathbf{V}(\mathbf{r})$, the system can be regarded as an equilibrium state. It is important to note that this assumption is not obvious, because generally a global flow causes some local effects such as string phases in shear flows [14–16,20] and possibly turbulent phases, and so on, which can destroy this assumption. However, these phases generally occur in far-from-equilibrium states so we may expect that our assumption is satisfied in a regime near equilibrium. Under this assumption, we introduce the canonical distribution

$$f(\mathbf{\Gamma}) = \Xi^{-1}\exp\{-\beta H^{(mov)}(\mathbf{\Gamma})\} \tag{9}$$

$$= \Xi^{-1}\exp\left\{-\beta\left[H^{(ine)}(\mathbf{\Gamma}) - \sum_{j=1}^{N}\mathbf{p}_j\cdot\mathbf{V}(\mathbf{q}_j)\right]\right\} \tag{10}$$

for steady flow, where β is the inverse temperature $1/(k_B T)$ with the Boltzmann constant k_B and the temperature T, and Ξ is the partition function $\Xi \equiv \int d\mathbf{\Gamma}\exp\{-\beta H^{(mov)}(\mathbf{\Gamma})\}$. For simplicity, we use units so that $k_B=1$ hereafter in this paper. It should be noted that the function $f(\mathbf{\Gamma})$ is the distribution of $\mathbf{p}^{(ine)}$ and $\mathbf{q}$ in the inertial frame $\mathcal{F}^{(ine)}$, as well as the distribution of $\mathbf{p}^{(mov)}$ and $\mathbf{q}$ in the moving frame $F^{(mov)}$, because the identity of the momenta implies $\mathbf{\Gamma}=(\mathbf{p}^{(ine)},\mathbf{q}) = (\mathbf{p}^{(mov)},\mathbf{q})$. Also notice that the canonical distribution (9) is stationary in time in the moving frame $\mathcal{F}^{(mov)}$, because $i\hat{\mathcal{L}}^{(mov)}f(\mathbf{\Gamma})=0$.

In this paper, we use the notation $\overline{X}$ for the ensemble average using the canonical distribution $f(\mathbf{\Gamma})$, namely

$$\overline{X} \equiv \int d\mathbf{\Gamma}X(\mathbf{\Gamma})f(\mathbf{\Gamma}) \tag{11}$$

for any function $X(\mathbf{\Gamma})$.

A typical example of the canonical distribution (10) is in rotating flows, as discussed in Appendix A. Applying it to rotating flows, we obtain the well known canonical distribution for the rotating flow, and therefore its thermodynamics [58].

The canonical distribution (10) is different from that obtained from the "local equilibrium assumption," which is popular in many texts on nonequilibrium statistical mechanics. In this approach, the canonical distribution function $g(\mathbf{\Gamma})$ is chosen as

$$g(\Gamma) \equiv \tilde{\Xi}^{-1} \exp\left\{ - \beta\left[\sum_{j=1}^{N} \frac{1}{2m}[\mathbf{p}_j - m\mathbf{V}(\mathbf{q}_j)]^2 + U(\mathbf{q}) \right]\right\} = \tilde{\Xi}^{-1} \exp\left\{ - \beta\left[H^{(mov)}(\Gamma) + \sum_{j=1}^{N} \frac{1}{2}m[\mathbf{V}(\mathbf{q}_j)]^2 \right]\right\} \quad (12)$$

with $\tilde{\Xi} \equiv \int d\Gamma \exp(-\beta\{\sum_{j=1}^{N}[\mathbf{p}_j - m\mathbf{V}(\mathbf{q}_j)]^2/(2m) + U(\mathbf{q})\})$. This type of distribution was actually used to calculate the shear viscosity [27,28,37,40,41], and its localized version was used as a canonical distribution under the local equilibrium assumption (see, for example, Ref. [42]). However, one of the problems is that the distribution (12) is not consistent with the thermodynamics of rotating flows. Therefore, the difference between the two distributions (10) and (12) is crucial to the subject of this paper, which is a statistical foundation for steady-state thermodynamics. This problem basically comes from the fact that the distribution $g(\Gamma)$ does not take into account the inertial force. Despite this point, one may also notice that the deviation of the distribution (12) from the distribution (10) is of order $\mathcal{O}(\mathbf{V}^2)$ in the global velocity, and near equilibrium this term may be small compared with the second term on the right-hand side of Eq. (7), which is of order $\mathcal{O}(\mathbf{V})$.

III. CANONICAL DISTRIBUTION APPROACH TO SHEAR FLOWS

In this section, we construct a nonequilibrium statistical mechanics for steady shear flows based on the canonical distribution (10). Considering the time evolution of the canonical distribution (10) in the inertial frame $\mathcal{F}^{(ine)}$, we get a nonequilibrium distribution function for shear flows in the form called the Kawasaki distribution. This leads to a linear-response formula for viscosity using a correlation function of the time-derivative of the Helfand moment for viscosity. We also discuss the work needed to sustain the steady shear flow as well as the viscous heat generated, which is consistent with the second law of thermodynamics. These points will be used to interpret the first law of thermodynamics for steady shear flows.

A. Shear flows and Helfand's moment of viscosity

We consider the shear flow system in which the global current is a linear velocity profile given by

$$\mathbf{V}(\mathbf{q}_j) = \gamma q_{jy}\mathbf{i}_x, \quad (13)$$

where q_{jy} is the y component of the position of the jth particle, and $\mathbf{i}_x$ is the unit vector in the x direction. Here, γ is the shear rate, a position-independent constant.

The shear flow system is proposed to describe a fluid between the two plates which move at different speeds, and is frequently used to calculate viscosity. The viscosity is given by the linear coefficient of $P_{xy}(\Gamma)$ with respect to the shear rate γ, where the pressure tensor $P_{\alpha\beta}(\Gamma)$ is defined by

$$P_{\alpha\beta}(\Gamma) \equiv \frac{1}{\mathcal{V}}\sum_{j=1}^{N} \left[\frac{1}{m}p_{j\alpha}p_{j\beta} - q_{j\beta}\frac{\partial U(\mathbf{q})}{\partial q_{j\alpha}} \right]. \quad (14)$$

Here $\mathcal{V}$ is the volume of the system, and $p_{j\alpha}$ ($q_{j\alpha}$) is the αth component of the momentum $\mathbf{p}_j$ (the position $\mathbf{q}_j$) of the jth particle. If particle-particle interactions in the system are given by a two-body interaction only, namely the potential $U(\mathbf{q})$ is expressed in the form $U(\mathbf{q}) = (1/2)\sum_{j\neq k}\phi(|\mathbf{q}_j - \mathbf{q}_k|)$, then Eq. (14) can be rewritten as

$$P_{\alpha\beta}(\Gamma) = \frac{1}{\mathcal{V}}\sum_{j=1}^{N} \left[\frac{1}{m}p_{j\alpha}p_{j\beta} + \frac{1}{2}\sum_{k=1}^{N} (q_{j\beta} - q_{k\beta})F_{jk\alpha} \right] \quad (15)$$

with $F_{jk\alpha} \equiv -\partial\phi(|\mathbf{q}_j - \mathbf{q}_k|)/\partial q_{j\alpha}$ interpreted as the αth component of the force acting on the jth particle due to the kth particle. The pressure tensor $P_{\alpha\beta}(\Gamma)$ comes from the balance equation for the momentum [20].

For the case of the global velocity distribution (13), Eq. (7) is given by [56]

$$H^{(mov)}(\Gamma) = H^{(ine)}(\Gamma) - \gamma Q(\Gamma), \quad (16)$$

where $Q(\Gamma)$ is defined by

$$Q(\Gamma) \equiv \sum_{j=1}^{N} q_{jy}p_{jx}. \quad (17)$$

It is essential to note that the quantity $Q(\Gamma)$ is connected to the shear stress $P_{xy}(\Gamma)$ as

$$i\hat{\mathcal{L}}^{(ine)}Q(\Gamma) = \mathcal{V}P_{xy}(\Gamma), \quad (18)$$

namely the quantity $Q(\Gamma)$ is Helfand's moment for viscosity [59,60]. [In the references, the name "Helfand's moment of viscosity" is used for the quantity $(T\mathcal{V})^{-1/2}Q(\Gamma)$, but in this paper, for convenience we use this name for the quantity Q itself without the factor $(T\mathcal{V})^{-1/2}$.] Helfand's moment of viscosity is used to calculate the viscosity by analogy with the Einstein formula for the diffusion constant [61,62].

B. Canonical distribution for shear flows

In the case of Eq. (13), the distribution function $f(\Gamma)$ is given by

$$f(\Gamma) = \Xi^{-1} \exp\{- \beta[H^{(ine)}(\Gamma) - \gamma Q(\Gamma)]\}. \quad (19)$$

This is the canonical distribution function for shear flow in a nonequilibrium steady state. This distribution can be attributed to the general form (2) of the canonical distribution when $H(\Gamma) = H^{(ine)}(\Gamma)$, $\tilde{n} = 1$, $A_1(\Gamma) = Q(\Gamma)$, and $\mu_1(\Gamma) = -\gamma$.

Now we mention some physical meanings for the shear flow canonical distribution function (19). For this purpose, we convert the distribution function (19) for the canonical variable Γ into the distribution function $f''(\mathbf{v}^{(mov)}, \mathbf{q})$ for the position $\mathbf{q}$ and the velocity $\mathbf{v}^{(mov)}$ in the moving frame $\mathcal{F}^{(mov)}$, and obtain

$$f''(\mathbf{v}^{(mov)},\mathbf{q}) = \Xi^{-1}\exp\left\{-\beta\left[\sum_{j=1}^{N}\frac{1}{2}m[\mathbf{v}_j^{(mov)}]^2+U(\mathbf{q})+u(\mathbf{q})\right]\right\}, \tag{20}$$

where the function $u(\mathbf{q})$ is defined by

$$u(\mathbf{q}) = -\frac{1}{2}m\gamma^2\sum_{j=1}^{N}q_{jy}^2. \tag{21}$$

Here $u(\mathbf{q})$ can be regarded as a potential corresponding to the inertial force which pushes particles in the direction of larger $|q_{jy}|$, namely the region of larger global current $\mathbf{V}$. In other words, this potential $u(\mathbf{q})$ expresses the effect of Bernoulli's theorem in the hydrodynamics. Another important point is, using the distribution $f''(\mathbf{v}^{(mov)},\mathbf{q})$ and the averaging defined by Eq. (11), we obtain

$$\overline{\sum_{j=1}^{N}\frac{1}{2}m[\mathbf{v}_j^{(mov)}]^2} = \frac{\tilde{d}NT}{2} \tag{22}$$

for any potential $U(\mathbf{q})$, where $\tilde{d}$ is the spatial dimension of the system. Therefore, T can be interpreted as the kinetic temperature [63]. It may be noted that the same relation with Eq. (22) is also derived from the distribution $g(\mathbf{\Gamma})$ defined by Eq. (12) by interpreting the average $\overline{X}$ of X as the average under the distribution $g(\mathbf{\Gamma})$.

It is essential to note that owing to Eq. (18), the distribution (19) is not stationary in the inertial frame $\mathcal{F}^{(ine)}$, namely $i\hat{\mathcal{L}}^{(ine)}f(\mathbf{\Gamma})\neq 0$, although it is stationary in time in the moving frame $\mathcal{F}^{(mov)}$, namely $i\hat{\mathcal{L}}^{(mov)}f(\mathbf{\Gamma})=0$. Physically speaking, this difference of the dynamics of the canonical distribution in the different frames $\mathcal{F}^{(ine)}$ and $\mathcal{F}^{(mov)}$ comes from the fact that we need some work to sustain the steady shear flows, but the effect of such work is not included in the canonical distribution $f(\mathbf{\Gamma})$. In order to include the effect of this work, we have to generalize the distribution (19), and introduce the distribution $\tilde{f}(\mathbf{\Gamma},t)$ at time t as

$$\tilde{f}(\mathbf{\Gamma},t) \equiv \exp\{-i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}f(\mathbf{\Gamma}) \tag{23}$$

$$= f(\mathbf{\Gamma})\exp\left\{-\beta\gamma\mathcal{V}\int_{t_0}^{t}ds\tilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)\right\}, \tag{24}$$

where t_0 is the initial time. Here, to derive Eq. (24) we used the relation (18), $i\hat{\mathcal{L}}^{(ine)}H^{(ine)}(\mathbf{\Gamma})=0$, and $\exp\{-i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}Q(\mathbf{\Gamma})=Q(\mathbf{\Gamma})-\mathcal{V}\int_{t_0}^{t}ds\tilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)$, and defined $\tilde{P}_{xy}(\mathbf{\Gamma},t)$ by

$$\tilde{P}_{xy}(\mathbf{\Gamma},t) \equiv \exp\{i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}P_{xy}(\mathbf{\Gamma}). \tag{25}$$

The distribution (23) corresponds to the distribution (3) in a general formulation of the nonequilibrium canonical distribution approach. Moreover, the form of the distribution (24) is called the Kawasaki distribution function for shear flows [20,40]. It may be noted that the distribution $\tilde{f}(\mathbf{\Gamma},t)$ is normalized, namely $\int d\mathbf{\Gamma}\tilde{f}(\mathbf{\Gamma},t)=1$, as well as $\int d\mathbf{\Gamma}f(\mathbf{\Gamma})=1$.

Using the distribution $\tilde{f}(\mathbf{\Gamma},t)$ defined by Eq. (23), we introduce the time average $\langle X(\mathbf{\Gamma})\rangle_t$ by

$$\langle X(\mathbf{\Gamma})\rangle_t \equiv \int d\mathbf{\Gamma}X(\mathbf{\Gamma})\tilde{f}(\mathbf{\Gamma},t) \tag{26}$$

for any function $X(\mathbf{\Gamma})$ of $\mathbf{\Gamma}$. This averaging is generally different from the averaging (11) given by the canonical distribution $f(\mathbf{\Gamma})$, except in special systems such as rotating systems where $\overline{X}=\langle X\rangle_t$ for any X is satisfied. We will discuss the difference between these two averages more concretely in Sec. IV C.

Noting from Eq. (24) that the difference between the distribution $\tilde{f}(\mathbf{\Gamma},t)$ and the distribution $f(\mathbf{\Gamma})$ appears as the factor $\exp\{-\beta\gamma\mathcal{V}\int_{t_0}^{t}ds\tilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)\}$, we will discuss the relation of this factor to the work needed to sustain the shear flow in Sec. III D. One may interpret the canonical distribution $f(\mathbf{\Gamma})$ as a steady distribution function in the moving frame $\mathcal{F}^{(mov)}$, but in order to calculate the work needed to sustain the steady flow, we have to investigate it in a different frame $\mathcal{F}^{(ine)}$, because the work to sustain the steady flow is information given by looking at the moving system in the inertial frame. Therefore, the canonical distribution $f(\mathbf{\Gamma})$ should not be regarded as an artificial test initial distribution, like in other canonical distribution approaches for linear-response theory [39,40]. The information about the work to sustain steady flows is essential to calculate transport coefficients such as the viscosity, as will be shown in Sec. III C.

C. Linear response formula for viscosity

To calculate the transport coefficient from the nonequilibrium canonical distribution approach is beyond the scope of this paper. However, many works have been devoted to this subject [37–42,49], so it may be meaningful to mention the consistency of the nonequilibrium canonical distribution (24) with the linear-response formula for viscosity.

Using the notation (26) and the quantity $P_{xy}(\mathbf{\Gamma})$ defined by Eq. (14), the viscosity η is given as

$$\eta \equiv -\lim_{\gamma\to 0}\frac{\langle P_{xy}(\mathbf{\Gamma})\rangle_\infty}{\gamma}. \tag{27}$$

Using the distribution $\tilde{f}(\mathbf{\Gamma},t)$ given by Eq. (24), the viscosity η is represented as

$$\eta = \beta\mathcal{V}\int_{t_0}^{\infty}dt\langle\tilde{P}_{xy}(\mathbf{\Gamma},t)P_{xy}(\mathbf{\Gamma})\rangle^{(eq)}, \tag{28}$$

where we introduced the notation $\langle X(\mathbf{\Gamma})\rangle^{(eq)}$ as the equilibrium average of $X(\mathbf{\Gamma})$ for any function $X(\mathbf{\Gamma})$, namely $\langle X(\mathbf{\Gamma})\rangle^{(eq)}\equiv\Xi^{(eq)-1}\int d\mathbf{\Gamma}X(\mathbf{\Gamma})\exp\{-\beta H^{(ine)}(\mathbf{\Gamma})\}$ with the equilibrium partition function $\Xi^{(eq)}$. The derivation of Eq. (28) is given in Appendix B. [In the same Appendix B, we also discuss two kinds of nonlinear-response formulas for $\langle P_{xy}(\mathbf{\Gamma})\rangle_\infty$ with respect to the shear rate γ, one of which can be regarded as a natural generalization of Eq. (28).] Here, it is important to note that

$$\overline{P_{xy}(\mathbf{\Gamma})} = 0, \quad (29)$$

at any shear rate γ, as also shown in Appendix B, so that we obtain the equation $-\lim_{\gamma\to 0}\overline{P_{xy}(\mathbf{\Gamma})}/\gamma=0$, meaning that the distribution $f(\mathbf{\Gamma})$ does not include information about the viscosity. Equation (28) is the well known linear-response formula for viscosity [49].

The factor $\exp\{-\beta\gamma\mathcal{V}\int_{t_0}^{t} ds\tilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)\}$ in the nonequilibrium canonical distribution (24) gives the difference between the two distributions $f(\mathbf{\Gamma})$ and $\tilde{f}(\mathbf{\Gamma},t)$, and plays an essential role in the derivation of the linear-response formula (28) for viscosity. It may be emphasized that this kind of factor can be derived from a different approach using the Sllod equation [20,50]. The Sllod equation expresses the dynamics of the velocity corresponding to $\mathbf{v}^{(mov)}$, and has been used in many numerical and analytical works on shear flow systems [20,52]. In the canonical distribution approach using the Sllod equations, the time evolution of a canonical distribution under Sllod dynamics is considered, and it leads to the distribution evolving a time integral of the shear stress, such as the distribution (24). These two approaches give the same formula (28) for the viscosity. A difference between this approach and the approach discussed in this paper is that the Sllod dynamics approach is based on distributions of the type (12), so that it does not take into account the inertial force. This make discussions of thermodynamic relations (for example, the first law of thermodynamics) rather more complicated than the approach used in this paper. It may also be noted that the Sllod dynamics is different from the dynamics for $\mathbf{v}^{(mov)}$ from the Hamiltonian $H^{(mov)}(\mathbf{\Gamma})$ in the moving frame $\mathcal{F}^{(mov)}$, and in the Sllod dynamics approach the distribution corresponding to $f(\mathbf{\Gamma})$ is just an initial test distribution and cannot be interpreted as a steady distribution in the moving frame $\mathcal{F}^{(mov)}$ like the Hamiltonian dynamics approach discussed in this paper. In the Sllod equation approach, the shear rate dependence appears in the dynamics itself, so that the response formula for viscosity is treated as a response formula to a mechanical perturbation. On the other hand, in the Hamiltonian dynamics approach the shear rate dependence appears in the distribution $f(\mathbf{\Gamma})$, not in the dynamics, and the formula (28) for viscosity can be regarded as a response formula to a thermodynamic perturbation, which does not have any potential form in the inertial frame Hamiltonian.

D. Work needed to sustain shear flows and the house-keeping heat

Now we discuss further the information involved in the distribution $\tilde{f}(\mathbf{\Gamma},t)$, which the canonical distribution $f(\mathbf{\Gamma})$ does not have. It is the information about the work required to sustain the steady shear flow.

First, the power $\langle\dot{W}\rangle_t$ to sustain the shear flow at time t is estimated by

$$\langle\dot{W}\rangle_t \equiv \frac{d\langle H^{(mov)}\rangle_t}{dt} = \frac{d\overline{\tilde{H}^{(mov)}(\mathbf{\Gamma},t)}}{dt} = -\gamma\mathcal{V}\langle P_{xy}\rangle_t, \quad (30)$$

where $\tilde{H}^{(mov)}(\mathbf{\Gamma},t)$ is defined as $\tilde{H}^{(mov)}(\mathbf{\Gamma},t)\equiv\exp\{i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}H^{(mov)}(\mathbf{\Gamma})$. Here, in order to derive Eq. (30) we used the equations $i\hat{\mathcal{L}}^{(ine)}H^{(ine)}(\mathbf{\Gamma})=0$ and $\partial\tilde{H}^{(mov)}(\mathbf{\Gamma},t)/\partial t =\exp\{i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}\mathcal{V}P_{xy}(\mathbf{\Gamma})$.

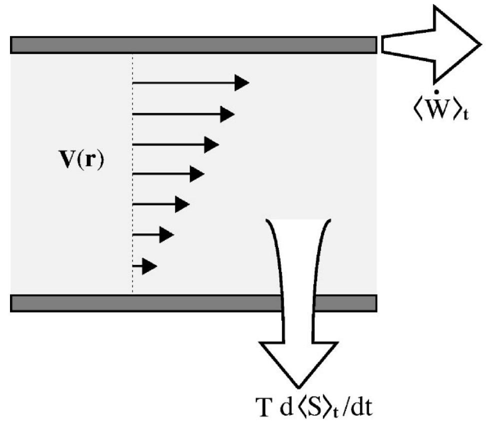

FIG. 1. Schematic illustration of the power $\langle\dot{W}\rangle_t$ required to sustain the shear flow and the house-keeping heat $T[d\langle S\rangle_t/dt]$. In this illustration, the power $\langle\dot{W}\rangle_t$ is represented as the power to move the upper boundary of the shearing system. This power supplies the energy to sustain the steady shear flow, which is eliminated from the system as the house-keeping heat.

In steady flow systems, the energy added to the system as the work needed to sustain the flow must be eliminated from the system as heat [33]. This type of heat is called the “house-keeping heat,” and its special role has been emphasized in the construction of a nonequilibrium steady-state thermodynamics [5,6]. Figure 1 is a schematic illustration of the power $\langle\dot{W}\rangle_t$ required to sustain the shear flow and the house-keeping heat. Now we estimate this house-keeping heat from the nonequilibrium canonical distribution approach. First, we introduce the observable $S(\mathbf{\Gamma})$ corresponding to entropy as

$$S(\mathbf{\Gamma}) \equiv -\ln\{f(\mathbf{\Gamma})\}. \quad (31)$$

[Note that $S(\mathbf{\Gamma})$ is actually used as the observable corresponding to the entropy in rotating flows, as shown in Appendix A.] Using this entropy observable we define the nonequilibrium entropy $\langle S\rangle_t$ as the ensemble average of $S(\mathbf{\Gamma})$ under the distribution $\tilde{f}(\mathbf{\Gamma},t)$. A similar kind of entropy to $\langle S\rangle_t$ was used in Refs. [37,39] for a different form of the distribution $f(\mathbf{\Gamma})$. Using Eq. (24), the entropy $\langle S\rangle_t$ is represented as

$$\begin{aligned}\langle S\rangle_t &= -\int d\mathbf{\Gamma} f(\mathbf{\Gamma})\ln\{\tilde{f}(\mathbf{\Gamma},-t+2t_0)\}\\ &= \overline{S} + \beta\gamma\mathcal{V}\int_{t_0}^{-t+2t_0} ds\overline{\tilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)}\\ &= \overline{S} - \beta\gamma\mathcal{V}\int_{t_0}^{t} ds\langle P_{xy}\rangle_s. \quad (32)\end{aligned}$$

Therefore, the house-keeping heat $T[d\langle S\rangle_t/dt]$ at time t is given by

$$T\frac{d\langle S\rangle_t}{dt} = -\gamma\mathcal{V}\langle P_{xy}\rangle_t \tag{33}$$

$$=\langle\dot{W}\rangle_t. \tag{34}$$

This is the balance equation that shows that the power needed to sustain the shear flow must be equal to the house-keeping heat. Using Eqs. (27), (33), and (34), the house-keeping heat and the ensemble averaged power $\langle\dot{W}\rangle_t$ to sustain the shear flow are connected to the viscosity η as $T[d\langle S\rangle_t/dt]=\langle\dot{W}\rangle_t=\mathcal{V}\eta\gamma^2+\mathcal{O}(\gamma^3)$.

The entropy $\langle S\rangle_t$ satisfies the inequality

$$\langle S\rangle_t \geqslant \langle S\rangle_{t_0} = \overline{S} \tag{35}$$

at any time $t(>t_0)$. The detail of the derivation of the inequality (35) is given in Appendix C. Noting that $\langle S\rangle_t - \langle S\rangle_{t_0}=\int_{t_0}^t dt[d\langle S\rangle_t/dt]$ and assuming that $d\langle S\rangle_t/dt$ is time-independent in a steady state, we obtain

$$\frac{d\langle S\rangle_t}{dt} \geqslant 0. \tag{36}$$

This is the expression of the second law of thermodynamics in the nonequilibrium canonical distribution approach. The inequality (36) means simply that the shear flow system produces a positive house-keeping heat constantly in time. In this sense, the total entropy production $\langle S\rangle_t-\langle S\rangle_{t_0}$ diverges as time t goes to infinity, because the total amount of heat produced by the steady viscoelastic shear flow in the infinite time interval is infinite [64]. In other words, the system is kept as a nonequilibrium steady state by discharging an amount of entropy constantly, which is transferred from the external work. Therefore, the inequality (36) must be distinguished from another type of second law of thermodynamics, meaning that an entropy increases in time and approaches a stable value in a relaxation process. This type of the second law of thermodynamics, or the thermodynamical stability condition, will be discussed in Sec. IV B. By combining the inequality (36) and $T>0$ with Eqs. (33) and (34), we have

$$\frac{\langle\dot{W}\rangle_\infty}{\mathcal{V}} = -\gamma\langle P_{xy}(\mathbf{\Gamma})\rangle_\infty \geqslant 0. \tag{37}$$

Namely, the averaged power $\langle\dot{W}\rangle_\infty$ needed to sustain the shear flow must be positive (or zero). This is one of the results, which can be checked by numerical simulation, as will actually be shown in Sec. V A. It may be noted that the inequality (37) implies the non-negativity of the viscosity η as a special case.

IV. THERMODYNAMICS FOR SHEAR FLOWS

As discussed in Sec. III D, the factor $\exp\{-\beta\gamma\mathcal{V}\int_{t_0}^t ds\tilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)\}$, which gives the difference between the distribution $\tilde{f}(\mathbf{\Gamma},t)$ and the canonical distribution $f(\mathbf{\Gamma})$, includes the effect of the work needed to sustain the shear flow, or the house-keeping heat. On the other hand, the expression for the first law of thermodynamics proposed by Evans and Hanley does not include this effect (otherwise it must include time-dependent terms for the sustaining work and the house-keeping heat). Moreover, Ref. [6] emphasized that we must subtract the contribution of the house-keeping heat from the entropy in order to obtain an expression for the first law of thermodynamics for steady states. Equation (32) implies that the entropy minus the contribution from the house-keeping heat is given by $\langle S\rangle_t-\int_{t_0}^t ds[d\langle S\rangle_s/ds]=\langle S\rangle_t+\beta\gamma\mathcal{V}\int_{t_0}^t ds\langle P_{xy}(\mathbf{\Gamma})\rangle_s=\overline{S}$, which is the entropy defined through the canonical distribution $f(\mathbf{\Gamma})$, not through the distribution $\tilde{f}(\mathbf{\Gamma},t)$. For these reasons (although it may be possible to construct a nonequilibrium steady-state thermodynamics explicitly including the effect of the house-keeping heat), in this section we construct a shear flow thermodynamics based on the canonical distribution $f(\mathbf{\Gamma})$ excluding the effect of the house-keeping heat, and show that it is consistent with the Evans-Hanley thermodynamics.

A. First law of thermodynamics

As the first thermodynamic property of the shear flow system, we consider the first law of thermodynamics. In the shear flow system, using Eq. (16) we obtain the relation

$$\overline{H^{(mov)}} = \overline{H^{(ine)}} - \gamma\overline{Q}, \tag{38}$$

which connects the average energies $\overline{H^{(mov)}}$ and $\overline{H^{(ine)}}$ in the two different frames $\mathcal{F}^{(mov)}$ and $\mathcal{F}^{(ine)}$, respectively. The entropy $\overline{S}$ based on the canonical distribution $f(\mathbf{\Gamma})$ is given by

$$\overline{S} = \ln\Xi + \beta\overline{H^{(mov)}} \tag{39}$$

$$=\ln\Xi + \beta[\overline{H^{(ine)}} - \gamma\overline{Q}] \tag{40}$$

using Eqs. (11), (19), and (31). The free energy $F^{(mov)}$ in the moving frame $\mathcal{F}^{(mov)}$ is introduced as

$$F^{(mov)} \equiv \overline{H^{(mov)}} - T\overline{S} \tag{41}$$

$$=-T\ln\Xi, \tag{42}$$

where we used Eq. (39) to derive Eq. (42). [Here, it may be noted that the free energy $F^{(mov)}$ can also be expressed as $F^{(mov)}=\langle H^{(mov)}(\mathbf{\Gamma})\rangle_t - T\langle S\rangle_t$ using the averaged energy $\langle H^{(mov)}(\mathbf{\Gamma})\rangle_t$ and entropy $\langle S\rangle_t$ related to the distribution $\tilde{f}(\mathbf{\Gamma},t)$ which includes information about the house-keeping heat.] Similarly, the free energy $F^{(ine)}$ in the inertial frame $\mathcal{F}^{(ine)}$ is also introduced as

$$F^{(ine)} \equiv \overline{H^{(ine)}} - T\overline{S} \tag{43}$$

$$=F^{(mov)} + \gamma\overline{Q} \tag{44}$$

$$=-T\left(\ln\Xi - \gamma\frac{\partial\ln\Xi}{\partial\gamma}\right) \tag{45}$$

using Eqs. (40) and $\partial\ln\Xi/\partial\gamma=\beta\overline{Q}$. Equation (44) connects the free energies $F^{(mov)}$ and $F^{(ine)}$ in the two different frames

$\mathcal{F}^{(mov)}$ and $\mathcal{F}^{(ine)}$, respectively. Using Eqs. (42) and (45), the free energies $F^{(mov)}$ and $F^{(ine)}$ can be calculated directly from the partition function Ξ.

Noting the definition of the partition function $\Xi \equiv \int d\mathbf{\Gamma}\ \exp\{-\beta H^{(mov)}\} = \int d\mathbf{\Gamma}\ \exp\{-\beta[H^{(ine)} - \gamma \mathcal{Q}]\}$ including the two parameters $T(=\beta^{-1})$ and γ explicitly, Eq. (42) implies that the free energy $F^{(mov)}$ is a function of the temperature T and the shear rate γ: $F^{(mov)} = F^{(mov)}(T,\gamma)$. Actually, by Eq. (42) we obtain

$$\frac{\partial[\beta F^{(mov)}]}{\partial \beta} = -\frac{\partial \ln \Xi}{\partial \beta} = \overline{H^{(mov)}}, \tag{46}$$

$$\frac{\partial[\beta F^{(mov)}]}{\partial \gamma} = -\frac{\partial \ln \Xi}{\partial \gamma} = -\beta \overline{Q}, \tag{47}$$

which are summarized as

$$d[\beta F^{(mov)}] = \overline{H^{(mov)}} d\beta - \beta \overline{Q} d\gamma. \tag{48}$$

Inserting Eqs. (41) and $d\beta = -T^{-2} dT$ into Eq. (48), we obtain

$$dF^{(mov)} = -\overline{S} dT - \overline{Q} d\gamma, \tag{49}$$

where the free energy $F^{(mov)}$ is an explicit function of T and γ. Equations (44) and (49) lead to

$$dF^{(ine)} = -\overline{S} dT + \gamma d\overline{Q}. \tag{50}$$

Equations (49) and (50) are also equivalent to

$$d\overline{H^{(mov)}} = T d\overline{S} - \overline{Q} d\gamma, \tag{51}$$

$$d\overline{H^{(ine)}} = T d\overline{S} + \gamma d\overline{Q}, \tag{52}$$

using the relations (41) and (43). The second term on the right-hand side of Eq. (51) can also be derived from the relation $\partial H^{(mov)}(\mathbf{\Gamma})/\partial\gamma = -Q(\mathbf{\Gamma})$ from Eq. (16), therefore $\partial \overline{H^{(mov)}}/\partial\gamma|_{\overline{S}} = -\overline{Q}$ under an adiabatic process. It is clear that the Evans-Hanley expression (1) for the first law of shear flow thermodynamics is the relation (51), where $\mathcal{E} = \overline{H^{(mov)}}$ and $\xi = -\overline{Q}$.

From Eq. (51), the energy $\overline{H^{(mov)}}$ in the moving frame $\mathcal{F}^{(mov)}$ is regarded as a function of $\overline{S}$ and γ, while the energy $\overline{H^{(ine)}}$ in the inertial frame $\mathcal{F}^{(ine)}$ is a function of $\overline{S}$ and $\overline{Q}$ by Eq. (51). The two energies $\overline{H^{(ine)}}$ and $\overline{H^{(mov)}}$ in the different frames are connected by a Legendre transformation, namely $\overline{H^{(ine)}} = \overline{H^{(mov)}} - \gamma \partial \overline{H^{(mov)}}/\partial\gamma|_{\overline{S}}$, as well as the two free energies in the different frames. Using Eq. (52), we obtain $\partial\overline{S}/\partial\overline{H^{(ine)}}|_{\overline{Q}} = 1/T$ and $\partial\overline{S}/\partial\overline{Q}|_{\overline{H^{(ine)}}} = -\gamma/T$ by regarding the entropy $\overline{S}$ as a function of $\overline{H^{(ine)}}$ and $\overline{Q}$. Therefore, the thermodynamic variable conjugate to the averaged Helfand moment of viscosity $\overline{Q}$ is the minus inverse temperature times the shear rate $-\gamma/T$, like the fact that the thermodynamic variable conjugate to the energy $\overline{H^{(ine)}}$ is the inverse temperature $1/T$. After all, thermodynamic functions such as the free energy $F^{(mov)}$ are calculated from the partition function Ξ, and by combining them with the first law of thermodynamics we can calculate thermodynamic quantities, for example the Helfand moment of viscosity $\overline{Q} = -\partial F^{(mov)}/\partial\gamma|_T$ and the entropy $\overline{S} = -\partial F^{(mov)}/\partial T|_\gamma$, and their relations including the equation of state are as in equilibrium thermodynamics.

B. Thermodynamic stability conditions

As the second thermodynamic property of the shear flow system, we consider a stability condition for shear flow [65]. We consider a small part $\mathcal{A}$ of the macroscopic shear flow system, in which averages of energy, entropy, and Helfand's moment of viscosity in the inertial frame $\mathcal{F}^{(ine)}$ are given by $\overline{H^{(ine)}}$, $\overline{S}$, and $\overline{Q}$, respectively. The other part $\mathcal{R}$ of the system, which is much bigger than the system $\mathcal{A}$ and is called the "environment" or "reservoir," has the thermodynamic values T_0, $\overline{S_0}$, and γ_0 of the temperature, the entropy, and the shear rate, respectively. Now, we consider moving an infinitesimal amount of energy as heat $-T_0 d\overline{S_0}$ from the reservoir $\mathcal{R}$ into the small system $\mathcal{A}$. In this process, the total entropy must increase: $d\overline{S} + d\overline{S_0} \geqslant 0$. By combining this inequality with the first law of thermodynamics $d\overline{H^{(ine)}} = -T_0 d\overline{S_0} + \gamma_0 d\overline{Q}$ based on Eq. (52), we have $d\overline{H^{(ine)}} - T_0 d\overline{S} - \gamma_0 d\overline{Q} = d(\overline{H^{(ine)}} - T_0 \overline{S} - \gamma_0 \overline{Q}) \leqslant 0$, using the fact that the reservoir $\mathcal{R}$ is so big that T_0 and γ_0 do not change in this process. This inequality means that the quantity $\overline{H^{(ine)}} - T_0\overline{S} - \gamma_0\overline{Q}$ always decreases and reaches a minimum in a stable state. In other words, if we force a change to the values of $\overline{H^{(ine)}}$, $\overline{S}$, and $\overline{Q}$ at the stable point by $\delta\overline{H^{(ine)}}$, $\delta\overline{S}$, and $\delta\overline{Q}$, respectively, then the inequality $\delta\overline{H^{(ine)}} - T_0\delta\overline{S} - \gamma_0\delta\overline{Q} \geqslant 0$ must be satisfied as the stability condition for the shear flow system. This simply leads to

$$\delta^2 \overline{H^{(ine)}} \geqslant 0 \tag{53}$$

for any infinitesimal deviations $\delta\overline{S}$ and $\delta\overline{Q}$. By a well known technique used in thermodynamics (see, for example, Ref. [58] or Appendix D), the condition (53) is equivalent to

$$\left.\frac{\partial \overline{S}}{\partial T}\right|_{\overline{Q}} > 0, \tag{54}$$

$$\left.\frac{\partial \overline{Q}}{\partial \gamma}\right|_{T} > 0. \tag{55}$$

The condition (54) simply means that the specific heat at constant $\overline{Q}$ is always positive at a positive temperature T. To understand the condition (55) we note

$$\left.\frac{\partial \overline{Q}}{\partial \gamma}\right|_{T} = \beta(\overline{Q^2} - \overline{Q}^2) \tag{56}$$

as shown in Appendix D. Therefore, combining Eq. (56) with the inequality (55), we obtain

$$\overline{Q^2} - \overline{Q}^2 > 0. \tag{57}$$

Namely, the stability condition (55) means the positivity of the correlation function for Helfand's moment $Q(\mathbf{\Gamma})$ of viscosity.

Based on Eq. (1), Evans and Hanley claimed the inequality $\partial\xi/\partial\gamma|_T > 0$ as a stability condition for shear flows [31,32]. This inequality is incompatible with the inequality (55) in the case of $\xi = -\overline{Q}$. This difference comes basically from the fact that they discussed a thermodynamic stability condition using the energy $\overline{H^{(mov)}}$, whereas we discussed it using the energy $\overline{H^{(ine)}}$. Obviously, the correlation function of Q cannot be negative because of $\overline{Q^2} - \overline{Q}^2 = \overline{(Q-\overline{Q})^2} \geqslant 0$, so noting Eq. (56) we cannot justify the stability condition claimed by Evans and Hanley in the canonical distribution approach.

C. Relations between canonical averages

So far we have introduced two types of canonical average $\overline{X}$ and $\langle X\rangle_t$, and in Sec. V we introduce the usual time average. It is very important to distinguish between these averages. The thermodynamic relations discussed in Secs. IV A and IV B are the relations for the ensemble average $\overline{X}$ of observable $X(\mathbf{\Gamma})$ using the canonical distribution $f(\mathbf{\Gamma})$. On the other hand, in numerical simulations using the Sllod equations with an isokinetic thermostat (as in Sec. V), the values obtained are the mixed ensemble-time average $\langle X\rangle_t$ for the distribution $\tilde{f}(\mathbf{\Gamma},t)$ in the limit $t\to\infty$. Therefore, it is important to obtain an explicit relation between these two different ensemble averages.

For any function $X(\mathbf{\Gamma})$, the relation between the two ensemble averages $\overline{X}$ and $\langle X\rangle_\infty$ is

$$\langle X\rangle_\infty = \overline{X} - \beta\gamma\mathcal{V}\int_{t_0}^{\infty} dt\overline{[\tilde{X}(\mathbf{\Gamma},t) - \overline{X}][P_{xy}(\mathbf{\Gamma}) - \overline{P_{xy}}]}, \quad (58)$$

where $\tilde{X}(\mathbf{\Gamma},t) \equiv \exp\{i\hat{L}^{(ine)}(t-t_0)\}X(\mathbf{\Gamma})$. The derivation of Eq. (58) is given in Appendix E. A similar equation for the canonical distribution approach using the Sllod equations is shown in Ref. [53].

From relation (58), if the fluctuation $\tilde{X}(\mathbf{\Gamma},t) - \overline{X}$ of X is weakly correlated to the shear stress $P_{xy}(\mathbf{\Gamma})$, then the ensemble average $\overline{X}$ can be nicely approximated by the average $\langle X\rangle_\infty$. However, notice that the justification for such an approximation strongly depends on the choice of the quantity X. A typical example is the case of $X = P_{xy}(\mathbf{\Gamma})$, in which we must not neglect the second term on the right-hand side of Eq. (58), because in this case the first term on the right-hand side of Eq. (58) is zero, namely $\overline{P_{xy}} = 0$, as shown in Appendix B. One should also notice that the second term in Eq. (58) is small near equilibrium, because it includes the nonequilibrium parameter γ as a factor.

V. NUMERICAL SIMULATIONS OF SHEAR FLOW

In this section, we show numerical results for some quantities which have appeared in the preceding Secs. III and IV, and we check the results obtained there.

For this numerical calculation, we use a two-dimensional square system of N particles with side length $L(=\sqrt{\mathcal{V}})$. The particle-particle interaction is given by the isotropic soft-core pair potential

$$\phi(r) = \begin{cases} \kappa\left(\dfrac{1}{r^{12}} - \dfrac{1}{r_0^{12}}\right) & \text{in } r < r_0 \\ 0 & \text{in } r \geqslant r_0 \end{cases} \quad (59)$$

with $r_0 = 1.5$ and $\kappa = 1$. The particle number density $\rho \equiv N/\mathcal{V}$ is 0.8. The mass m of the particle and the kinetic temperature T are both chosen as 1. The number of particles is $N = 450$, except in Sec. V D, where the N dependence of quantities will be discussed. We use the Sllod equations with Lees-Edwards boundary conditions and the Gaussian isokinetic thermostat so that the kinetic temperature [given by Eq. (22)] is kept constant [20]. A fourth-order predictor-corrector method [66] is used to carry out these numerical simulations with a time step of $\Delta t = 0.001$. In this algorithm, the sum of the "thermal momentum" $\tilde{\mathbf{P}}_j \equiv \mathbf{p}_j - m\mathbf{V}(\mathbf{q}_j)$ is zero in both coordinate directions.

We use the notation $\langle X\rangle$ for the time-averaged value of any quantity X given by this numerical simulation. To calculate this average, we used data over more than 10^6 time steps omitting the first 10^4 time steps. (We checked that 10^4 time steps is much longer than the relaxation time of the time-correlation function for the thermal momentum.) This should correspond to the ensemble average $\langle X\rangle_\infty$ used so far. This is supposed by the fact that we can calculate the viscosity from the time average $\langle P_{xy}\rangle$ in this simulation, based on Eq. (27) assuming $\langle P_{xy}\rangle_\infty = \langle P_{xy}\rangle$. We calculate γ dependences of three quantities: $\langle P_{xy}\rangle$, $\langle Q\rangle$, and $\langle Q^2\rangle$. We use $\langle P_{xy}\rangle$ to discuss the power to sustain the flow and the house-keeping heat given by Eq. (33). The quantities $\langle Q\rangle$ and $\langle Q^2\rangle$ are used to discuss the behavior of Helfand's moment of viscosity and the thermodynamic stability condition (55). Here, it is assumed that the quantities Q and P_{xy} are not strongly correlated with each other because of the relation (18), and in the case of $X = Q$ or Q^2 the second term on the right-hand side of Eq. (58) may be small compared to the first term in the small shear rate case. This implies that the behavior of the time averages of Helfand's moment of viscosity and its correlation function are not so different from the ones for $\overline{Q}$ and $\overline{Q^2} - \overline{Q}^2$, respectively, near equilibrium.

A. Work needed to sustain the shear flow

The first numerical result is for the power $\dot{W}/\mathcal{V}$ per unit volume ($\mathcal{V} = 562.499\cdots$) for the work required to sustain the shear flow, or equivalently, the house-keeping heat per unit volume. It is given as the time average of $\dot{W}/\mathcal{V} \equiv -\gamma P_{xy}(\Gamma)$, based on Eqs. (33) and (34). Figure 2 shows the shear rate γ dependence of the time-averaged power $\langle\dot{W}\rangle/\mathcal{V}$ per unit volume. The inset is the same graph except showing it in a wider shear rate region. (Note that we used a linear-log scale in this inset, whereas we use a linear-linear scale for the main figure.) Following from the inequality (37), the power to sustain the flow shown in Fig. 2 is always positive (or zero).

It may be noted that the average power $\langle\dot{W}\rangle$ needed to sustain the shear flow should be an even function of γ, be-

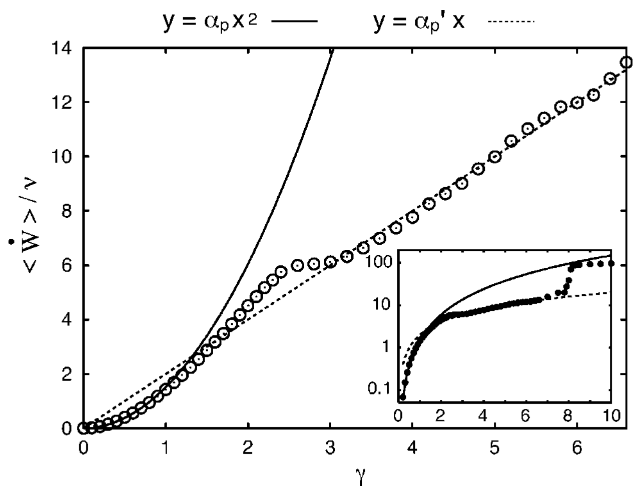

FIG. 2. The average power per unit volume $\langle\dot{W}\rangle/\mathcal{V}$ needed to sustain the shear flow, as a function of shear rate γ as a linear-linear plot. The solid line is the fit to a quadratic function and the dashed line is the fit to a linear function (valid for $\gamma>3$). Inset: the same graph as a linear-log plot including a wider range of γ.

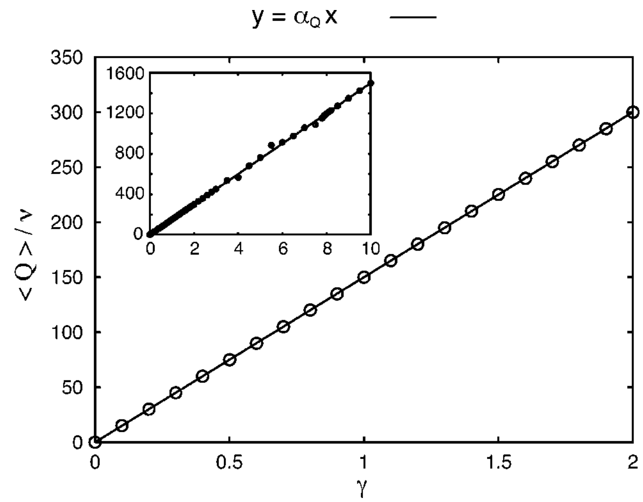

FIG. 3. Time average of Helfand's moment of viscosity per unit volume $\langle Q\rangle/\mathcal{V}$ as a function of shear rate γ. The solid line is the fit to a linear function. Inset: the same graph including a wider range of γ.

cause it should be invariant under a change in sign of the shear rate γ. In Fig. 2, we fitted the numerical data to a quadratic function $y=\alpha_P x^2$ with the fitting parameter $\alpha_P=1.513\,09$. Near equilibrium $\gamma<0.5$, the graph is nicely fitted by this quadratic function. As the shear rate increases, a region in which the value of $\langle P_{xy}(\Gamma)\rangle$ is almost independent of γ (namely the region fitted by a linear function $y=\alpha_P' x$ with the fitting parameter $\alpha_P'=2.000\,05$) appears [15], and after that the string phase region appears [14–16] (the region $\gamma>8$ approximately in the inset to Fig. 2). The string phase can be checked not only by the string-type arrangement of particle positions, but also by the strong time-oscillating behavior of the time-correlation functions for quantities such as the potential energy, the shear stress, and so on [16]. For an isokinetic thermostat, the house-keeping heat is also given as the time average of the thermostat term. We checked numerically that this quantity is equal to the time average of $-\gamma P_{xy}(\Gamma)$.

B. Helfand's moment of viscosity

Figure 3 shows the graph of the time average of Helfand's moment of viscosity per unit volume $\langle Q\rangle/\mathcal{V}$ as a function of shear rate γ. It (almost) takes the value 0 at equilibrium $\gamma=0$, and increases linearly as a function of γ. In this figure, we also give a fit to a linear function $y=\alpha_Q\gamma$, with the parameter value $\alpha_Q=150.043$.

To explain this linear behavior for Helfand's moment of viscosity as a function of shear rate, we simply note that

$$\langle Q\rangle = \sum_{j=1}^{N}\langle q_{jy}\tilde{p}_{jx}\rangle + \gamma\sum_{j=1}^{N}\langle q_{jy}^2\rangle \tag{60}$$

with the x component $\tilde{p}_{jx}\equiv p_{jx}-\gamma q_{jy}$ of the thermal momentum of the jth particle. Our numerical calculations show that the value of the first term on the right-hand side of Eq. (60) is extremely small (or zero) compared to the value of its second term, namely $\sum_{j=1}^{N}\langle q_{jy}\tilde{p}_{jx}\rangle\approx 0$. Moreover, using a homogeneous continuum assumption for the fluid, the value of the quantity $\sum_{j=1}^{N}\langle q_{jy}^2\rangle$ appearing in the second term on the right-hand side of Eq. (60) can be estimated as $\sum_{j=1}^{N}\langle q_{jy}^2\rangle\approx NL^{-1}\int_0^L dy y^2=NL^2/3$. These estimations lead to $\langle Q\rangle/\mathcal{V}\approx(N/3)\gamma=150\gamma$, which explains the value of the fitting parameter α_Q.

The time-averaged Helfand's moment of viscosity $\langle Q\rangle$ should be at least an odd function of shear rate γ, because the infinitesimal deviation $\gamma\overline{dQ}$ giving the energy change $\overline{dH^{(ine)}}$ in the inertial frame by Eq. (52) must be invariant under the change of sign of the shear rate. It may be noted that this linear dependence for the time average of Helfand's moment Q of viscosity with respect to shear rate is satisfied not only in the near-equilibrium region but also even in the string phase region, shown in the inset to Fig. 3, possibly because the Sllod equations are a homogeneous shear algorithm.

It may be noted that in our simulations, Helfand's moment of viscosity can change discontinuously in time, when a particle steps over a boundary in the direction orthogonal to the global shear flow. However, it should be a small boundary effect which can be neglected in the thermodynamic limit $N\to\infty$ and $\rho=$const, and our numerical calculations gave a good convergence for the long time average of Helfand's moment of viscosity.

C. Correlation function for Helfand's moment of viscosity

As the last example, Fig. 4 shows the shear rate dependence of the correlation function $(\langle Q^2\rangle-\langle Q\rangle^2)/\mathcal{V}$ of Helfand's moment of viscosity divided by the volume $\mathcal{V}$. This figure shows that this correlation function is always positive at least for $\gamma<10$, consistent with the thermodynamic stability condition (55).

The correlation function for Helfand's moment of viscosity should be an even function of the shear rate. Noting this

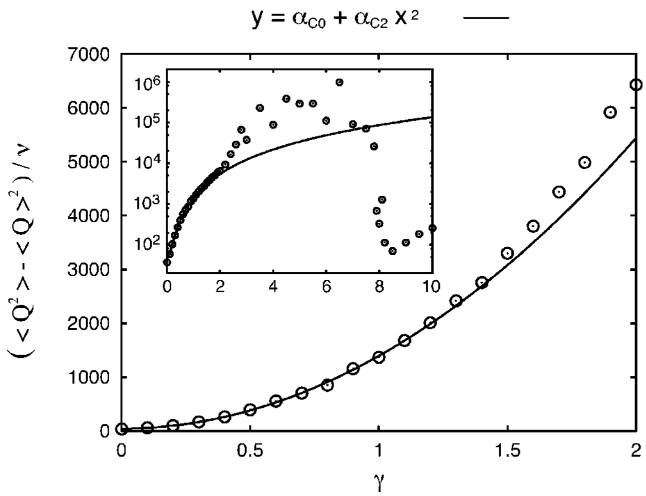

FIG. 4. Correlation function $(\langle Q^2\rangle - \langle Q\rangle^2)/\mathcal{V}$ of Helfand's moment of viscosity per unit volume as a function of shear rate γ in a linear-linear plot. The solid line is the fit to a quadratic function. The inset: the same graph except that it includes a wider region of γ and is a linear-log plot.

point, in the small shear rate region of Fig. 4 we give the fit of numerical data to the function $y=\alpha_{C0}+\alpha_{C2}x^2$ with the fitting parameter values $\alpha_{C0}=46.749$ and $\alpha_{C2}=1349.38$. The graph is nicely fitted by this quadratic function in the small shear rate region. This point may be explained by noting

$$\langle Q^2\rangle - \langle Q\rangle^2 \approx \sum_{j=1}^{N}\sum_{k=1}^{N}\langle q_{jy}q_{ky}\tilde{p}_{jx}\tilde{p}_{kx}\rangle + \gamma^2\sum_{j=1}^{N}\sum_{k=1}^{N}(\langle q_{jy}^2 q_{ky}^2\rangle - \langle q_{jy}^2\rangle\langle q_{ky}^2\rangle) \quad (61)$$

using the thermal momentum component $\tilde{p}_{jx}$. Here we assumed that the time average of the linearly dependent terms for the thermal momentum can be neglected. As the two terms $\Sigma_{j=1}^{N}\Sigma_{k=1}^{N}\langle q_{jy}q_{ky}\tilde{p}_{jx}\tilde{p}_{kx}\rangle$ and $\Sigma_{j=1}^{N}\Sigma_{k=1}^{N}\Sigma_{j=1}^{N}\langle q_{jy}^2 q_{ky}^2\rangle$ can be considered γ-independent, the correlation $\langle Q^2\rangle - \langle Q\rangle^2$ can be fitted by a quadratic function of γ.

In the inset to Fig. 4, we give the shear rate dependence of the time average of the correlation function for Helfand's moment of viscosity per unit volume in a much wider region of shear rate on a linear-log scale. (Note that we used a linear-linear scale in the main figure of Fig. 4.) It should be noted that a rapid drop of the value of this correlation function occurs in the string phase region. In the intermediate region, which is approximately the region $2.5<\gamma<8$ in Fig. 4, between the region fitted by the quadratic function of γ and the string phase region, fluctuations in the value $\langle Q^2\rangle - \langle Q\rangle^2$ become much larger than in the other regions, and their values in Fig. 4 are less reliable.

D. Remarks in connection with the isokinetic thermostat dynamics and the canonical distribution approach

Sllod dynamics with the isokinetic thermostat is regularly used to simulate shear flows. It is supposed to reproduce the value of shear stress predicted by a canonical distribution approach [51], and succeeded to reproduce some real experimental values [12]. However, we note that, strictly speaking, the time average from Sllod dynamics with the isokinetic thermostat does not always reproduce the ensemble average for the nonequilibrium canonical distribution used in this paper, even in the equilibrium state where $\gamma=0$ after taking the thermodynamic limit $N\to\infty$ (and $\rho=$const). Now we discuss a couple of examples illustrating these ensemble differences.

First, in the numerical simulations used in this section, the sum of the thermal momentum $\tilde{\mathbf{p}}_j \equiv (\tilde{p}_{jx},\tilde{p}_{jy}) \equiv \mathbf{p}_j - m\mathbf{V}(\mathbf{q}_j)$ over particle number j in each direction is zero at all times, meaning that there is a constraint on the values of the thermal momenta, that is, $\Sigma_{j=1}^{N}\tilde{p}_{jx}=0$. On the other hand, in the canonical distribution approach, all components of momenta can be treated as independent variables. This difference, for example, causes the different averaged values for $\Sigma_{j=1}^{N}\Sigma_{k=1}^{N}\langle\tilde{p}_{jx}\tilde{p}_{kx}\rangle$ and $\Sigma_{j=1}^{N}\Sigma_{k=1}^{N}\overline{\tilde{p}_{jx}\tilde{p}_{kx}}$. Actually, the value of $\Sigma_{j=1}^{N}\Sigma_{k=1}^{N}\langle\tilde{p}_{jx}\tilde{p}_{kx}\rangle = \langle(\Sigma_{j=1}^{N}\tilde{p}_{jx})(\Sigma_{k=1}^{N}\tilde{p}_{kx})\rangle$ is zero as each bracketed sum is individually zero. The value of $\Sigma_{j=1}^{N}\Sigma_{k=1}^{N}\overline{\tilde{p}_{jx}\tilde{p}_{kx}}$, however, is given by mNT in the canonical distribution because of $\overline{\tilde{p}_{jx}\tilde{p}_{kx}}=mT\delta_{jk}$.

Second, the isokinetic thermostat used here keeps the kinetic energy constant so that the distribution of kinetic energy is a δ function. This is different from the distribution of kinetic energy in the canonical distribution, where there is always a nonzero fluctuation of the kinetic energy around its mean value. References [67,68] modify the distribution to give consistency with the isokinetic thermostat, but it is not obvious that we can justify the shear flow thermodynamics based on such a modified distribution.

As a concrete example of these ensemble differences, let us consider the first term $\tilde{\Psi}_{xy} \equiv \Sigma_{j=1}^{N}\Sigma_{k=1}^{N}\langle q_{jy}q_{ky}\tilde{p}_{jx}\tilde{p}_{kx}\rangle|_{\gamma=0}$ appearing on the right-hand side of Eq. (61) at equilibrium $\gamma=0$. Assuming that the variables q_{jy} and $\tilde{p}_{jx}$ are independent, and that $\langle q_{jy}q_{ky}\rangle$ only depends upon whether $j=k$ or $j\neq k$, then

$$\sum_{j=1}^{N}\sum_{k=1}^{N}\langle q_{jy}q_{ky}\tilde{p}_{jx}\tilde{p}_{kx}\rangle \approx \langle q_{1y}^2\rangle\sum_{j=1}^{N}\langle\tilde{p}_{jx}^2\rangle + \langle q_{1y}q_{2y}\rangle\sum_{j=1}^{N}\sum_{k=1(k\neq j)}^{N}\langle\tilde{p}_{jx}\tilde{p}_{kx}\rangle. \quad (62)$$

If q_{1y} is uniformly distributed between 0 and L, then $\langle q_{1y}^2\rangle \approx L^2/3$ and $\langle q_{1y}q_{2y}\rangle \approx L^2/4$. Now, if this time average appearing in the quantity $\tilde{\Psi}_{xy}$ in Sllod dynamics could be replaced by its ensemble average in the canonical distribution $f(\Gamma)$, then the average value $\tilde{\Psi}_{xy}$ should be equal to $\overline{\Psi}_{xy} \equiv mT\Sigma_{j=1}^{N}\langle q_{jy}^2\rangle|_{\gamma=0}$ because of $\overline{\tilde{p}_{jx}\tilde{p}_{kx}}=0$ in $j\neq k$ for the canonical average. However, the quantities $\tilde{\Psi}_{xy}$ and $\overline{\Psi}_{xy}$ actually take different values, because the time average $\Sigma_{j\neq k}\langle\tilde{p}_{jx}\tilde{p}_{kx}\rangle$ is not zero but takes the value $-\Sigma_{j=1}^{N}\langle\tilde{p}_{jx}^2\rangle$. It follows that $\overline{\Psi}_{xy}\approx mNTL^2/3$ and $\tilde{\Psi}_{xy}\approx mNTL^2/12$, so $\Phi_{xy} \equiv |\tilde{\Psi}_{xy}-\overline{\Psi}_{xy}|/\overline{\Psi}_{xy}\approx 3/4$. Figure 5 is the graph of the normalized difference Φ_{xy} as a function of system size N for square

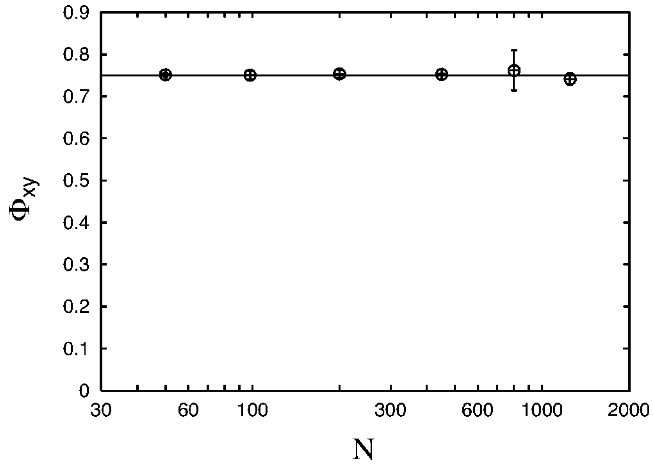

FIG. 5. Time-averaged quantity $\Phi_{xy} \equiv |\tilde{\Psi}_{xy} - \overline{\Psi_{xy}}| / \overline{\Psi_{xy}}$ as a function of particle number N for Sllod dynamics with an isokinetic thermostat in a square at equilibrium $\gamma=0$ with the particle density $\rho=0.8$ as a log-linear plot. Here $\tilde{\Psi}_{xy}$ and $\overline{\Psi_{xy}}$ are defined by $\tilde{\Psi}_{xy} \equiv \Sigma_{j=1}^{N}\Sigma_{k=1}^{N} \langle q_{jy}q_{ky}\tilde{p}_{jx}\tilde{p}_{kx}\rangle|_{\gamma=0}$ and $\overline{\Psi_{xy}} \equiv mT\Sigma_{j=1}^{N} \langle q_{jy}^2\rangle|_{\gamma=0}$, respectively. The length of error bars in this figure is given by $2|\Phi_{xy} - \Phi_{yx}|$. The solid line is the value 3/4, which is explained in the text.

systems at fixed density $\rho=0.8$. The length of error bars in this figure is given by $2|\Phi_{xy} - \Phi_{yx}|$, which must be zero in the square cases. Figure 5 suggests that Φ_{xy} is in excellent agreement with the value of 3/4 given above.

VI. CONCLUSION AND REMARKS

In this paper, we have discussed a canonical distribution approach to nonequilibrium steady-flows and constructed a steady-state thermodynamics from solid statistical mechanical foundations. Using the Lagrangian technique of classical mechanics, we introduced the energy in the moving frame by separating the velocity of the global steady flow. A canonical distribution based on this internal energy was introduced. Our special concern was to describe steady shear flows and their thermodynamics based on this canonical distribution approach. Evans and Hanley proposed a first law of thermodynamics of the form $d\mathcal{E}=TdS-\mathcal{Q}d\gamma$ relating energy $\mathcal{E}$, temperature T, entropy S, and shear rate γ. Here we derived this shear flow thermodynamics based on our canonical distribution approach, and showed that the quantity $\mathcal{Q}$ is given by the average of Helfand's moment of viscosity, the temperature T is the kinetic temperature derived from the thermal kinetic energy, and $\mathcal{E}$ can be interpreted as an internal energy. We show the consistency of our approach with the Kawasaki distribution from which the linear-response formula for viscosity is derived. The work required to sustain the shear flow and the heat removed to compensate it (the house-keeping heat) were discussed. We introduced a nonequilibrium entropy, and showed that it increases in time and the house-keeping heat based on this entropy has the same magnitude as the power needed to sustain the steady flow. This discussion led to the non-negativity of average of $-\gamma P_{xy}$, where P_{xy} is the shear stress, meaning that the power needed to sustain the shear flow and the house-keeping heat is always non-negative. Our first law of thermodynamics for steady shear flows does not include the effect of the house-keeping heat. We discussed the thermodynamic stability condition for the shear flows, one of which is equivalent to the positivity of the correlation function of Helfand's moment of viscosity. Our results were investigated in numerical simulations of two-dimensional many-particle systems with soft-core interactions, with Sllod equations and an isokinetic thermostat.

Our interest in this paper was to apply the canonical distribution approach using the moving frame Hamiltonian to steady shear flow systems. On the other hand, this approach is also applicable to rotating systems, as briefly discussed in Appendix A. We summarize the similarities and differences between these two systems in the canonical distribution approach. Both of these systems are steady flows whose magnitude is proportional to a component of position vector: the distance from the rotating axis in the rotating system or the position component orthogonal to the flow in the shear system. Both systems have parameters to characterize their currents: the angular velocity ω in the rotating flow and the shear rate γ in the shear flow. In the rotating flow, the response function for the internal energy $\overline{H^{(\mathrm{mov})}}$ with respect to the angular velocity ω is minus the average of the total angular momentum $\mathbf{M}$, while in shear flow the response function of the internal energy with respect to the shear rate γ is minus the averaged Helfand moment of viscosity $\overline{Q}$. On the other hand, we must also emphasize some differences between these two systems. The biggest difference is that the total angular momentum $\mathbf{M}$ of the rotating flow is a conserved quantity, whereas Helfand's moment of viscosity Q appearing in the shear flow is not constant in time and its time derivative gives the shear stress P_{xy} (times volume of the system). Physically speaking, this difference comes from the fact that we need work to sustain the steady current in the shear flow, whereas such work is not necessary in the rotational system. Because of this conserved total momentum in the rotating flow, the nonequilibrium canonical distribution $\tilde{f}(\Gamma,t)$ coincides with the canonical distribution $f(\Gamma)$ itself. In addition, the relation $\langle X(\Gamma)\rangle_t=\overline{X(\Gamma)}$ for any function $X(\Gamma)$ is satisfied. This means that the nonequilibrium canonical distribution $\tilde{f}(\Gamma,t)$ is stationary in time, not only in the moving frame but also in the inertial frame. In shear flow systems, such simple relations are not satisfied. In shear flow, the nonequilibrium canonical distribution $\tilde{f}(\Gamma,t)$ is not stationary in time in the inertial frame, and is given by a Kawasaki distribution, which is the canonical distribution function $f(\Gamma)$ multiplied by the factor $\exp\{-\beta\gamma\mathcal{V}\int_{t_0}^{t} ds\tilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)\}$. This point plays an essential role in a derivation of the response formula for viscosity in the shear flow. Moreover, this multiplicative factor in the distribution function $\tilde{f}(\mathbf{\Gamma},t)$ includes information about the work needed to sustain steady flow and the house-keeping heat. The comparison between rotating systems and shear flow systems in the canonical distribution approach is also summarized in Table I.

One may notice that the canonical distribution approach discussed in this paper can be generalized to more general steady flows than the rotating system and the shear flow

TABLE I. Comparison between rotating flows and shear flows in the canonical distribution approach.

	Rotating flow	Shear flow
Nonequilibrium parameter ζ	angular velocity ω	shear flow γ
Response function to ζ	angular momentum M $[i\hat{\mathcal{L}}^{(ine)}\mathbf{M}(\Gamma)=0]$	Helfand moment of viscosity Q $[i\hat{\mathcal{L}}^{(ine)}Q(\Gamma)=\mathcal{V}P_{xy}(\Gamma)]$
Global current $\mathbf{V}(\mathbf{q}_j)$	$\omega\times\mathbf{q}_j$	$\gamma q_{jy}\mathbf{i}_x$
Canonical distribution $f(\Gamma)$	$\Xi^{-1}\exp\{-\beta[H^{(ine)}(\Gamma)-\omega\cdot\mathbf{M}(\Gamma)]\}$	$\Xi^{-1}\exp\{-\beta[H^{(ine)}(\Gamma)-\gamma Q(\Gamma)]\}$
Nonequilibrium distribution $\overline{f}(\Gamma,t)$	$f(\Gamma)$	$f(\Gamma)\exp\{-\beta_\gamma\mathcal{V}\int_{t_0}^{t}ds\widetilde{P}_{xy}(\Gamma,-s+2t_0)\}$
First law of thermodynamics	$d\overline{H^{(mov)}}=Td\overline{S}-\overline{\mathbf{M}}\cdot d\omega$	$d\overline{H^{(mov)}}=Td\overline{S}-\overline{Q}d\gamma$

system. One of the restrictions in our canonical distribution approach is that we have to know the global velocity distribution $\mathbf{V}$ *a priori*. In this sense, this approach is not appropriate to determine the global velocity distribution under some external constraints, etc. It is also crucial that we know *a priori* an external parameter that specifies the amount of the global flow, like the angular velocity or the shear rate. This parameter is treated as a thermodynamic quantity in the expression for the first law of thermodynamics.

An important future problem in shear flow thermodynamics using this approach is to discuss the changes in the pressure. References [30–33] introduced the pressure $\mathcal{P}$ simply by adding the term $-\mathcal{P}d\mathcal{V}$ on the right-hand side of Eq. (1). For this term, it was conjectured that the pressure $\mathcal{P}$ would be equal to the minimum eigenvalue of the pressure tensor [35]. However, one should notice that nonequilibrium systems such as the shear flow system are not generally isotropic, so that the pressure defined by $-\partial\mathcal{E}/\partial\mathcal{V}$ may depend on the direction in which we change the volume $\mathcal{V}$. Actually, as shown in Fig. 6, the numerical simulations using Sllod dynamics in Sec. V show that the time averages of $P_{xx}(\mathbf{\Gamma}')$ and $P_{yy}(\mathbf{\Gamma}')$ are different from each other at nonzero shear rate. [Here $\mathbf{\Gamma}'$ is the "thermal phase-space vector" given by replacing the momentum $\mathbf{p}_j$ with the thermal momentum $\tilde{\mathbf{p}}_j \equiv \mathbf{p}_j - m\mathbf{V}(\mathbf{q}_j)$ in the phase-space vector $\mathbf{\Gamma}$.] Noting that usually the pressure is calculated by the arithmetic average of these time averages (or ensemble averages) (see Ref. [20], also Ref. [42] for its justification using the microcanonical distribution), this suggests that if the pressures in the x and the y directions are given by averages of $P_{xx}(\mathbf{\Gamma}')$ and $P_{yy}(\mathbf{\Gamma}')$, respectively, then the pressure is direction-dependent in shear flow systems. The quantity $\langle P_{xx}(\mathbf{\Gamma}')\rangle - \langle P_{yy}(\mathbf{\Gamma}')\rangle$ is called the "normal stress" and a nonzero value is one of the important properties of viscoelastic fluids [9,20,72]. Therefore, it is important to understand whether such a property is compatible with the thermodynamic framework discussed in this paper, in other words to discuss the first law of thermodynamics in which the averages $\overline{P_{xx}(\mathbf{\Gamma}')}$ and $\overline{P_{yy}(\mathbf{\Gamma}')}$ are included as the x and y components of the pressure, respectively. It may be noted that a similar question can be asked for rotating flows. We leave discussion of these points for the future.

As mentioned in Sec. IV C, the thermodynamic relations, Eqs. (52) and (57) derived in this paper, are relations for the ensemble average (11) under the canonical distribution $f(\mathbf{\Gamma})$. On the other hand, the numerical calculations discussed in Sec. V give the average (26) under the distribution $\tilde{f}(\mathbf{\Gamma},\infty)$. Although these two averages are related by Eq. (58), it is still an open question to calculate the canonical average (11), required for the thermodynamic relations, from the dynamical evolved canonical average (26) in numerical calculations.

Originally, Evans and Hanley introduced their shear flow thermodynamics to discuss the nonanalytical properties of the pressure, viscosity, and the internal energy as functions of the shear rate. Such nonanalytical properties are predicted by mode-coupling theory [41,69], and are supported by some numerical calculations [20,70,71]. However, recently some numerical works suggest that the shear rate dependence of the pressure is analytic near equilibrium, except close to the triple point [12,13]. Moreover, even at the triple point, the nonanalytic dependence of the pressure is not completely convincing [10]. It may also be noted that some theories that predict an analytic dependence of the pressure and the viscosity with respect to the shear rate have been proposed [4,10,72]. In this sense, it is still an interesting problem to discuss shear rate dependences of the pressure, the viscosity, and so on using shear flow thermodynamics.

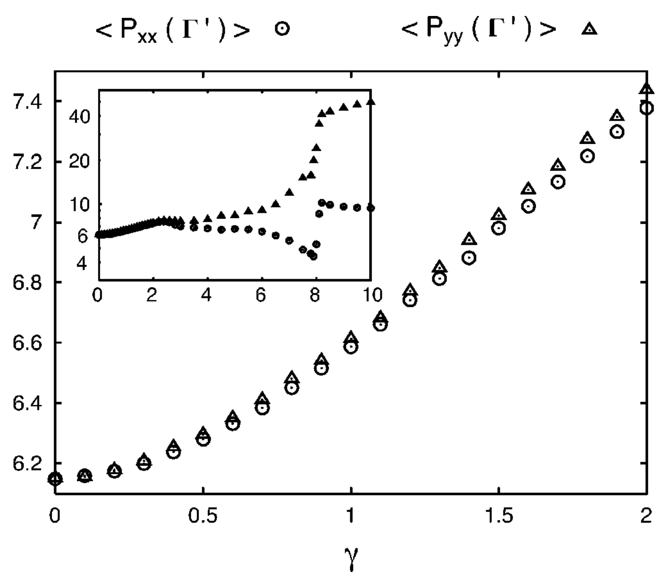

FIG. 6. Time averages of the diagonal components $\langle P_{xx}(\mathbf{\Gamma}')\rangle$ (circles) and $\langle P_{yy}(\mathbf{\Gamma}')\rangle$ (triangles) of the pressure tensor with the thermal phase-space vector $\mathbf{\Gamma}'$ as functions of shear rate γ in Sllod dynamics with an isokinetic thermostat in a linear-linear plot. The inset: the same graph except for including a wider region of shear rate and in a linear-log plot.

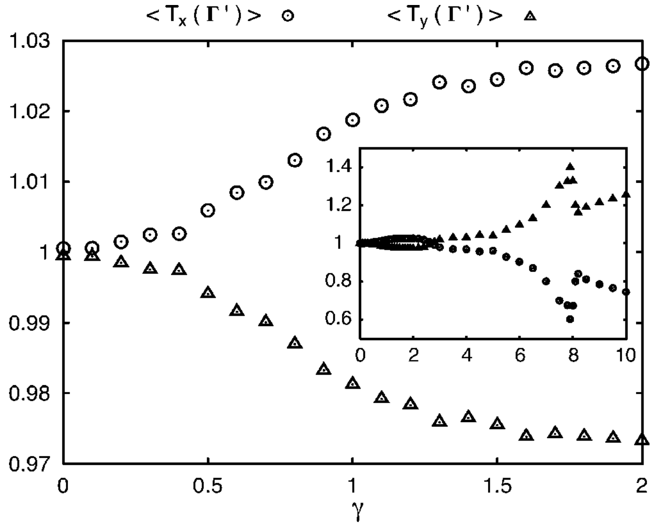

FIG. 7. x component $\langle T_x(\mathbf{\Gamma}')\rangle$ (circles) and y component $\langle T_y(\mathbf{\Gamma}')\rangle$ (triangles) of the kinetic temperature with the thermal phase-space vector $\mathbf{\Gamma}'$ as functions of shear rate γ in the Sllod dynamics with the isokinetic thermostat. The inset: the same graph except for including a wider range of shear rate.

There are also questions about the numerical simulations of shear flow themselves, from the point of view of the canonical distribution approach. Some such problems were already mentioned in Sec. V D. As another potential problem, we mention the direction dependence of the thermal kinetic energy. To discuss this point, we introduce the quantities $T_x(\mathbf{\Gamma}')$ and $T_y(\mathbf{\Gamma}')$ as $T_k(\mathbf{\Gamma}')\equiv(2/N)\Sigma_{j=1}^N\tilde{p}_{jk}^2/(2m)$ with the thermal momentum component $\tilde{p}_{jk}\equiv p_{jk}-mV_k(\mathbf{q}_j)$, where V_k is the k component of the global current density $\mathbf{V}$. The arithmetic average of ensemble averages of $\{T_k(\mathbf{\Gamma}')\}_k$ over the component k gives the kinetic temperature, so we may interpret the quantity $T_k(\mathbf{\Gamma}')$ as the observable for the "k component of the temperature." The canonical distribution approach discussed in this paper claims that the ensemble average $\overline{T_k(\mathbf{\Gamma}')}$ of the quantity $T_k(\mathbf{\Gamma}')$ is k-independent, in other words the kinetic temperature is direction-independent, although we should note a difference in the two averages $\overline{T_k(\mathbf{\Gamma}')}$ and $\langle T_k(\mathbf{\Gamma}')\rangle_\infty$. Figure 7 shows the graphs of $\langle T_x(\mathbf{\Gamma}')\rangle$ and $\langle T_y(\mathbf{\Gamma}')\rangle$ as functions of shear rate γ from numerical simulations using the Sllod dynamics with an isokinetic thermostat, used in Sec. V. This figure shows that the kinetic temperature is direction-dependent at least in large shear rate cases. As a related point, we note that the isokinetic thermostat removes heat from any component of kinetic energy of any particle uniformly. This is a great simplification in the formula and numerical calculations and preserves a similar dynamical structure to Hamiltonian dynamics leading to the numerical observation of the conjugate pairing rule for the Lyapunov spectrum [73], but its physical justification as a mechanical thermostat is not completely convincing. For example, one may use other types of thermostats in which the heat is removed from the particles near the walls or from the kinetic energy component orthogonal to the walls [74,75]. These different thermostats might give, for example, different values of $\langle T_x(\mathbf{\Gamma}')\rangle$ and $\langle T_y(\mathbf{\Gamma}')\rangle$ from the isokinetic thermostat. Checking the shear flow thermodynamics for such types of thermostat remains an open problem.

ACKNOWLEDGMENTS

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APPENDIX A: CANONICAL DISTRIBUTION APPROACH TO ROTATING FLOWS

In this appendix, we give a derivation of the well known canonical distribution and the thermodynamics for uniformly rotating flows, based on the formalism given in Sec. II. The detailed derivation of them is quite similar to that for the shear flow system discussed in Secs. III A, III B, and IV A in the text of this paper, so it is given rather briefly.

We consider a rotating flow with a constant angular velocity vector ω. We assume that the Hamiltonian $H^{(ine)}(\mathbf{\Gamma})$ is invariant under rotation about the axis of rotation. In this appendix, the origin of the spatial coordinates and the axis of rotation is taken at the center of mass of the system. Under these conditions, the global velocity distribution function $\mathbf{V}$ is given by

$$\mathbf{V}(\mathbf{q}_j) = \omega \times \mathbf{q}_j, \quad \text{(A1)}$$

where $\times$ is the usual vector product. Using Eq. (A1), relation (7) is rewritten as [57,58]

$$H^{(mov)}(\mathbf{\Gamma}) = H^{(ine)}(\mathbf{\Gamma}) - \boldsymbol{\omega}\cdot\mathbf{M}(\mathbf{\Gamma}) \quad \text{(A2)}$$

with the total angular momentum $\mathbf{M}(\mathbf{\Gamma})\equiv\Sigma_{j=1}^N\mathbf{q}_j\times\mathbf{p}_j$. In comparison with shear flow systems discussed in Sec. III it is important to note that the total angular momentum $\mathbf{M}(\mathbf{\Gamma})$ is conserved in the inertial frame $\mathcal{F}^{(ine)}$, namely

$$i\hat{\mathcal{L}}^{(ine)}\mathbf{M}(\mathbf{\Gamma}) = 0. \quad \text{(A3)}$$

Because of this conserved property of the total angular momentum, this global velocity distribution $\mathbf{V}$ can be sustained without any external effect in isolated systems. Using Eqs. (10) and (A2), the canonical distribution for the rotating flow is represented as [58]

$$f(\mathbf{\Gamma}) = \Xi^{-1}\exp\{-\beta[H^{(ine)}(\mathbf{\Gamma}) - \boldsymbol{\omega}\cdot\mathbf{M}(\mathbf{\Gamma})]\}. \quad \text{(A4)}$$

The distribution (A4) is stationary, namely $i\hat{\mathcal{L}}^{(ine)}f(\mathbf{\Gamma}) = i\hat{\mathcal{L}}^{(mov)}f(\mathbf{\Gamma})=0$, in both frames $\mathcal{F}^{(mov)}$ and $\mathcal{F}^{(ine)}$. The distribution (A4) has the general form (2) of the canonical distribution in the case that $H(\mathbf{\Gamma})=H^{(ine)}(\mathbf{\Gamma})$, $\tilde{n}=\tilde{d}$, and $A_j(\mathbf{\Gamma})$ is the component of $\mathbf{M}(\mathbf{\Gamma})$, and $\mu_j(\mathbf{\Gamma})$ is the component of $-\omega$ in the $\tilde{d}$-dimensional system. It is valuable to note that from the canonical distribution (A4) we can derive the distribution function $f'(\mathbf{v}^{(mov)},\mathbf{q})$ for the position $\mathbf{q}$ and the velocity $\mathbf{v}^{(mov)}$ in the moving frame $\mathcal{F}^{(mov)}$ as

$$f'(\mathbf{v}^{(mov)},\mathbf{q}) = \Xi^{-1}\exp\left\{-\beta\left[\sum_{j=1}^{N}\frac{1}{2}m[\mathbf{v}_j^{(mov)}]^2 + U(\mathbf{q}) + u_c(\mathbf{q})\right]\right\} \tag{A5}$$

using Eq. (6), where $u_c(\mathbf{q})$ is given by $u_c(\mathbf{q}) \equiv -\sum_{j=1}^{N} m\omega^2 r_j^2/2$ with $r_j \equiv |\omega\times\mathbf{q}_j|/|\omega|$. The function $f'(\mathbf{v}^{(mov)},\mathbf{q})$ is the distribution for a rotating flow including explicitly the effect of the centrifugal potential $u_c(\mathbf{q})$. We cannot derive the distribution (A5) from the distribution (12).

Now we discuss the first law of thermodynamics for rotating flows. Using Eq. (A2), we obtain the relation

$$\overline{H^{(mov)}} = \overline{H^{(ine)}} - \boldsymbol{\omega}\cdot\overline{\mathbf{M}}. \tag{A6}$$

The entropy $\overline{S} \equiv -\overline{\log\{f(\boldsymbol{\Gamma})\}}$ is given by

$$\overline{S} = \ln\Xi + \beta\overline{H^{(mov)}} \tag{A7}$$

using Eq. (A4). Using Eq. (A7), the free energy $F^{(mov)} \equiv \overline{H^{(mov)}} - T\overline{S}$ in the moving frame $\mathcal{F}_{(mov)}$ is given by

$$F^{(mov)} = -T\ln\Xi. \tag{A8}$$

Similarly, the free energy $F^{(ine)} \equiv \overline{H^{(ine)}} - T\overline{S}$ in the inertial frame $\mathcal{F}^{(ine)}$ is given by $-T[\ln\Xi - \omega\cdot(\partial\ln\Xi/\partial\omega)]$ and is connected to the moving frame free energy $F^{(mov)}$ as

$$F^{(ine)} = F^{(mov)} + \boldsymbol{\omega}\cdot\overline{\mathbf{M}}. \tag{A9}$$

Using Eq. (A8), we obtain $\partial[\beta F^{(mov)}]/\partial\beta = \overline{H^{(mov)}}$ and $\partial[\beta F^{(mov)}]/\partial\omega = -\beta\overline{\mathbf{M}}$, namely $d[\beta F^{(mov)}] = \overline{H^{(mov)}}d\beta - \beta\overline{\mathbf{M}}\cdot d\omega$, which leads to

$$dF^{(mov)} = -\overline{S}dT - \overline{\mathbf{M}}\cdot d\boldsymbol{\omega}. \tag{A10}$$

Noting the relations (A6) and (A9), and $\overline{H^{(mov)}} = F^{(mov)} + T\overline{S}$, Eq. (A10) is also equivalent to

$$dF^{(ine)} = -\overline{S}dT + \boldsymbol{\omega}\cdot d\overline{\mathbf{M}}. \tag{A11}$$

$$d\overline{H^{(mov)}} = Td\overline{S} - \overline{\mathbf{M}}\cdot d\boldsymbol{\omega}, \tag{A12}$$

$$d\overline{H^{(ine)}} = Td\overline{S} + \boldsymbol{\omega}\cdot d\overline{\mathbf{M}}. \tag{A13}$$

The relation (A13) is the first law of thermodynamics for the rotating flow, which is well known [58].

APPENDIX B: RESPONSE FORMULA FOR THE VISCOSITY FROM THE CANONICAL DISTRIBUTION APPROACH

In this appendix, we give a derivation of the linear-response formula (28) for viscosity from the definition (27), as well as a derivation of Eq. (29). We also discuss the two kinds of nonlinear response formulas for $\langle P_{xy}(\boldsymbol{\Gamma})\rangle_\infty$ with respect to the shear rate γ, one of which is a simple generalization of the formula (28).

First we note that the partition function Ξ can be rewritten as

$$\begin{aligned}\Xi &\equiv \int d\boldsymbol{\Gamma}\,\exp\{-\beta H^{(mov)}(\boldsymbol{\Gamma})\}\\ &= \int d\boldsymbol{\Gamma}\,\exp\{-i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}\exp\{-\beta H^{(mov)}(\boldsymbol{\Gamma})\}\\ &= \int d\boldsymbol{\Gamma}\,\exp\{-\beta H^{(mov)}(\boldsymbol{\Gamma})\}\\ &\quad\times\exp\left\{-\beta\gamma\mathcal{V}\int_{t_0}^{t} ds\tilde{P}_{xy}(\boldsymbol{\Gamma},-s+2t_0)\right\},\end{aligned} \tag{B1}$$

or equivalently

$$\overline{\exp\left\{-\beta\gamma\mathcal{V}\int_{t_0}^{t} ds\tilde{P}_{xy}(\boldsymbol{\Gamma},-s+2t_0)\right\}} = 1, \tag{B2}$$

where we used the definition of the average (11) and the relations $\exp\{-i\hat{\mathcal{L}}^{(\mathrm{ine})}(t-t_0)\}1=1$, $(i\hat{\mathcal{L}}^{(\mathrm{ine})})^\dagger = -i\hat{\mathcal{L}}^{(\mathrm{ine})}$ († meaning to take its Hermitian conjugate), and a similar derivation to that in Eq. (24). Equation (B1) means that both the distributions $f(\boldsymbol{\Gamma})$ and $\tilde{f}(\boldsymbol{\Gamma},t)$ are normalized with the same partition function Ξ. The partition function Ξ given by Eq. (B1) must be time-independent, so that we obtain

$$\begin{aligned}0 = \frac{\partial\Xi}{\partial t} &= -\beta\gamma V\int d\boldsymbol{\Gamma}\tilde{P}_{xy}(\boldsymbol{\Gamma},-t+2t_0)\exp\{-\beta H^{(mov)}(\boldsymbol{\Gamma})\}\\ &\qquad\times\exp\left\{-\beta\gamma\mathcal{V}\int_{t_0}^{t} ds\tilde{P}_{xy}(\boldsymbol{\Gamma},-s+2t_0)\right\}\\ &= -\beta\gamma\mathcal{V}\Xi\int d\boldsymbol{\Gamma}\tilde{P}_{xy}(\boldsymbol{\Gamma},-t+2t_0)\\ &\qquad\times\exp\{-i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}f(\boldsymbol{\Gamma})\\ &= -\beta\gamma\mathcal{V}\Xi\int d\boldsymbol{\Gamma}\,\exp\{-i\hat{\mathcal{L}}(t-t_0)\}P_{xy}(\boldsymbol{\Gamma})f(\boldsymbol{\Gamma})\\ &= -\beta\gamma\mathcal{V}\Xi\overline{P_{xy}(\boldsymbol{\Gamma})}\end{aligned} \tag{B3}$$

noting the average (11). From Eq. (B3) we obtain Eq. (29), implying that the viscosity calculated from the canonical distribution $f(\boldsymbol{\Gamma})$ is zero.

On the other hand, using the average (26) from the distribution $\tilde{f}(\boldsymbol{\Gamma},t)$ given by Eq. (24) we have

$$\begin{aligned}\langle P_{xy}(\mathbf{\Gamma})\rangle_{\infty} &= \lim_{t\to\infty}\int d\mathbf{\Gamma} P_{xy}(\mathbf{\Gamma}) f(\mathbf{\Gamma}) \exp\left\{-\beta\gamma\mathcal{V}\int_{t_0}^{t} ds \widetilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)\right\} \\ &= \int d\mathbf{\Gamma} P_{xy}(\mathbf{\Gamma}) f(\mathbf{\Gamma}) - \beta\gamma\mathcal{V}\int_{t_0}^{\infty} ds \int d\mathbf{\Gamma} P_{xy}(\mathbf{\Gamma}) f(\mathbf{\Gamma}) \widetilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0) + \mathcal{O}(\gamma^2) \\ &= \overline{P_{xy}(\mathbf{\Gamma})} - \beta\gamma\mathcal{V}\int_{t_0}^{\infty} ds \int d\mathbf{\Gamma} P_{xy}(\mathbf{\Gamma}) f^{(eq)}(\mathbf{\Gamma}) \widetilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0) + \mathcal{O}(\gamma^2) \\ &= -\beta\gamma\mathcal{V}\int_{t_0}^{\infty} ds \int d\mathbf{\Gamma} P_{xy}(\mathbf{\Gamma}) f^{(eq)}(\mathbf{\Gamma}) \exp\{-i\hat{\mathcal{L}}^{(ine)}(s-t_0)\} P_{xy}(\mathbf{\Gamma}) + \mathcal{O}(\gamma^2) \\ &= -\beta\gamma\mathcal{V}\int_{t_0}^{\infty} ds \int d\mathbf{\Gamma} [\exp\{i\hat{\mathcal{L}}^{(ine)}(s-t_0)\} P_{xy}(\mathbf{\Gamma}) f^{(eq)}(\mathbf{\Gamma})] P_{xy}(\mathbf{\Gamma}) + \mathcal{O}(\gamma^2) \\ &= -\beta\gamma\mathcal{V}\int_{t_0}^{\infty} ds \langle \widetilde{P}_{xy}(\mathbf{\Gamma},s) P_{xy}(\mathbf{\Gamma})\rangle^{(eq)} + \mathcal{O}(\gamma^2) \end{aligned} \quad \text{(B4)}$$

with the notation $f^{(eq)}(\mathbf{\Gamma}) \equiv \lim_{\gamma\to 0} f(\mathbf{\Gamma})$, where we used Eq. (29), the relation $(i\hat{\mathcal{L}}^{(ine)})^{\dagger} = -i\hat{\mathcal{L}}^{(ine)}$, and $\exp\{i\hat{\mathcal{L}}^{(ine)}(s-t_0)\} f^{(eq)}(\mathbf{\Gamma}) = f^{(eq)}(\mathbf{\Gamma})$. Equation (B4) leads to the linear-response formula (28) for viscosity.

Next, using Eq. (24) we have

$$\frac{\partial \widetilde{f}(\mathbf{\Gamma},t)}{\partial t} = -\beta\gamma\mathcal{V}\widetilde{P}_{xy}(\mathbf{\Gamma},-t+2t_0)\widetilde{f}(\mathbf{\Gamma},t). \quad \text{(B5)}$$

The solution of the time-differential equation (B5) of the function $\widetilde{f}(\mathbf{\Gamma},t)$ with the initial condition

$$\widetilde{f}(\mathbf{\Gamma},t_0) = f(\mathbf{\Gamma}) \quad \text{(B6)}$$

is represented as

$$\widetilde{f}(\mathbf{\Gamma},t) = f(\mathbf{\Gamma}) + \sum_{n=1}^{\infty} (-\beta\gamma\mathcal{V})^n \int_{t_0}^{t} ds_1 \int_{t_0}^{s_1} ds_2 \int_{t_0}^{s_2} ds_3 \cdots \int_{t_0}^{s_{n-1}} ds_n \widetilde{P}_{xy}(\mathbf{\Gamma},-s_1+2t_0)\widetilde{P}_{xy}(\mathbf{\Gamma},-s_2+2t_0)\cdots\widetilde{P}_{xy}(\mathbf{\Gamma},-s_n+2t_0) f(\mathbf{\Gamma}). \quad \text{(B7)}$$

From Eqs. (29) and (B7), we derive

$$\langle P_{xy}(\mathbf{\Gamma})\rangle_{\infty} = \sum_{n=1}^{\infty} (-\beta\gamma\mathcal{V})^n \int_{t_0}^{\infty} ds_1 \int_{t_0}^{s_1} ds_2 \int_{t_0}^{s_2} ds_3 \cdots \int_{t_0}^{s_{n-1}} ds_n \overline{P_{xy}(\mathbf{\Gamma})\widetilde{P}_{xy}(\mathbf{\Gamma},-s_1+2t_0)\widetilde{P}_{xy}(\mathbf{\Gamma},-s_2+2t_0)\cdots\widetilde{P}_{xy}(\mathbf{\Gamma},-s_n+2t_0)}. \quad \text{(B8)}$$

This expresses a nonlinear response formula for an average of the shear stress $P_{xy}(\mathbf{\Gamma})$ with respect to the shear rate γ in the form of its multiple time-correlation function. The formula (28) can be derived directly from Eq. (B8), using the relations $\overline{X(\mathbf{\Gamma})}|_{\gamma=0} = \langle X(\mathbf{\Gamma})|_{\gamma=0}\rangle^{(eq)}$ in any function $X(\mathbf{\Gamma})$ of $\mathbf{\Gamma}$ and $(i\hat{\mathcal{L}}^{(ine)})^{\dagger} = -i\hat{\mathcal{L}}^{(ine)}$. It may be noted that the multitime integral functions on the right-hand side of Eq. (B8) can be γ-dependent because of the γ dependence of the function $f(\mathbf{\Gamma})$, so strictly speaking Eq. (B8) is not an expansion formula for $\langle P_{xy}(\mathbf{\Gamma})\rangle_{\infty}$ with respect to the shear rate γ.

It may be meaningful to show another type of nonlinear response formula for the average of the quantity $P_{xy}(\mathbf{\Gamma})$ with respect to the shear rate γ, using a Green's function $\hat{G}$ defined by

$$\hat{G} \equiv \lim_{\epsilon\to +0} [\hat{\mathcal{L}}^{(ine)} + i\epsilon]^{-1}. \quad \text{(B9)}$$

For this purpose, first we note a formal identity

$$\lim_{t\to+\infty}\exp\{i\hat{\mathcal{L}}^{(ine)}t\} = \lim_{\epsilon\to+0}\epsilon\int_0^{+\infty}dt\,\exp\{-\epsilon t\}\cdot\exp\{i\hat{\mathcal{L}}^{(ine)}t\}$$
$$= \lim_{\epsilon\to+0}\epsilon[\epsilon - i\hat{\mathcal{L}}^{(ine)}]^{-1} = 1 - \hat{G}\hat{\mathcal{L}}^{(ine)}. \tag{B10}$$

Equation (B10) is an analogous technique to that used in quantum scattering theory [76] in which the Hamiltonian operator instead of the Liouville operator $\hat{\mathcal{L}}^{(ine)}$ is used. Using Eq. (B10), we have

$$\langle P_{xy}(\mathbf{\Gamma})\rangle_\infty = \lim_{t-t_0\to\infty}\int d\mathbf{\Gamma} f(\mathbf{\Gamma})\exp\{i\hat{\mathcal{L}}^{(ine)}(t-t_0)\}P_{xy}(\mathbf{\Gamma})$$
$$= \int d\mathbf{\Gamma} f(\mathbf{\Gamma})[1 - \hat{G}\hat{\mathcal{L}}^{(ine)}]P_{xy}(\mathbf{\Gamma})$$
$$= \sum_{n=0}^{\infty}\frac{(\beta\gamma)^n}{n!}\langle[Q(\mathbf{\Gamma})]^n[1 - \hat{G}\hat{\mathcal{L}}^{(ine)}]P_{xy}(\mathbf{\Gamma})\rangle^{(eq)}. \tag{B11}$$

This is the formula which we wanted to derive. It may be noted that the quantity $\langle[Q(\mathbf{\Gamma})]^n[1-\hat{G}\hat{\mathcal{L}}^{(ine)}]P_{xy}(\mathbf{\Gamma})\rangle^{(eq)}$ appearing on the right-hand side of Eq. (B11) is γ-independent, so Eq. (B11) can be regarded as a real expansion of $\langle P_{xy}(\mathbf{\Gamma})\rangle_\infty$ with respect to the shear rate γ, different from the formula (B8). Another merit of the formula (B11) is that we do not have to calculate a time-integral in the interval $[0,\infty]$, which is required in the formula (B8). As a special case of the formula (B11), using Eq. (27) and the fact that zeroth order of the quantity $\langle P_{xy}(\mathbf{\Gamma})\rangle_\infty$ must be zero, we obtain

$$\langle[1 - \hat{G}\hat{\mathcal{L}}^{(ine)}]P_{xy}(\mathbf{\Gamma})\rangle^{(eq)} = 0, \tag{B12}$$

$$\eta = -\beta\langle Q(\mathbf{\Gamma})[1 - \hat{G}\hat{\mathcal{L}}^{(ine)}]P_{xy}(\mathbf{\Gamma})\rangle^{(eq)}. \tag{B13}$$

Equation (B13) is another type of the linear-response formula for the viscosity.

APPENDIX C: SECOND LAW OF THERMODYNAMICS IN THE NONEQUILIBRIUM CANONICAL DISTRIBUTION APPROACH

In this appendix, we give a derivation of the inequality (35) satisfied at any time $t(>t_0)$.

We start our derivation from the inequality

$$x\ln x - x + 1 \geqslant 0 \tag{C1}$$

satisfied by any positive real number x (>0). The equality in Eq. (C1) is satisfied only when $x=1$. Using the inequality (C1) in the case $x=\tilde{f}(\mathbf{\Gamma},t)/f(\mathbf{\Gamma})$, we have

$$\frac{\tilde{f}(\mathbf{\Gamma},t)}{f(\mathbf{\Gamma})}\ln\frac{\tilde{f}(\mathbf{\Gamma},t)}{f(\mathbf{\Gamma})} - \frac{\tilde{f}(\mathbf{\Gamma},t)}{f(\mathbf{\Gamma})} + 1 \geqslant 0, \tag{C2}$$

which is equivalent to

$$\tilde{f}(\mathbf{\Gamma},t)\ln\tilde{f}(\mathbf{\Gamma},t) - \tilde{f}(\mathbf{\Gamma},t)\ln f(\mathbf{\Gamma}) \geqslant \tilde{f}(\mathbf{\Gamma},t) - f(\mathbf{\Gamma}). \tag{C3}$$

Now we note

$$\int d\mathbf{\Gamma}\tilde{f}(\mathbf{\Gamma},t) = \int d\mathbf{\Gamma} f(\mathbf{\Gamma})(=1), \tag{C4}$$

$$\int d\mathbf{\Gamma}\tilde{f}(\mathbf{\Gamma},t)\ln\tilde{f}(\mathbf{\Gamma},t) = \int d\mathbf{\Gamma} e^{-i\hat{\mathcal{L}}^{(ine)}(t-t_0)}[f(\mathbf{\Gamma})\ln f(\mathbf{\Gamma})]$$
$$= \int d\mathbf{\Gamma} f(\mathbf{\Gamma})\ln f(\mathbf{\Gamma}). \tag{C5}$$

By taking an integral with respect to $\mathbf{\Gamma}$ on both sides of the inequality (C3), and by using Eqs. (31), (C4), and (C5) we obtain

$$\int d\mathbf{\Gamma}\tilde{f}(\mathbf{\Gamma},t)S(\mathbf{\Gamma}) \geqslant \int d\mathbf{\Gamma} f(\mathbf{\Gamma})S(\mathbf{\Gamma}). \tag{C6}$$

Using the equation $\overline{S}=\int d\mathbf{\Gamma} f(\mathbf{\Gamma})S(\mathbf{\Gamma})=\langle S\rangle_{t_0}$ in the inequality (C6), we obtain the inequality (35).

APPENDIX D: STABILITY CONDITION FOR THE SHEAR FLOW

In this appendix, we show the equivalence between the condition (53) and the conditions (54) and (55). We also give a derivation of Eq. (56).

Noting that the energy $\overline{H^{(ine)}}$ is the function of $\overline{S}$ and $\overline{Q}$ by Eq. (52), we have

$$\delta T = \delta\frac{\partial\overline{H^{(ine)}}}{\partial\overline{S}} = \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}^2}\delta\overline{S} + \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\delta\overline{Q}. \tag{D1}$$

Using Eq. (D1), we also have

$$\delta\gamma = \delta\frac{\partial\overline{H^{(ine)}}}{\partial\overline{Q}}$$
$$= \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\delta\overline{S} + \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{Q}^2}\delta\overline{Q}$$
$$= \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}^2}\right)^{-1}\left[\delta T - \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\delta\overline{Q}\right] + \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{Q}^2}\delta\overline{Q}$$
$$= \left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}^2}\right)^{-1}\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\delta T$$
$$+ \left[\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{Q}^2} - \left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}^2}\right)^{-1}\left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\right)^2\right]\delta\overline{Q}, \tag{D2}$$

which leads to

$$\left.\frac{\partial\gamma}{\partial\overline{Q}}\right|_T = \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{Q}^2} - \left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}^2}\right)^{-1}\left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\right)^2. \tag{D3}$$

Using Eq. (D1) and (D3), we obtain

$$\begin{aligned}
\delta^2\overline{H^{(ine)}} &= \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}^2}(\delta\overline{S})^2 + 2\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\delta\overline{S}\delta\overline{Q} + \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{Q}^2}(\delta\overline{Q})^2 \\
&= \left(\delta T + \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\delta\overline{Q}\right)\delta\overline{S} + \frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{Q}^2}(\delta\overline{Q})^2 \\
&= \left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}^2}\right)^{-1}(\delta T)^2 + \left[\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{Q}^2} - \left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}^2}\right)^{-1}\left(\frac{\partial^2\overline{H^{(ine)}}}{\partial\overline{S}\partial\overline{Q}}\right)^2\right](\delta\overline{Q})^2 \\
&= \left(\left.\frac{\partial T}{\partial\overline{S}}\right|_{\overline{Q}}\right)^{-1}(\delta T)^2 + \left.\frac{\partial\gamma}{\partial\overline{Q}}\right|_T(\delta\overline{Q})^2. \qquad \text{(D4)}
\end{aligned}$$

The inequality (53) must be satisfied by any infinitesimal deviations δT and $\delta\overline{Q}$, so using Eq. (D4) we obtain the conditions (54) and (55).

Now, using the canonical distribution (19), we calculate the derivative of $\overline{Q}$ with respect to γ at constant temperature T,

$$\begin{aligned}
\left.\frac{\partial\overline{Q}}{\partial\gamma}\right|_T &= \frac{\partial}{\partial\gamma}\Xi^{-1}\int d\mathbf{\Gamma}Q(\mathbf{\Gamma})\exp\{-\beta[H^{(ine)}(\mathbf{\Gamma}) - \gamma Q(\mathbf{\Gamma})]\} \\
&= \beta\Xi^{-1}\int d\mathbf{\Gamma}[Q(\mathbf{\Gamma})]^2\exp\{-\beta[H^{(ine)}(\mathbf{\Gamma}) - \gamma Q(\mathbf{\Gamma})]\} \\
&\quad - \Xi^{-2}\frac{\partial\Xi}{\partial\gamma}\int d\mathbf{\Gamma}Q(\mathbf{\Gamma})\exp\{-\beta[H^{(ine)}(\mathbf{\Gamma}) - \gamma Q(\mathbf{\Gamma})]\} \\
&= \beta(\overline{Q^2} - \overline{Q}^2), \qquad \text{(D5)}
\end{aligned}$$

where we used $\Xi^{-1}\partial\Xi/\partial\gamma = \beta\overline{Q}$. Therefore we obtain Eq. (56).

APPENDIX E: RELATION BETWEEN THE TWO AVERAGES

In this appendix we give a derivation of Eq. (58).

Using the expression (24) for the distribution $\tilde{f}(\mathbf{\Gamma},t)$ used in the average $\langle X(\mathbf{\Gamma})\rangle_t$ for any function $X(\mathbf{\Gamma})$, we have

$$\begin{aligned}
\langle X\rangle_t &= \overline{X} + \langle(X-\overline{X})\rangle_t \\
&= \overline{X} + \int_{t_0}^{t} ds \frac{\partial\langle(X-\overline{X})\rangle_s}{\partial s} \\
&= \overline{X} - \beta\gamma\mathcal{V}\int_{t_0}^{t} ds\langle[X(\mathbf{\Gamma}) - \overline{X}]\tilde{P}_{xy}(\mathbf{\Gamma},-s+2t_0)\rangle_s \\
&= \overline{X} - \beta\gamma\mathcal{V}\int_{t_0}^{t} ds\overline{[\tilde{X}(\mathbf{\Gamma},s) - \overline{X}]P_{xy}(\mathbf{\Gamma})} \\
&= \overline{X} - \beta\gamma\mathcal{V}\int_{t_0}^{t} ds\overline{[\tilde{X}(\mathbf{\Gamma},s) - \overline{X}][P_{xy}(\mathbf{\Gamma}) - \overline{P_{xy}}]}, \qquad \text{(E1)}
\end{aligned}$$

where we used Eqs. (29), $\langle(X-\overline{X})\rangle_{t_0}=0$, and $(i\hat{\mathcal{L}}^{(ine)})^\dagger = -i\hat{\mathcal{L}}^{(ine)}$. By taking the limit $t\to\infty$ in Eq. (E1), we obtain Eq. (58). Concerning Eq. (E1), one may notice

$$\overline{[\tilde{X}(\mathbf{\Gamma},s) - \overline{X}][P_{xy}(\mathbf{\Gamma}) - \overline{P_{xy}}]} = \overline{\tilde{X}(\mathbf{\Gamma},s)P_{xy}(\mathbf{\Gamma})} \qquad \text{(E2)}$$

because of Eq. (29), so the integral function in the second term of the right-hand side of Eq. (E1) can be replaced by the right-hand side of Eq. (E2).

It may also be noted that from Eqs. (29), (E1), and (E2), we can derive a formula for P_{xy} as

$$\langle P_{xy}(\mathbf{\Gamma})\rangle_\infty = -\beta\gamma\mathcal{V}\int_{t_0}^{\infty} dt\overline{\tilde{P}_{xy}(\mathbf{\Gamma},t)P_{xy}(\mathbf{\Gamma})} \qquad \text{(E3)}$$

which is correct in any shear rate γ. The linear-response formula (28) for viscosity is easily derived from Eqs. (27) and (E3).

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[64] The divergence of a nonequilibrium entropy in a steady shear flow in thermostated dynamics has been considered; for example, see Ref. [35]. However, note that the explanation for the entropy divergence in that case is different from that used here.
[65] As a related point, one can notice that the canonical distribution $f(\mathbf{\Gamma})$ can be derived from the extremum condition for the entropy $\overline{S}=-\int d\mathbf{\Gamma} f(\mathbf{\Gamma})\ln f(\mathbf{\Gamma})$ under the constraints of $\overline{H^{(int)}}=\text{const}$, $\overline{Q}=\text{const}$, and $1=\text{const}$. Actually, using the method of Lagrange's undetermined multipliers with constants a_j, $j=1, 2, 3$ we have $0=\delta(\overline{S}+a_1\overline{H^{(int)}}+a_2\overline{Q}+a_3)$, namely, $0=-\ln f(\mathbf{\Gamma})+1+a_1H^{(int)}(\mathbf{\Gamma})+a_2Q(\mathbf{\Gamma})+a_3$. In the case where $a_1=-\beta$, $a_2=\beta\gamma$, and $a_3=-\ln\Xi-1$, we obtain the form (19) for the canonical distribution for shear flow.
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