All- and one-particle distribution functions at nonequilibrium steady state under thermal gradient

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We provide a concrete expression for the phase-space distribution function at nonequilibrium steady state under a constant thermal gradient, which is a typical system of the nonequilibrium molecular dynamics simulation of heat conduction. First, the phase-space distribution function of all particles in a local volume is formulated. Our formulation explicitly takes into account the entropy production due to the change in equilibrium thermodynamic variables in addition to the traditional entropy production described by the spatial gradients and fluxes of equilibrium thermodynamic variables. This treatment is necessary to explain the nonequilibrium response of a quantity that has no equilibrium correlation with mass and heat fluxes and is essential to correctly deduce one-particle distribution functions from the all-particle one. From the all-particle distribution function, we derive the Green–Kubo relations that express the one-particle distribution functions of density and velocity in terms of equilibrium correlation functions and verify these expressions using the molecular dynamics simulation of a Lennard-Jones liquid. These nonequilibrium one-particle distribution functions are sufficiently tractable for practical use, such as for the analytical evaluation of the nonequilibrium average of physical quantities.

I. INTRODUCTION

Nonequilibrium molecular dynamics (NEMD) simulation of heat conduction has been widely used to study the microscopic mechanism of thermal transport properties, including thermal conductivity [1], thermal boundary resistance [2], the Soret coefficient [3,4], etc. In the most common situation, the NEMD analysis is performed in a nonequilibrium steady state under a constant thermal gradient generated by various methodologies [5–9]. The phase-space distribution function of this nonequilibrium state is a crucial factor of the statistical mechanical foundation for such NEMD analysis.

Finding an appropriate phase-space distribution function, which describes the probability of a particular microscopic state appearing in a given thermodynamic state, is a fundamental issue in nonequilibrium statistical mechanics. Various formulations have been proposed for such nonequilibrium distribution functions [10]. The linear response theory [11] describes the linear change in the equilibrium distribution function caused by a small perturbation and offers the Green–Kubo relations, which enable us to derive the linear transport coefficients from equilibrium fluctuations. In addition to other formulations for near equilibrium states [12,13], extensions to nonlinear response or far-from-equilibrium states were made [10,14,15]. Such studies led to an active research field concerning the fluctuation theorem [16,17], and the experimental application of the theorem is currently a hot research topic [18,19]. Efforts have been continued to devise expressions that have higher affinity for experiments and numerical simulations [20–23].

Although these studies expanded the applicability of nonequilibrium statistical mechanics, the concrete expression of a nonequilibrium phase-space distribution function is not sufficiently developed for the steady state of a constant thermal gradient. In particular, a tractable form of the one-particle distribution function as typified by the Maxwell-Boltzmann (MB) velocity distribution function is missing. The linear response theory provides a traditional expression for the distribution function of all particles in this steady state. However, the concrete way to reduce the all-particle distribution function to one-particle ones is discussed here.

The present paper describes how one can achieve this reduction within the linear response regime and provides concrete expressions for the nonequilibrium distribution functions of one-particle density and velocity under a constant thermal gradient. In the rest of the paper, revising our previous theory [24], we first formulate the phase-space distribution function of all particles in a local volume under a thermal gradient. From the all-particle distribution function, we derive the linear responses of the one-particle density and velocity distribution functions in the Green–Kubo form. Finally, these one-particle distribution functions are verified using the MD simulation of a Lennard-Jones (LJ) liquid.

II. THEORY

A. All-particle distribution function for a local volume

As a model of the NEMD system, let us consider a classical system of a single component as in Fig. 1(a) where the number of particles N_{tot}, volume V_{tot}, and internal energy E_{tot} are fixed, and there is no macroscopic particle flow. The system is at an equilibrium state of temperature T_0 for time $t \leqslant 0$, and then for $t > 0$, energy is injected at constant rate into the hot slab and removed at the same rate from the cold slab so that a constant heat flux is imposed without changing E_{tot}. For $t \to \infty$, the system reaches a nonequilibrium steady state where the hot and cold slabs have a higher and a
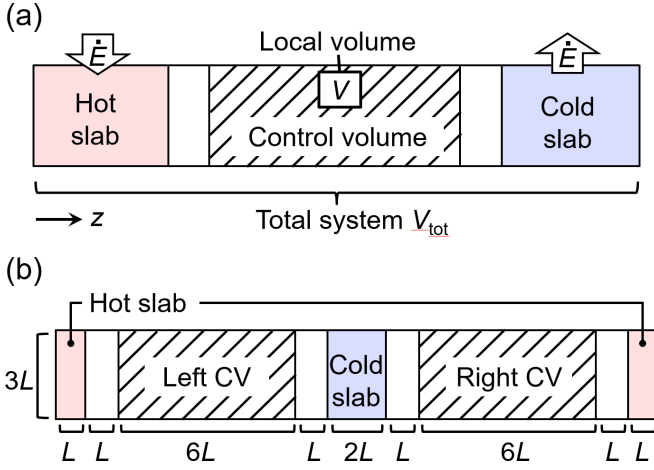
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FIG. 1. (a) Schematic of the system under the thermal gradient. (b) System of our NEMD simulation for the Lennard-Jones liquid. $L = 3.19\sigma$.

FIG. 2. Geometric representation of the entropy production terms on the left hand side and the right hand side of Eq. (2).

lower temperature $T_0 + \Delta T$ and $T_0 - \Delta T$, respectively. We pay attention to a constant local volume V in the control volume (CV), which is a region not involved in and around the hot and cold slabs. The location $\mathbf{r}$ and size V of the local volume are arbitrary as long as they are inside the CV. The local volume is an open system, and the remaining part of the system is seen as the reservoir of energy and particles. Here and hereafter, a variable with respect to the total system and reservoir are denoted by the subscripts "tot" and "res," respectively, otherwise the variable means that of the local volume. We use the notation $X(\Gamma, t)$ for a variable X under the condition that the microstate of the local volume containing N particles is Γ at t, where $\Gamma = \mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N$ is the phase-space coordinates, and $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and momentum vectors of the ith particle, respectively. We note that the argument Γ in $X_{\text{res}}(\Gamma, t)$ or $X_{\text{tot}}(\Gamma, t)$ indicates the microstate of the local volume not those of the reservoir or the total volume. The variation from the initial value is expressed as $\delta X(\Gamma, t) = X(\Gamma, t) - X(\Gamma, 0)$.

Following the previous formulation [24], we consider that the phase-space distribution function in the local volume $f(\Gamma, t)$ is proportional to $\exp[S_{\text{tot}}(\Gamma, t)/k_B]$, where k_B is the Boltzmann constant and $S_{\text{tot}}(\Gamma, t) = S_{\text{res}}(\Gamma, t) + S(\Gamma, t)$ is the entropy of the total system. Since Γ completely specifies the microstate of the local volume, we assume that $S(\Gamma, t) = 0$. Then, the linear approximation for the time variation in $f(\Gamma, t)$ is expressed as

$$\delta f(\Gamma, t) \sim \left[\frac{\delta S_{\text{res}}(\Gamma, t) - \delta S_{\text{tot}}(t)}{k_B} \right] f(\Gamma, 0), \quad (1)$$

where the total entropy production $\delta S_{\text{tot}}(t)$ is defined as $\delta S_{\text{tot}}(t) = \sum_{N=1}^{\infty} \int \delta S_{\text{res}}(\Gamma, t) f(\Gamma, 0) d\Gamma / N!$ so as to satisfy the normalization condition $\int f(\Gamma, t) d\Gamma = 1$.

In order to rewrite $\delta S_{\text{res}}(\Gamma, t)$ in terms of the variables of the local volume, we performed the following decomposition:

$$\delta S_{\text{res}}(\Gamma, t) = \{S_{\text{res}}(\Gamma, t) - S_{\text{res}}[\Gamma(-t), 0]\}$$
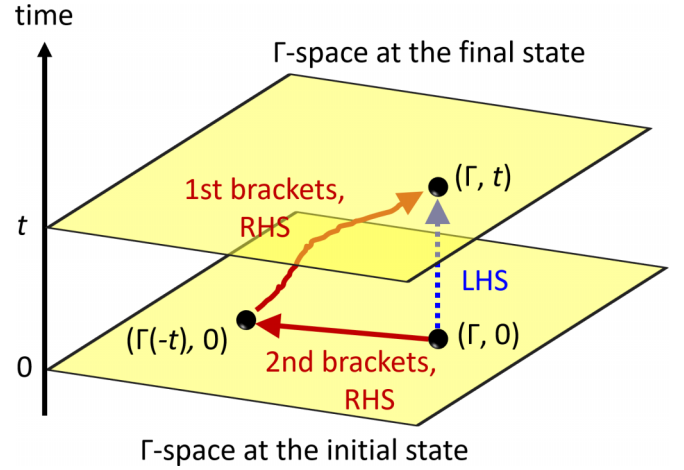$$+ \{S_{\text{res}}[\Gamma(-t), 0] - S_{\text{res}}(\Gamma, 0)\}, \quad (2)$$

where $\Gamma(-t)$ is the phase point that reaches Γ at time t according to the equation of motion under the constant heat flux. The diagram of this decomposition is shown in Fig. 2.

The first curly brackets on the right hand side of Eq. (2) can be interpreted as the amount of entropy acquired by the reservoir along this trajectory. This is equal to the amount of entropy flowing out from the local volume through the volume boundaries, and its rate at a phase point Γ is reasonably given by [25]

$$\nabla \cdot \mathbf{J}_S(\Gamma) V = \sum_{X=E,N} k_B \left[\nabla \beta_{X,\infty}^{\text{res}} \cdot \mathbf{J}_X(\Gamma) V + \beta_{X,\infty}^{\text{res}} \nabla \cdot \mathbf{J}_X(\Gamma) V \right]$$

$$= \sum_{X=E,N} k_B \left[\nabla \beta_{X,\infty}^{\text{res}} \cdot \mathbf{J}_X(\Gamma) V - \beta_{X,\infty}^{\text{res}} \dot{X}(\Gamma) \right], \quad (3)$$

invoking the conservation law $\dot{X} = -\nabla \cdot \mathbf{J}_X V$, where $\mathbf{J}_X$ and $\dot{X}$ are the flux and time derivative of X and β_X is the intensive variable conjugate to X, i.e., $\beta_E = 1/(k_B T)$, $\beta_\mu = -\mu \beta_E$, and μ is the chemical potential.

The β_X of the reservoir and its gradient for $t > 0$ were denoted as $\beta_{X,\infty}^{\text{res}}$ and $\nabla \beta_{X,\infty}^{\text{res}}$, respectively, which are approximated to be independent of time and equal to the β_X and $\nabla \beta_X$ of the local volume at the final state. From the time integration of Eq. (3) along the trajectory from $[\Gamma(-t), 0]$ to (Γ, t), we obtain the expression for the first curly brackets as

$$\{S_{\text{res}}(\Gamma, t) - S_{\text{res}}[\Gamma(-t), 0]\}/k_B$$

$$= \sum_{X=E,N} \nabla \beta_{X,\infty}^{\text{res}} \cdot \int_0^t \mathbf{J}_X[\Gamma(-\tau)] V \, d\tau$$

$$+ \sum_{X=E,N} \beta_{X,\infty}^{\text{res}} \{X[\Gamma(-t)] - X(\Gamma)\}. \quad (4)$$

The second brackets on the right hand side of Eq. (2) are the entropy difference between two microstates in the initial equilibrium state. Using equilibrium thermodynamics and the fact that for $X = E$ and N, $X_{\text{tot}} = X_{\text{res}}(\Gamma) + X(\Gamma)$ is

independent of Γ, we have

$$\{S_{\text{res}}[\Gamma(-t), 0] - S_{\text{res}}(\Gamma, 0)\}\big/k_{\text{B}}$$
$$= \sum_{X=E,N} \beta_{X,0}^{\text{res}}\{X[\Gamma(-t)] - X(\Gamma)\}, \qquad (5)$$

where $\beta_{X,0}^{\text{res}}$ is the β_X of the reservoir for $t \leqslant 0$ and is independent of time. Combining Eqs. (2), (4), and (5), and taking the limit of $t \to \infty$, $\delta S_{\text{res}}(\Gamma, \infty)$ is expressed as

$$\delta S_{\text{res}}(\Gamma, \infty)\big/k_{\text{B}} = \sum_{X=E,N} \nabla \beta_{X,\infty}^{\text{res}} \cdot \int_0^\infty \mathbf{J}_X[\Gamma(-t)]V \, dt$$
$$- \sum_{X=E,N} \delta\beta_{X,\infty}^{\text{res}}\{X(\Gamma) - X[\Gamma(-\infty)]\},$$
$$(6)$$

where $\delta\beta_{X,\infty}^{\text{res}} = \beta_{X,\infty}^{\text{res}} - \beta_{X,0}^{\text{res}}$. Together with Eq. (6), $\delta f(\Gamma, \infty)$ in Eq. (1) describes a general form of the linear response of the local distribution function to thermal gradient. Correspondingly, the linear response $\delta A(\infty) = \langle A \rangle_\infty - \langle A \rangle_0$ of a phase variable $A(\Gamma)$ is given by the ensemble average with $\delta f(\Gamma, \infty)$ as

$$\delta A(\infty) = \int A(\Gamma)\delta f(\Gamma, \infty)d\Gamma$$
$$= \sum_{X=E,N} \nabla \beta_{X,\infty}^{\text{res}} \cdot \int_0^\infty \langle \Delta\mathbf{J}_X(-t)V \Delta A \rangle_0 dt$$
$$- \sum_{X=E,N} \delta\beta_{X,\infty}^{\text{res}} \langle \Delta X \, \Delta A \rangle_0, \qquad (7)$$

where $\langle \ldots \rangle_t$ means the ensemble average with respect to $f(\Gamma, t)$, $\langle \Delta B(-t)\Delta A \rangle_0 = \langle B(-t)A \rangle_0 - \langle B \rangle_0 \langle A \rangle_0$ with $\langle B(-t)A \rangle_0 = \sum_{N=1}^\infty \int B[\Gamma(-t)]A(\Gamma)f(\Gamma, 0)d\Gamma/N!$ is the time correlation function between B and A at the initial equilibrium state, and the short notation $\langle \Delta B \, \Delta A \rangle_0$ is used for the case of no time difference. In addition, we assumed that the correlation vanishes after a long time so that $\langle B(-\infty)A \rangle_0 = \langle B \rangle_0 \langle A \rangle_0$.

In Eq. (6), the first term on the right hand side represents the entropy production associated with the appearance of nonequilibrium thermodynamic variables, i.e., spatial gradients and fluxes, and is referred to as the nonequilibrium term here. The second term in contrast explains the equilibrium part of entropy production, and we call it the equilibrium term. In the traditional linear response formulation [10], the nonequilibrium term only is considered since the main interest there is the transport coefficients, such as thermal conductivity and viscosity, which are correctly described without the equilibrium term. The inclusion of the equilibrium term is, however, essential to explain the response in a variable that has no equilibrium correlation with $\mathbf{J}_X$ and is also necessary for the case where the final state is another equilibrium state of different temperature with $\nabla \beta_{X,\infty}^{\text{res}} = \mathbf{0}$. From the nature of the equilibrium correlation function [26], if A changes sign under time reversal, the equilibrium term vanishes, and Eq. (7) reduces to the Onsager reciprocal relation [27], otherwise the nonequilibrium term vanishes, and Eq. (7) gives the fluctuation formula in equilibrium thermodynamics.

B. One-particle density distribution

Now, in order to derive the one-particle density and velocity distributions, we suppose that β_E and β_N form a constant gradient in the z direction at the final steady state so that the profiles in the CV are given by

$$\beta_{E,\infty}^{\text{res}}(\mathbf{r}) = \frac{1}{k_{\text{B}}T_0} - \frac{\nabla_z T_\infty}{k_{\text{B}}T_0^2}\Delta z, \qquad (8)$$

and

$$\beta_{N,\infty}^{\text{res}}(\mathbf{r}) = -\frac{\mu_0}{k_{\text{B}}T_0} + h_0\frac{\nabla_z T_\infty}{k_{\text{B}}T_0^2}\Delta z, \qquad (9)$$

where $\nabla_z T_\infty$ is the constant temperature gradient, h is the specific enthalpy, $\Delta z = z - z_{\text{c}}$, and z_{c} is the z coordinate in the middle of the CV. The initial equilibrium values are denoted by the subscript 0. In Eq. (9), we utilized the Gibbs-Duhem relation $\nabla_z \beta_N = -h\nabla_z\beta_E$, assuming uniform normal pressure in the z direction. The linear response of the number density $\delta\rho_N(\mathbf{r}, \infty)$ is obtained by applying Eq. (7) to the small local volume at $\mathbf{r}$ together with Eqs. (8) and (9) and choosing ρ_N as A. The result is given by

$$\delta\rho_N(\mathbf{r}, \infty) = \frac{\langle \Delta E \, \Delta\rho_N \rangle_0 - h_0\langle \Delta N \, \Delta\rho_N \rangle_0}{k_{\text{B}}T_0^2}\nabla_z T_\infty \Delta z$$
$$= -\langle\rho_N\rangle_0 \alpha_p \nabla_z T_\infty \Delta z, \,, \qquad (10)$$

where ρ_X is the density of X and α_p is the thermal expansion coefficient at the initial equilibrium state and the second equality can be shown by thermodynamic manipulations [28]. Equation (10) gives the Green–Kubo relation for the one-particle density. This result is also consistent with the consequence of the local equilibrium hypothesis that [29] $\alpha_p = -\nabla_z \ln \rho_N(\mathbf{r}, \infty)/\nabla_z T_\infty$. It is well known that an application of heat flux induces spatial gradient not only in temperature, but also in particle density as can be clearly shown by NEMD simulations [29,30]. However, this response cannot be directly deduced from the all-particle distribution function if Eq. (7) does not contain the equilibrium term since $\mathbf{J}_X$ does not have an equilibrium correlation with ρ_N.

C. One-particle velocity distribution

Next, we consider the response of the one-particle velocity distribution $f(\mathbf{v}, \infty)$, where $\mathbf{v}$ is the one-particle velocity $\mathbf{v} = (v_x, v_y, v_z)$. At the initial equilibrium state, the distribution is given by the MB distribution: $f(\mathbf{v}, 0) = \prod_{\alpha=x,y,z} f(v_\alpha, 0)$, where $f(v_\alpha, 0) = \exp(-\hat{v}_\alpha^2)/(v_{\text{p}}\sqrt{\pi})$, $\hat{v}_\alpha = v_\alpha/v_{\text{p}}$, $v_{\text{p}} = \sqrt{2k_{\text{B}}T_0/m}$, and m is the particle mass. The linear response $\delta f(\mathbf{v}, \infty)$ is formally obtained by integrating out the phase-space coordinates other than $\mathbf{v}$ from $\delta f(\Gamma, \infty)$ as

$$\delta f(\mathbf{v}, \infty) = \frac{1}{m^3}\sum_{N=1}^\infty \frac{1}{N!}\int \delta f(\Gamma, \infty)d\mathbf{r}_1 \cdots d\mathbf{r}_N d\mathbf{p}_2 \cdots d\mathbf{p}_N$$
$$\equiv g(\mathbf{v})f(\mathbf{v}, 0). \qquad (11)$$

We expand the unknown function $g(\mathbf{v})$ in a series of Hermite polynomials as

$$g(\mathbf{v}) = \sum_i \sum_j \sum_k c_{ijk} H_{ijk}(\hat{\mathbf{v}}), \qquad (12)$$

where i, j, and k run through non-negative integers and $H_{ijk}(\hat{\mathbf{v}}) = H_i(\hat{v}_x) H_j(\hat{v}_y) H_k(\hat{v}_z)$. The ith order Hermite polynomial $H_i(\hat{v}_\alpha)$ has $f(v_\alpha, 0)$ as the weight function and fulfills the orthogonalization condition $\int_{-\infty}^{\infty} H_i(\hat{v}_\alpha) H_{i'}(\hat{v}_\alpha) f(v_\alpha, 0) dv_\alpha = \langle H_i(\hat{v}_\alpha) H_{i'}(\hat{v}_\alpha) \rangle_0 = \delta_{ii'} 2^i i!$. This orthogonality gives the coefficient c_{ijk} as

$$c_{ijk} = \frac{\delta H_{ijk}(\infty)}{2^{i+j+k} i! j! k!}, \qquad (13)$$

where $\delta H_{ijk}(\infty)$ is the linear response of $H_{ijk}(\hat{\mathbf{v}})$, which can be evaluated by Eq. (7) choosing $H_{ijk}(\hat{\mathbf{v}})$ as A. Since the equilibrium correlation between velocity and X for $X = N$ or E is zero, only the flux correlation term can make a nonzero contribution to $\delta H_{ijk}(\infty)$. Furthermore, the grand canonical correlation $\langle \Delta J_{X,z} V \, \Delta H_{ijk}(t) \rangle_0$ can be reasonably approximated by the microcanonical correlation $\langle \Delta J_{X,z} V \, \Delta H_{ijk}(t) \rangle_{NVE}$ on the basis of the ensemble transformation theory [31] to vanish the $X = N$ term [24], where $J_{X,z}$ is the z component of $\mathbf{J}_X$. Removing Δ using $\langle J_{E,z} \rangle_{NVE} = 0$ and using the relation $\langle J_{E,z}(-t) V H_{ijk} \rangle_{NVE} = \langle J_{E,z}(t) V H_{ijk} \rangle_{NVE}$, $\delta H_{ijk}(\infty)$ is finally expressed as

$$\delta H_{ijk}(\infty) = -\frac{\nabla_z T_\infty}{k_B T_0^2} \int_0^\infty \langle J_{E,z}(t) V H_{ijk} \rangle_{NVE} dt. \qquad (14)$$

Because the correlation in Eq. (14) gives zero when $n = i + j + k$ is 1 or an even number, the third-order expansion [in a series of $H_{ijk}(\hat{\mathbf{v}})$'s with $n \leqslant 3$] is the lowest nontrivial approximation, and its explicit form is as follows:

$$\delta f(\mathbf{v}, \infty) \sim -\frac{\nabla_z T_\infty}{k_B T_0^2} \left[\frac{d_{201}}{2} H_2(\hat{v}_x) H_1(\hat{v}_z) \right.$$
$$\left. + \frac{d_{021}}{2} H_2(\hat{v}_y) H_1(\hat{v}_z) + \frac{d_{003}}{6} H_3(\hat{v}_z) \right] f(\mathbf{v}, 0), \qquad (15)$$

where

$$d_{lmn} = \int_0^\infty \langle J_{E,z}(t) V \hat{v}_x^l \hat{v}_y^m \hat{v}_z^n \rangle_{NVE} dt. \qquad (16)$$

The distribution function for the x, y, or z component can be obtained by integrating out the other two components. This integration results in $\delta f(v_x, \infty) = \delta f(v_y, \infty) = 0$. Actually, this relation holds for the approximation of an arbitrary order because each term in Eq. (12) must have $H_k(\hat{v}_z)$ with $k \geqslant 3$ for c_{ijk} to be nonzero, but such a function vanishes when integrated with v_z due to the orthogonality of a Hermite polynomial. Thus, in the current formulation, the velocity distribution shows the response only in the gradient direction z, and its third-order approximation is given as follows:

$$\delta f(v_z, \infty) = -\frac{\nabla_z T_\infty}{k_B T_0^2} d_{003} \left[\frac{4}{3} \hat{v}_z^3 - 2\hat{v}_z \right] f(v_z, 0). \qquad (17)$$

The new information necessary for the third-order approximation is d_{003} only. In general, the kth-order approximation only requires $d_{00k'}$'s for $k' \leqslant k$, where k and k' are odd.

III. VALIDATION WITH MD SIMULATION

In order to validate our formulation, the above expressions for the one-particle distribution functions were examined with MD simulations. Specifically, we calculated the one-particle density and velocity distributions by the NEMD simulation of a LJ liquid under the thermal gradient. These distributions were compared with the Green–Kubo relations Eqs. (10) and (17) where the necessary equilibrium correlations were calculated from EMD simulations. All MD simulations were performed using LAMMPS software [32]. In the following, physical quantities are written in LJ units [energy, distance, and time are scaled by the LJ parameters ε, σ, and $\tau = (m/\varepsilon)^{1/2}\sigma$, respectively]. For the NEMD simulation, the MD system contained 4311 LJ particles in the volume of $V_{tot} = 9.571 \times 9.571 \times 63.81\sigma^3$ with the three-dimensional periodic boundary conditions. The actual arrangement of the CVs, hot slab, and cold slab were as shown in Fig. 1(b). Here, in this paper, to make our discussion clear, we refer to the results only for the left half of the MD system (the equivalent results were obtained for the right half). The interaction potential $\phi_{IJ} = 4\varepsilon[(\sigma/r_{IJ})^{12} - (\sigma/r_{IJ})^6]$ with the cutoff distance of 3.217σ was used, where r_{IJ} is the distance between particles I and J. A time step of 0.001485τ was used. The NEMD system was initially brought to an equilibrium state at temperature $T_0 = 0.9074\varepsilon/k_B$. A constant heat flux was then imposed using the enhanced heat exchange algorithm [8] by injecting energy into the hot slab at the constant rate of $dE/dt = 5.04\varepsilon/\tau$ and removing the same amount from the cold slab. The one-particle density and velocity distributions were averaged over 5×10^8 steps after 10^7 steps for equilibration. The velocity distribution was obtained as a spatially averaged value over the entire left CV. That is, the entire left CV was considered as the local volume of temperature T_0 and temperature gradient $\nabla_z T_\infty$. The temperature gradient formed in the NEMD simulation was calculated as $\nabla_z T_\infty = -5.41 \pm 0.02[10^{-3}\varepsilon/(k_B\sigma)]$.
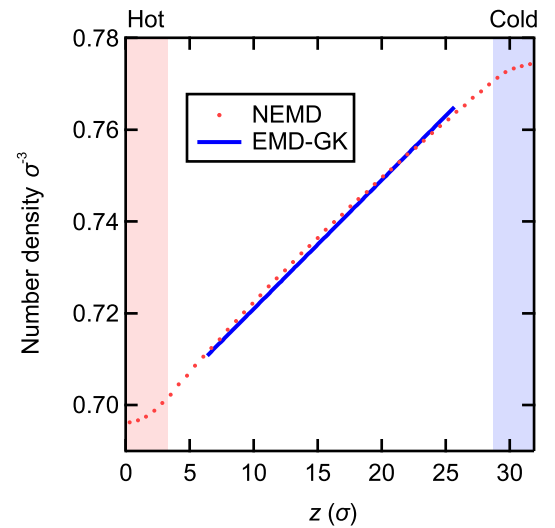

FIG. 3. Number density distribution for a LJ liquid under thermal gradient (for the left half of the MD system), where z is the coordinates in the gradient direction. The result of the NEMD simulation and the prediction by the Green–Kubo relation are compared.
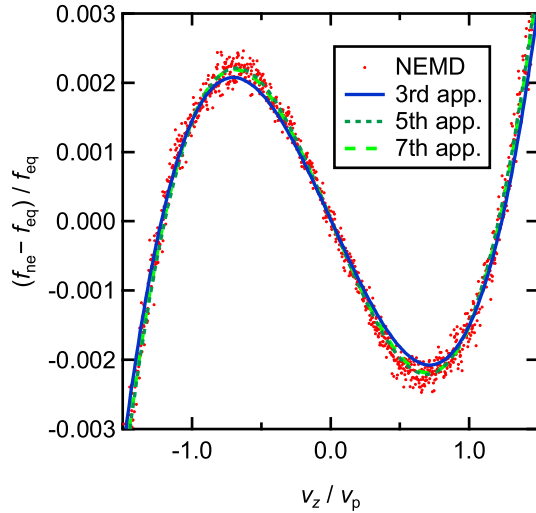
FIG. 4. Velocity distribution f_{ne} for a LJ liquid under thermal gradient as the relative deviation from the Maxwell-Boltzmann distribution f_{eq} (for the left CV). The horizontal axis is the velocity v_z in the gradient direction, scaled by $v_p = \sqrt{2k_B T_0/m}$. The NEMD result and the predictions by the third- to seventh-order Hermite polynomial approximation are compared.

The EMD simulations were performed using the same number density of particles and temperature as those of the NEMD simulation, but a cubic volume of $18.01^3\sigma^3$ was used. After equilibration, we carried out an NpT (isothermal-isobaric) simulation for 10^7 steps from which the thermal expansion coefficient was evaluated as $\alpha_p = 0.71 \pm 0.01 k_B/\varepsilon$ using the fluctuation formula $\alpha_p = \langle \Delta H\, \Delta V \rangle_{NpT}/(k_B T^2 V)$. Separately from the NpT run, we executed a 10^9 step NVE (microcanonical) simulation to obtain d_{003} using Eq. (16). In the NVE run, d_{003} was computed from the cross correlation between $J_{E,\alpha}$ and the particle average of $\hat{v}_\alpha^3$, $\frac{1}{N}\sum_{I=1}^{N}\hat{v}_{\alpha,I}^3$, and the average of the $\alpha = x, y,$ and z directions was taken, where I is the particle index. The value was calculated to be $d_{003} = 0.336 \pm 0.008 \varepsilon\sigma$.

Figure 3 shows the results for the one-particle number density. The density distribution was almost linear inside the left CV and is well reproduced by the Green–Kubo relation represented by Eq. (10). We note that the fluctuation formula tends to overestimate α_p typically by a few percent due to the discontinuous cutoff of the LJ potential [29]. In Fig. 3, this error appears as a slightly higher gradient of the EMD line,

but it is sufficiently small to confirm Eq. (10). The results for the one-particle velocity distribution function in the left CV are displayed in Fig. 4 as the relative deviation from the MB distribution function $\delta f(v_z, \infty)/f(v_z, 0)$. In the figure, the predictions by the Hermite polynomial approximation in Eqs. (11) and (12) are included up to the seventh order. The relative deviation has the form of a cubic function, and a similar velocity distribution was reported for a liquid-vapor coexisting system under a thermal gradient [33]. The third-order approximation Eq. (17) already works quite well despite its simplicity, although a small deviation from the NEMD curve can be found near the extrema [at $v_z/v_p = 2^{-1/2}$ according to Eq. (17)]. This deviation is eliminated in the fifth-order approximation, which is indistinguishable from the seventh-order approximation within the scale of this figure. The results in Figs. 3 and 4 support our formulation of nonequilibrium distribution functions.

IV. CONCLUSIONS

In conclusion, we have formulated a concrete way to describe the phase-space distribution functions in the nonequilibrium steady states under a constant thermal gradient, which is a typical system of NEMD simulation of heat conduction. We have demonstrated that our expression of the all-particle distribution function correctly reduces to the one-particle distribution functions of density and velocity. This result indicates that, in order to describe a comprehensive form of the distribution function, one has to include both the equilibrium and the nonequilibrium terms in entropy production. In addition, the one-particle distribution functions derived here are tractable for the investigation of the nature of nonequilibrium states and analytical evaluation of the nonequilibrium average of physical quantities. These distribution functions also are useful for judging if a nonequilibrium state generated by NEMD simulation is actually in the linear response regime or not. In the present paper, we concentrated on a single component system under a constant thermal gradient. The underlying idea is not specific to this system, and extensions to multicomponent systems and systems with particle flow are also expected.

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