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Generalization of the homogeneous nonequilibrium molecular dynamics method for calculating thermal conductivity to multibody potentials

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This work provides a generalization of Evans' homogeneous nonequilibrium method for estimating thermal conductivity to molecular systems that are described by general multibody potentials. A perturbed form of the usual Nose-Hoover equations of motion is formally constructed and is shown to satisfy the requirements of Evans' original method. These include adiabatic incompressibility of phase space, equivalence of the dissipative and heat fluxes, and momentum preservation.

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I. INTRODUCTION

Estimating the thermal conductivity $\boldsymbol{\kappa}$ is essential for modeling the flow of heat using Fourier's law. The thermal conductivity can be computed using molecular dynamics (MD) simulations, given sufficient information regarding the inherent molecular structure and interactions among the particles in the system [1–3]. Commonly, such interactions are modeled with empirical potentials describing the bonding energy of neighboring atoms. While many materials can be adequately described with pair potentials based simply on interatomic distances, semiconductor materials such as Si and GaN require additional terms that reflect the relative orientation between triplets of neighboring atoms [4–6]. Moreover, four-body terms measuring dihedral angles and torsion are also employed to describe polymers [7–9] and the surface and cluster phases of silicon [10].

In this Brief Report, a homogeneous nonequilibrium molecular dynamics (HNEMD) method is formulated for any system consisting of N identical particles described by potentials containing up to M-body terms. This method was originally proposed by Evans for systems modeled by pair potentials [11], applied to molecular liquids with distance and angle constraints as well as an intramolecular four-body energy in [12,13], generalized to mixtures of arbitrarily complex nonidentical molecules in [14], and was later extended to solid systems modeled by three-body potentials in [15]. The HNEMD method is synthetic, in the sense that a fictitious external force field is applied to the system in order to mimic the thermal transport process. Since the method requires only the time average of the heat flux, it is free of difficulties involving the calculation and integration of the heat flux autocorrelation tensor necessary for estimating $\boldsymbol{\kappa}$ using the Green-Kubo (GK) method. Also, it is free of strong size effects, such as the GK method, and does not involve large temperature gradients both of which plague the direct method [2,15]. For these reasons, the HNEMD method is a practical means for computing statistically accurate estimates of thermal conductivity. The most challenging task in the HNEMD method, which is addressed in this paper, is to formulate the field-dependent equations of motion so that the flux induced is commensurate with the microscopic heat flux vector [16].

The organization of the paper is as follows. The linear response theory of Nose-Hoover (NH) thermostatted systems is derived systematically in Sec. II. This is accomplished in a straightforward manner by appealing to a direct linearization of the Liouville equation, as in the case of adiabatic linear response theory [16], instead of linearizing the propagator of the perturbed distribution function, as in [17]. The main result of the paper is obtained in Sec. III, where the equations of motion necessary for computing thermal conductivity are derived for an M-body potential consistent with the HNEMD method of Sec. II.

II. LINEAR RESPONSE THEORY WITH NH THERMOSTAT

The generic form of the NH-thermostatted equations of motion linearly perturbed by an external field $\mathbf{F}_e$ is

$$\dot{\mathbf{r}}_i = \frac{\mathbf{p}_i}{m} + \mathbf{C}_i(\boldsymbol{\Gamma})\mathbf{F}_e(t),$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i(\boldsymbol{\Gamma})\mathbf{F}_e(t) - \zeta\mathbf{p}_i,$$

$$\dot{\zeta} = \frac{1}{Q}\left(\sum_i \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{m} - 3Nk_BT\right). \quad (1)$$

Here, k_B is the Boltzmann constant, T is the temperature, $\boldsymbol{\Gamma} = \{(\mathbf{r}_i,\mathbf{p}_i),\ i=1,2,\ldots,N\}$ is the phase space with $\mathbf{r}_i$ and $\mathbf{p}_i$ being the position and momentum vectors of atom i respectively. Also, $\mathbf{F}_i$ is the interatomic force, $\mathbf{C}_i(\boldsymbol{\Gamma})$ and $\mathbf{D}_i(\boldsymbol{\Gamma})$ are the tensor phase variables, which describe the coupling of the system to the applied external field $\mathbf{F}_e$, ζ is the thermodynamic friction coefficient associated with the NH thermostat, and Q is a parameter that affects the amplitude and period of thermal fluctuations. It is well known that the NH thermostat preserves the canonical distribution in the absence of external field [17,18]. When $\mathbf{F}_e=0$, the phase space distribution follows the extended canonical distribution [18]

$$f_c(\boldsymbol{\Gamma},\zeta) = \frac{e^{-\beta(H_0(\boldsymbol{\Gamma})+1/2Q\zeta^2)}}{z(\beta)}, \quad (2)$$

where H_0 is the total internal energy of the system and $z(\beta)=\int e^{-\beta[H_0(\boldsymbol{\Gamma})+(1/2)Q\zeta^2]}d\boldsymbol{\Gamma}d\zeta$ is the partition function with

$\beta = \frac{1}{k_B T}$. The total internal energy H_0 is given by

$$H_0 = \sum_i \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} + \Phi(\mathbf{r}), \tag{3}$$

where $\Phi(\mathbf{r})$ is the potential that describes interactions among the particles such that the interatomic force is given by $\mathbf{F}_i = -\frac{\partial}{\partial \mathbf{x}_i}\Phi$. Assuming the external field $\mathbf{F}_e$ is applied at time $t = 0$, the perturbed distribution $f(\mathbf{\Gamma}, \zeta, t)$ is obtained by solving the Liouville equation

$$\begin{aligned}\frac{\partial f(\mathbf{\Gamma},\zeta,t)}{\partial t} &= -\left[\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} + \dot{\mathbf{\Gamma}} \cdot \frac{\partial}{\partial \mathbf{\Gamma}} + \dot{\zeta}\frac{\partial}{\partial \zeta} + \frac{\partial}{\partial \zeta}\dot{\zeta}\right] f(\mathbf{\Gamma},\zeta,t) \\ &= -iLf(\mathbf{\Gamma},\zeta,t),\end{aligned} \tag{4}$$

with initial condition $f(\mathbf{\Gamma},\zeta,0) = f_c(\mathbf{\Gamma},\zeta)$. Here, iL represents the Liouvillean. Assuming the external field $\mathbf{F}_e$ to be small enough, the Liouvillean iL and the perturbed distribution function $f(\mathbf{\Gamma},\zeta,t)$ may be approximated by

$$iL = iL_0 + i\Delta L(t),$$

$$f(\mathbf{\Gamma},\zeta,t) = f_c(\mathbf{\Gamma},\zeta) + \Delta f(\mathbf{\Gamma},\zeta,t), \tag{5}$$

where $i\Delta L(t)$ and $\Delta f(\mathbf{\Gamma},\zeta,t)$ are linear perturbations to the field-free Liouvillean iL_0 and the extended canonical distribution $f_c(\mathbf{\Gamma},\zeta)$, respectively, due to the presence of the external field $\mathbf{F}_e$. Here, iL_0 corresponds to the field-free equations of motion, i.e., Eq. (1) with $\mathbf{F}_e = \mathbf{0}$, while f_c satisfies $\frac{\partial}{\partial t} f = -iL_0 f$. Using the approximations given by Eq. (5), the Liouville Eq. (4) can be linearized as

$$\frac{\partial}{\partial t}\Delta f(\mathbf{\Gamma},\zeta,t) + iL_0 \Delta f(\mathbf{\Gamma},\zeta,t) = -i\Delta L(t) f_c(\mathbf{\Gamma},\zeta). \tag{6}$$

The solution $\Delta f(\mathbf{\Gamma},\zeta,t)$ of the linearized Liouville Eq. (6) can be obtained formally as

$$\Delta f(\mathbf{\Gamma},\zeta,t) = -\int_0^t \exp[-iL_0(t-s)] i\Delta L(s) f_c(\mathbf{\Gamma},\zeta) ds, \tag{7}$$

where $i\Delta L(s) f_c(\mathbf{\Gamma},\zeta) = iL(s) f_c(\mathbf{\Gamma},\zeta) - iL_0 f_c(\mathbf{\Gamma},\zeta)$ [16]. Since $f_c(\mathbf{\Gamma},\zeta)$ is the steady-state solution of the equation $\frac{\partial}{\partial t} f = -iL_0 f$, it follows that $iL_0 f_c(\mathbf{\Gamma},\zeta) = 0$ [18], hence $i\Delta L(s) f_c(\mathbf{\Gamma},\zeta) = iL(s) f_c(\mathbf{\Gamma},\zeta)$. Using Eqs. (4) and (2), it can be shown that for the field-dependent equations of motion given by Eq. (1)

$$\begin{aligned} i\Delta L(s) f_c(\mathbf{\Gamma},\zeta) &= \left[\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} + \dot{\mathbf{\Gamma}} \cdot \frac{\partial}{\partial \mathbf{\Gamma}} + \dot{\zeta}\frac{\partial}{\partial \zeta} + \frac{\partial}{\partial \zeta}\dot{\zeta}\right] f_c(\mathbf{\Gamma},\zeta) \\ &= \left[\sum_i \frac{\partial}{\partial \mathbf{r}_i} \cdot \mathbf{C}_i \mathbf{F}_e + \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot \mathbf{D}_i \mathbf{F}_e\right] f_c(\mathbf{\Gamma},\zeta) \\ &\quad + \beta\left[-\sum_i \mathbf{D}_i^T \frac{\mathbf{p}_i}{m} + \sum_i \mathbf{C}_i^T \mathbf{F}_i\right] \cdot \mathbf{F}_e(t) f_c(\mathbf{\Gamma},\zeta). \end{aligned} \tag{8}$$

At this stage, the equations of motion are assumed to satisfy the condition of adiabatic incompressibility of phase space (AIΓ) [16], i.e.,

$$\sum_i \frac{\partial}{\partial \mathbf{r}_i} \cdot (\mathbf{C}_i \mathbf{F}_e) + \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot (\mathbf{D}_i \mathbf{F}_e) = 0. \tag{9}$$

Note that, in the absence of a thermostat, the AIΓ condition is identical to the incompressibility of the full phase space, i.e., $\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} = 0$. Also, the AIΓ condition is always satisfied if the equations of motion are derivable from a Hamiltonian. However, here the AIΓ is assumed to hold even if, as in the present case, the equations of motion (1) are not derivable from a general Hamiltonian. Using Eq. (9), Eq. (8) may be further reduced to

$$\begin{aligned} i\Delta L(s) f_c(\mathbf{\Gamma},\zeta) &= \beta\left[-\sum_i \mathbf{D}_i^T \frac{\mathbf{p}_i}{m} + \sum_i \mathbf{C}_i^T \mathbf{F}_i\right] \cdot \mathbf{F}_e(t) f_c(\mathbf{\Gamma},\zeta) \\ &= -\beta \mathbf{J}(\mathbf{\Gamma}) \cdot \mathbf{F}_e(t) f_c(\mathbf{\Gamma},\zeta), \end{aligned} \tag{10}$$

where $\mathbf{J}(\mathbf{\Gamma})$ is defined as the *dissipative flux*. Substituting Eq. (10) into Eq. (7), the perturbed distribution function $f(\mathbf{\Gamma},\zeta,t)$ is obtained as

$$\begin{aligned} f(\mathbf{\Gamma},\zeta,t) = f_c(\mathbf{\Gamma},\zeta) + \beta \int_0^t & \exp[-iL_0(t-s)] \\ & \times [\mathbf{J}(\mathbf{\Gamma}) \cdot \mathbf{F}_e(s)] f_c(\mathbf{\Gamma},\zeta) ds. \end{aligned} \tag{11}$$

The ensemble average of the microscopic virial heat flux vector $\mathbf{J}_Q(\mathbf{\Gamma}(t)) = \tilde{\mathbf{J}}_Q(t)$ derived from the field-free equations of motion using the Irving-Kirkwood procedure [19], but evolving with the field-dependent equations of motion Eq. (1), is given by

$$\begin{aligned} \langle \tilde{\mathbf{J}}_Q(t) \rangle &= \int \mathbf{J}_Q(\mathbf{\Gamma}) f(\mathbf{\Gamma},\zeta,t) d\mathbf{\Gamma} d\zeta \\ &= \langle \tilde{\mathbf{J}}_Q(0) \rangle_c + \beta \int_0^t \left(\int \mathbf{J}_Q(\mathbf{\Gamma}) \{\exp[-iL_0(t-s)] \right. \\ &\qquad \left. \times [\mathbf{J}(\mathbf{\Gamma}) \cdot \mathbf{F}_e] f_c(\mathbf{\Gamma},\zeta)\} d\mathbf{\Gamma} d\zeta \right) ds, \end{aligned} \tag{12}$$

where $\langle \tilde{\mathbf{J}}_Q(0) \rangle_c = \int \mathbf{J}_Q(\mathbf{\Gamma}) f_c(\mathbf{\Gamma},\zeta) d\mathbf{\Gamma} d\zeta$. Assuming the external field $\mathbf{F}_e$ to be independent of time, the inner integral on the right-hand side of Eq. (12) can be written as

$$\begin{aligned} &\int \mathbf{J}_Q(\mathbf{\Gamma}) \{\exp[-iL_0(t-s)][\mathbf{J}(\mathbf{\Gamma}) \cdot \mathbf{F}_e] f_c(\mathbf{\Gamma},\zeta)\} d\mathbf{\Gamma} d\zeta \\ &\quad = \langle \tilde{\mathbf{J}}_Q[(t-s)_0] \otimes \tilde{\mathbf{J}}(0) \rangle_c \mathbf{F}_e, \end{aligned} \tag{13}$$

where $\otimes$ denotes the tensor product, $\langle \tilde{\mathbf{J}}_Q((t-s)_0) \otimes \tilde{\mathbf{J}}(0) \rangle_c$ is the correlation function of the heat flux vector $\mathbf{J}_Q$ and the dissipative flux $\mathbf{J}$ with respect to the extended canonical distribution, and $\tilde{\mathbf{J}}(t) = \mathbf{J}(\mathbf{\Gamma}(t))$ [15]. The subscript "0" in Eq. (13) indicates that $\tilde{\mathbf{J}}((t-s)_0)$ in the correlation function is obtained by solving the field-free equations of motion, see [16,15]. Using Eq. (13), Eq. (12) reduces to

$$\langle \tilde{\mathbf{J}}_Q(t) \rangle = \left(\beta \int_0^t \langle \tilde{\mathbf{J}}_Q((s)_0) \otimes \tilde{\mathbf{J}}(0) \rangle_c ds \right) \mathbf{F}_e, \tag{14}$$

where $\langle \tilde{\mathbf{J}}_Q(0) \rangle_c = \mathbf{0}$ since there is no heat flux when the system is in canonical equilibrium.

The HNEMD method requires that the equations of motion Eq. (1) are constructed so that the dissipative flux is equivalent to the heat flux vector obtained by using the field-free equations of motion, i.e., $\mathbf{J} = \mathbf{J}_Q$, and Eq. (14) can be written as

$$\frac{\langle \tilde{\mathbf{J}}_Q(\infty) \rangle}{VT} = \left(\frac{1}{V k_B T^2} \int_0^\infty \langle \tilde{\mathbf{J}}_Q((s)_0) \otimes \tilde{\mathbf{J}}_Q(0) \rangle_c ds \right) \mathbf{F}_e, \tag{15}$$

where V is the volume of the system. The dynamics used to obtain $\tilde{\mathbf{J}}_Q((s)_0)$ in Eq. (15) generates the ensemble of starting states following $f_c(\mathbf{\Gamma}, \zeta)$, thus, making the theory ergodically consistent. In the range of $\mathbf{F}_e$ where the linear response theory is valid, Eq. (15) indicates that $\frac{\langle \tilde{\mathbf{J}}_Q(\infty) \rangle}{VT}$ is linearly proportional to $\mathbf{F}_e$ once the steady state is reached with the constant of proportionality being the thermal conductivity tensor $\boldsymbol{\kappa}$ as in the GK method. Since the system has been assumed to be ergodic, the ensemble average $\langle \tilde{\mathbf{J}}_Q(\infty) \rangle$ is equivalent to the time average of $\tilde{\mathbf{J}}_Q(t)$ with respect to the field-dependent dynamics once the linear nonequilibrium steady state is reached. In the following section, the equations of motion, consistent with the preceding HNEMD method, to compute the thermal conductivity of a system consisting of N identical particles modeled by a potential with up to M-body terms are proposed.

III. EQUATIONS OF MOTION

The interaction potential of a system of N identical particles is of the general form

$$\Phi(\mathbf{r}) = \frac{1}{2!} \sum_{i_1, i_2} u_2(\mathbf{r}_{i_1}, \mathbf{r}_{i_2}) + \frac{1}{3!} \sum_{i_1, i_2, i_3} u_3(\mathbf{r}_{i_1}, \mathbf{r}_{i_2}, \mathbf{r}_{i_3}) + \cdots + \frac{1}{M!} \sum_{i_1, i_2, \ldots, i_M} u_M(\mathbf{r}_{i_1}, \mathbf{r}_{i_2}, \ldots, \mathbf{r}_{i_M}), \tag{16}$$

where $M \le N$ and $u_M(\mathbf{r}_{i_1}, \mathbf{r}_{i_2}, \ldots, \mathbf{r}_{i_M})$ describes the M-body interactions [20]. The total interatomic force $\mathbf{F}_i$ on atom i is given by

$$\mathbf{F}_i = -\frac{\partial \Phi}{\partial \mathbf{r}_i} = \frac{1}{1!} \sum_{i_2} \mathbf{F}_{ii_2} + \frac{1}{2!} \sum_{i_2, i_3} \mathbf{F}_{ii_2 i_3} + \cdots + \frac{1}{(M-1)!} \times \sum_{i_2, \ldots, i_M} \mathbf{F}_{ii_2, \ldots, i_M}, \tag{17}$$

where $\mathbf{F}_{ii_2, \ldots, i_M} = -\frac{\partial}{\partial \mathbf{r}_i} u_M(\mathbf{r}_i, \mathbf{r}_{i_2}, \ldots, \mathbf{r}_{i_M})$ is the M-body force contribution on atom i. The energy E_i of atom i is taken to be of the form

$$E_i = \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m} + \frac{1}{2!} \sum_{i_2} u_2(\mathbf{r}_i, \mathbf{r}_{i_2}) + \frac{1}{3!} \sum_{i_2, i_3} u_3(\mathbf{r}_i, \mathbf{r}_{i_2}, \mathbf{r}_{i_3}) + \cdots + \frac{1}{M!} \sum_{i_2, \ldots, i_M} u_M(\mathbf{r}_i, \mathbf{r}_{i_2}, \ldots, \mathbf{r}_{i_M}), \tag{18}$$

based on the assumption that the energy from any K-body term $u_K(\mathbf{r}_{i_1}, \mathbf{r}_{i_2}, \ldots, \mathbf{r}_{i_K})$ is divided equally among the atoms $i_1, i_2, \ldots, i_K$. For this choice of the energy, the heat flux vector with the field-free equations of motion is given by

$$\mathbf{J}_Q = \sum_i \frac{\mathbf{p}_i E_i}{m} + \frac{1}{2!} \sum_{i_1, i_2} \mathbf{r}_{i_1 i_2} \left(\frac{\mathbf{F}_{i_1 i_2} \cdot \mathbf{p}_{i_1}}{m} \right) + \frac{1}{6!} \sum_{i_1, i_2, i_3} (\mathbf{r}_{i_1 i_2} + \mathbf{r}_{i_1 i_3}) \times \left(\frac{\mathbf{F}_{i_1 i_2 i_3} \cdot \mathbf{p}_{i_1}}{m} \right) + \cdots + \frac{1}{M!} \sum_{i_1, i_2, \ldots i_M} (\mathbf{r}_{i_1 i_2} + \mathbf{r}_{i_1 i_3} + \ldots + \mathbf{r}_{i_1 i_M}) \left(\frac{\mathbf{F}_{i_1 i_2 \ldots i_M} \cdot \mathbf{p}_{i_1}}{m} \right), \tag{19}$$

where $\mathbf{r}_{i_1 i_2} = \mathbf{r}_{i_1} - \mathbf{r}_{i_2}$, provided the system momentum is zero [19]. Note that other partitions of energy are possible but the choice does not appear to significantly affect the thermal conductivity estimate in practice [21]. The heat flux vector can be rewritten in tensorial form as

$$\mathbf{J}_Q = \sum_{i_1} \left[E_{i_1} \mathbf{I} + \frac{1}{2!} \sum_{i_2} (\mathbf{r}_{i_1 i_2} \otimes \mathbf{F}_{i_1 i_2}) + \frac{1}{6!} \sum_{i_2, i_3} [(\mathbf{r}_{i_1 i_2} + \mathbf{r}_{i_1 i_3}) \otimes \mathbf{F}_{i_1 i_2 i_3}] + \cdots + \frac{1}{M!} \sum_{i_2, \ldots i_M} [(\mathbf{r}_{i_1 i_2} + \mathbf{r}_{i_1 i_3} + \cdots + \mathbf{r}_{i_1 i_M}) \otimes \mathbf{F}_{i_1 i_2 \ldots i_M}] \right] \frac{\mathbf{p}_{i_1}}{m}, \tag{20}$$

where $\mathbf{I}$ is the identity tensor.

The criteria for generating the field-dependent equations of motion Eq. (1) are (a) adiabatic incompressibility (AIΓ), (b) equivalence of virial heat flux and dissipative heat flux ($\mathbf{J} = \mathbf{J_Q}$), and (c) momentum preservation. Recalling the definition for dissipative flux $\mathbf{J} = \Sigma_i \mathbf{D}_i^T \frac{\mathbf{p}_i}{m} - \Sigma_i \mathbf{C}_i^T \mathbf{F}_i$ in Eq. (10) and comparing it with the tensorial form of the heat flux vector in Eq. (20), suggests the form

$$\mathbf{D}_i = E_i \mathbf{I} + \frac{1}{2!} \sum_{i_2} \mathbf{F}_{ii_2} \otimes \mathbf{r}_{ii_2} + \frac{1}{3!} \sum_{i_2, i_3} \mathbf{F}_{ii_2 i_3} \otimes (\mathbf{r}_{ii_2} + \mathbf{r}_{ii_3}) + \cdots + \frac{1}{M!} \sum_{i_2, \ldots, i_M} \mathbf{F}_{ii_2 \ldots i_M} \otimes (\mathbf{r}_{ii_2} + \ldots + \mathbf{r}_{ii_M}) \tag{21}$$

with $\mathbf{C}_i = \mathbf{0}$. However, this form violates momentum preservation

$$\sum_i \dot{\mathbf{p}}_i = \sum_i \mathbf{F}_i + \sum_i \mathbf{D}_i \mathbf{F}_e = \mathbf{0}, \tag{22}$$

which requires $\Sigma_i \mathbf{D}_i = \mathbf{0}$. This can be remedied by subtracting the mean of each term, as in Evans' original formula [11], leading to

$$\begin{aligned}\mathbf{D}_i = (E_i - \bar{E})\mathbf{I} + \frac{1}{2!}\sum_{i_2} \mathbf{F}_{ii_2} \otimes \mathbf{r}_{ii_2} - \frac{1}{2\,!\,N}\sum_{i_1,i_2} \mathbf{F}_{i_1i_2} \otimes \mathbf{r}_{i_1i_2} \\ + \frac{1}{3!}\sum_{i_2,i_3} \mathbf{F}_{ii_2i_3} \otimes (\mathbf{r}_{ii_2} + \mathbf{r}_{ii_3}) - \frac{1}{3\,!\,N}\sum_{i_1,i_2,i_3} \mathbf{F}_{i_1i_2i_3} \otimes (\mathbf{r}_{i_1i_2} \\ + \mathbf{r}_{i_1i_3}) + \ldots + \frac{1}{M!}\sum_{i_2,\ldots,i_M} \mathbf{F}_{ii_2,\ldots,i_M} \otimes (\mathbf{r}_{ii_2} + \ldots + \mathbf{r}_{ii_M}) \\ - \frac{1}{M\,!\,N}\sum_{i_1,i_2,\ldots,i_M} \mathbf{F}_{i_1i_2\ldots i_M} \otimes (\mathbf{r}_{i_1i_2} + \cdots + \mathbf{r}_{i_1i_M}), \qquad (23)\end{aligned}$$

where $\bar{E}=\frac{1}{N}\Sigma_i E_i$ is the average instantaneous internal energy. This form of $\mathbf{D}_i$ in Eq. (23) induces no net momentum and also satisfies the AIΓ condition

$$\sum_i \frac{\partial}{\partial \mathbf{r}_i} \cdot (\mathbf{C}_i\mathbf{F}_e) + \sum_i \frac{\partial}{\partial \mathbf{p}_i} \cdot (\mathbf{D}_i\mathbf{F}_e) = \sum_i \frac{\partial}{\partial \mathbf{p}_i}(E_i - \bar{E}) \cdot \mathbf{F}_e = \mathbf{0}, \qquad (24)$$

since $\mathbf{C}_i=\mathbf{0}$. Using Eq. (23), the dissipative heat flux may be now written as

$$\begin{aligned}\mathbf{J} = \sum_i \mathbf{D}_i^T\frac{\mathbf{p}_i}{m} - \sum_i \mathbf{C}_i^T\mathbf{F}_i \\ = \sum_i \Bigg[E_i\mathbf{I} + \frac{1}{2!}\sum_{i_2} \mathbf{r}_{ii_2} \otimes \mathbf{F}_{ii_2} + \frac{1}{3!}\sum_{i_2,i_3} (\mathbf{r}_{ii_2} + \mathbf{r}_{ii_3}) \otimes \mathbf{F}_{ii_2i_3} \\ + \ldots + \frac{1}{M!}\sum_{i_2,\ldots,i_M} (\mathbf{r}_{ii_2} + \ldots + \mathbf{r}_{ii_M}) \otimes \mathbf{F}_{ii_2\ldots i_M}\Bigg]\frac{\mathbf{p}_i}{m} \\ - \Bigg[\bar{E} + \frac{1}{2\,!\,N}\sum_{i_1,i_2} \mathbf{r}_{i_1i_2} \otimes \mathbf{F}_{i_1i_2} + \frac{1}{3\,!\,N}\sum_{i_1,i_2,i_3} (\mathbf{r}_{i_1i_2} + \mathbf{r}_{i_1i_3}) \\ \otimes \mathbf{F}_{i_1i_2i_3} + \frac{1}{M\,!\,N}\sum_{i_1,i_2,\ldots,i_M} (\mathbf{r}_{i_1i_2} + \cdots + \mathbf{r}_{i_1i_M}) \\ \otimes \mathbf{F}_{i_1i_2,\ldots,i_M}\Bigg]\sum_i \frac{\mathbf{p}_i}{m}. \qquad (25)\end{aligned}$$

Since $\Sigma_i\frac{\mathbf{p}_i}{m}=\mathbf{0}$, Eq. (25) reduces to Eq. (19), hence $\mathbf{J}=\mathbf{J}_Q$. Thus, given Eqs. (24), (25), and (22), the form Eq. (23) with $\mathbf{C}_i=\mathbf{0}$ is a viable HNEMD method for calculating the thermal conductivity of a material described with multibody potentials.

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