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Daichi Torii,[a)] Takeo Nakano, and Taku Ohara
Institute of Fluid Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

The molecular dynamics expression of heat flux, originally derived by Irving and Kirkwood [J. Chem. Phys. **18**, 817 (1950)] for pairwise potentials, is generalized in this paper for systems with many-body potentials. The original formula consists of a kinetic part and a potential part, and the latter term is found in the present study to be expressible as a summation of contributions from all the many-body potentials defined in the system. The energy transfer among a set of sites for which a many-body potential is defined is discussed and evaluated by the rate of increase in the kinetic energy of each site due to the potential, and its accumulation over all the potentials in the system is shown to make up the potential part of the generalized expression. A molecular dynamics simulation for liquid *n*-octane was performed to demonstrate the applicability of the new expression obtained in this study to measure the heat flux and to elucidate the contributions of inter- and intramolecular potentials to heat conduction. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2821963]

I. INTRODUCTION

There has been increasing interest recently in the transport properties and dynamic structures of complex organic molecules and biomolecules, such as proteins and lipids, and of the bulk materials composed of these molecules. Molecular dynamics (MD) simulations are a powerful tool to investigate such systems. The remarkable development of computer performance has made feasible the application of complex many-body potentials which accurately reproduce intramolecular degrees of freedom.

Heat conduction is a fundamental thermal phenomenon and heat flux is the most important quantity in thermophysical engineering. The molecular dynamics expression of the heat flux vector was first derived by Irving and Kirkwood.[1] By modifying this expression under the assumptions of uniformity of the system and no macroscopic fluid flow, one can obtain the instantaneous heat flux in the *x* direction J_x in the control volume *V* as

$$J_x V = \sum_i v_{x,i} E_i + \frac{1}{2} \sum_i \sum_{j>i} \{ \boldsymbol{F}_{ij} \cdot (\boldsymbol{v}_i + \boldsymbol{v}_j) \} (x_i - x_j), \qquad (1)$$

where $\boldsymbol{v}_i$ and x_i are the velocity vector and *x* coordinate of a particle *i*. $\boldsymbol{F}_{ij}$ is the intermolecular force acting on *i* due to the pair potential defined between *i* and *j*. $v_{x,i}$ is the *x* component of the velocity vector. E_i is the total contribution of mechanical energy of the particle *i* to the internal energy of the fluid (i.e., whole mechanical energy of the particle if the streaming velocity is zero), which is called internal energy hereafter. Equation (1) has been introduced in many textbooks and is widely utilized to measure heat flux in thermally nonequilibrated systems via MD simulation. However, it is only valid for pair potentials such as the Lennard-Jones

(LJ) type, and is not applicable to systems with many-body potentials, which are usually included in molecular models for diamond-structured materials or organic compounds and biomolecules.

In order only to obtain the thermal conductivity of a system, as a matter of fact, it is not necessary to calculate the heat flux directly or straightforwardly with many-body potentials taken into account, even though they are defined in the system. One alternative method that is useful in the measurement of the thermal conductivity of a fluid composed of polyatomic molecules is to calculate "molecular heat flux,"[2] i.e., a heat flux whose description is based on the view that the individual atomic contributions to the local energy density are localized at the molecular centers of mass, rather than to calculate "atomic heat flux" similar to those dealt in the present paper where all the intramolecular energy transfer is taken into account. The expression of the molecular heat flux does not contain explicit contributions of intramolecular interactions that are described by many-body potentials and succeeds to avoid the complexities to handle them. The absolute value of molecular heat flux is indeed different from that of atomic heat flux even if they are ensemble averaged,[2] but they are proven to represent the identical thermal conductivity when calculated by Green-Kubo formula[2] or via the method called Evans nonequilibrium MD algorithm.[3,4] In such ways, molecular heat flux is effective in obtaining the thermal conductivity of polyatomic fluids; however, in order to measure the net heat flux and to analyze the contribution of an arbitrary inter- and intramolecular interactions to it, it is essential to employ atomic heat flux in which all many-body interactions defined in the system are taken into consideration.

To the best of the authors' knowledge, three papers have been published that proposed a formula for calculating the heat flux vector with a contribution of a many-body potential included. One is the work of Zhang and Todd,[5] who extended their own expression previously derived for pairwise

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a)Author to whom correspondence should be addressed. Tel.: +81-22-217-5872. Fax: +81-22-217-5252. Electronic mail: torii@microheat.ifs.tohoku.ac.jp.

potentials[6] to those for an arbitrary three-body potential. They introduced a control surface through which the heat flux was measured, rather than measuring the heat flux vector in a control volume. The method was called the "method of planes" by the authors and has a great advantage when the system is nonuniform, for which the original Irving-Kirkwood formula[1] presents difficulties in treating the differential operator. Another work has been done by Chen,[7] whose expression is for a local heat flux vector rather than space-averaged ones. Chen followed the idea and method of formulation developed by Hardy[8] and extended them for three-body potentials of the Tersoff type[9,10] and the Stillinger-Weber type.[11] The third paper that treats the measurement of heat flux with many-body potentials was written by Marechal and Ryckaert.[2] In their expression of atomic heat flux in butane, the contribution of torsional degrees of freedom described by a four-body potential is included. However, these works referenced above are limited to certain types of interactions[2,7] or specific numbers of interacting bodies[2,5,7] and are not applicable to many-body potentials, in general.

On the other hand, one of the authors has investigated molecular mechanisms of macroscopic heat conduction with a focus on intermolecular energy transfer.[12,13] He considered two mechanisms to generate heat flux through a control surface; the first is the kinetic energy of molecules transported via molecular motions crossing the control surface, and the other is the transfer of kinetic energy of molecules between a pair of molecules separated by the control surface. He obtained the latter element called "intermolecular energy transfer" from the rate of increase in the kinetic energy of each molecule due to intermolecular forces and showed that its accumulation over all pairs of molecules plus the abovementioned contribution of the kinetic energy of molecules crossing the control surface were consistent with the conventional expression of heat flux, as expressed by Eq. (1). This concept of the intermolecular energy transfer is a powerful tool to analyze molecular-scale factors governing thermal properties of dense materials, and extension of this concept to the cases of many-body potentials has been required to analyze thermal properties of systems of complex molecules.

The present paper deals with the heat flux as an accumulation of molecular-scale thermal energy transfer caused by many-body potentials, paying significant attention to the above intermolecular energy transfer concept. By using the formula derived in the present paper, one can specify the contributions to heat flux of both the inter- and intramolecular energy transfers in a specific part of molecules. In the next section, Eq. (1) is generalized for systems with many-body potentials. In Sec. III, the concept of intermolecular energy transfer is extended to the energy transfer among sites in which an arbitrary many-body potential is defined, and the molecular-scale mechanism of the energy transfer due to a many-body potential is discussed. It is shown that the accumulation of the inter- and intramolecular energy transfers defined here makes up the potential part of the expression derived in Sec. II. Finally in Sec. IV, a MD simulation is performed for a system of liquid n-octane molecules to demonstrate the applicability of the expression.

II. EXPRESSION OF HEAT FLUX INVOLVING MANY-BODY POTENTIALS

In this section, we extend the molecular dynamics expression of heat flux for pairwise potentials [Eq. (1)] to derive a generalized form for many-body potentials. The system considered here is a three-dimensional one containing atomic sites, which only have three degrees of translational freedom. The total potential of the system is assumed to be the superposition of n-body potentials, in which the potential is given by the relative positions of arbitrary n sites. Let N be the number of sites in the system and let s represent a site. ϕ_U and $F_{s_i,U}$ are the potential energy defined among a set of sites named U and the force acting on a site $s_i \in U$ due to the potential, respectively. According to the definition widely used in mass systems, the heat flux in the direction of x, described as J_x, in the volume of the system V is

$$J_x V = \frac{d}{dt} \sum_{s_0=1}^{N} x_{s_0} E_{s_0}, \tag{2a}$$

$$= \sum_{s_0=1}^{N} \frac{dx_{s_0}}{dt} E_{s_0} + \sum_{s_0=1}^{N} \frac{dE_{s_0}}{dt} x_{s_0}, \tag{2b}$$

$$= \sum_{s_0=1}^{N} v_{x,s_0} E_{s_0} + \sum_{s_0=1}^{N} \frac{dE_{s_0}}{dt} x_{s_0}. \tag{2c}$$

Here, x_{s_0}, v_{x,s_0}, and E_{s_0} are the x coordinate, the x component of the velocity vector, and the internal energy of a site s_0, respectively. E_{s_0} is the sum of the kinetic energy $E_{s_0}^{\text{kinetic}}$ and the potential energy $E_{s_0}^{\text{pot}}$ of the site. By assuming that a potential energy ϕ_{U_0} ($U_0=\{s_0,s_1,s_2,\ldots,s_{n-1}\}$) is distributed over the constituent sites by the ratio $p_{s_0,U_0}:p_{s_1,U_0}:p_{s_2,U_0}:\cdots:p_{s_{n-1},U_0}$, one would obtain

$$E_{s_0} = E_{s_0}^{\text{kinetic}} + E_{s_0}^{\text{pot}} = \frac{1}{2}m_{s_0}\boldsymbol{v}_{s_0}^2 + \sum_{\substack{\text{all } n\text{-body} \\ \text{potentials}}} \sum_{s_1=1}^{N-n+2} \sum_{s_2=s_1+1}^{N-n+3} \sum_{s_3=s_2+1}^{N-n+4} \cdots \sum_{s_{n-2}=s_{n-3}+1}^{N-1} \sum_{s_{n-1}=s_{n-2}+1}^{N} p_{s_0,U_0} \cdot \phi_{U_0}, \tag{3}$$

where m_{s_0} and $\boldsymbol{v}_{s_0}$ are the mass and the velocity vector of the site s_0, and $p_{s_i,U}$ ($U=\{s_1,s_2,\ldots,s_n\}$) satisfies

$$\sum_{i=1}^{n} p_{s_i,U} = 1. \tag{4}$$

The time derivative of Eq. (3) can be described as the summation of the contributions of the many-body potentials that involve the site s_0. The terms of a n-body potential become

$$\left(\frac{dE_{s_0}}{dt}\right)_n = \left\{\frac{d}{dt}\left(\frac{1}{2}m_{s_0}\boldsymbol{v}_{s_0}^2\right)\right\}_n + \sum_{s_1=1}^{N-n+2}\sum_{s_2=s_1+1}^{N-n+3}\cdots\sum_{s_{n-1}=s_{n-2}+1}^{N} p_{s_0,U_0}\frac{d\phi_{U_0}}{dt}, \tag{5a}$$

$$= m_{s_0}\boldsymbol{v}_{s_0}\cdot\left(\frac{d\boldsymbol{v}_{s_0}}{dt}\right)_n + \sum_{s_1=1}^{N-n+2}\sum_{s_2=s_1+1}^{N-n+3}\cdots\sum_{s_{n-1}=s_{n-2}+1}^{N} p_{s_0,U_0}\left(\sum_{\beta=0}^{n-1}\frac{\partial\phi_{U_0}}{\partial\boldsymbol{r}_{s_\beta}}\cdot\frac{d\boldsymbol{r}_{s_\beta}}{dt}\right), \tag{5b}$$

$$= \boldsymbol{v}_{s_0}\cdot\sum_{s_1=1}^{N-n+2}\sum_{s_2=s_1+1}^{N-n+3}\cdots\sum_{s_{n-1}=s_{n-2}+1}^{N}\boldsymbol{F}_{s_0,U_0} - \sum_{s_1=1}^{N-n+2}\sum_{s_2=s_1+1}^{N-n+3}\cdots\sum_{s_{n-1}=s_{n-2}+1}^{N} p_{s_0,U_0}\left(\sum_{\beta=0}^{n-1}\boldsymbol{F}_{s_\beta,U_0}\cdot\boldsymbol{v}_{s_\beta}\right), \tag{5c}$$

$$= \sum_{s_1=1}^{N-n+2}\sum_{s_2=s_1+1}^{N-n+3}\cdots\sum_{s_{n-1}=s_{n-2}+1}^{N}\left[\boldsymbol{F}_{s_0,U_0}\cdot\boldsymbol{v}_{s_0} - p_{s_0,U_0}\left(\sum_{\beta=0}^{n-1}\boldsymbol{F}_{s_\beta,U_0}\cdot\boldsymbol{v}_{s_\beta}\right)\right], \tag{5d}$$

for $U_0 = \{s_0, s_1, s_2, \ldots, s_{n-1}\}$, where $\boldsymbol{r}$ is the position vector. Multiplying both sides by x_{s_0} and taking the summation over all the sites in the system, Eq. (5d) becomes

$$\sum_{s_0=1}^{N}\left(\frac{dE_{s_0}}{dt}\right)_n x_{s_0} = \sum_{s_0=1}^{N}\sum_{s_1=1}^{N-n+2}\sum_{s_2=s_1+1}^{N-n+3}\cdots\sum_{s_{n-1}=s_{n-2}+1}^{N}\left(\boldsymbol{F}_{s_0,U_0}\cdot\boldsymbol{v}_{s_0} - p_{s_0,U_0}\sum_{\beta=0}^{n-1}\boldsymbol{F}_{s_\beta,U_0}\cdot\boldsymbol{v}_{s_\beta}\right)x_{s_0}, \tag{6a}$$

$$= \sum_{s_0=1}^{N-n+1}\sum_{s_1=s_0+1}^{N-n+2}\sum_{s_2=s_1+1}^{N-n+3}\cdots\sum_{s_{n-1}=s_{n-2}+1}^{N}\left[\sum_{\alpha=0}^{n-1}\left(\boldsymbol{F}_{s_\alpha,U_0}\cdot\boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U_0}\sum_{\beta=0}^{n-1}\boldsymbol{F}_{s_\beta,U_0}\cdot\boldsymbol{v}_{s_\beta}\right)x_{s_\alpha}\right], \tag{6b}$$

$$= \sum_{s_0}\sum_{s_1>s_0}\sum_{s_2>s_1}\cdots\sum_{s_{n-1}>s_{n-2}}\left[\sum_{\alpha=0}^{n-1}\left(\boldsymbol{F}_{s_\alpha,U_0}\cdot\boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U_0}\sum_{\beta=0}^{n-1}\boldsymbol{F}_{s_\beta,U_0}\cdot\boldsymbol{v}_{s_\beta}\right)x_{s_\alpha}\right], \tag{6c}$$

$$= \sum_{s_1}\sum_{s_2>s_1}\sum_{s_3>s_2}\cdots\sum_{s_n>s_{n-1}}\left[\sum_{\alpha=1}^{n}\left(\boldsymbol{F}_{s_\alpha,U}\cdot\boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U}\sum_{\beta=1}^{n}\boldsymbol{F}_{s_\beta,U}\cdot\boldsymbol{v}_{s_\beta}\right)x_{s_\alpha}\right], \tag{6d}$$

for $U_0 = \{s_0, s_1, s_2, \ldots, s_{n-1}\}$, $U = \{s_1, s_2, \ldots, s_n\}$. The expression in the outer parentheses in Eq. (6d) can be transformed as (see Appendix A for details)

$$\sum_{\alpha=1}^{n}\left(\boldsymbol{F}_{s_\alpha,U}\cdot\boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U}\sum_{\beta=1}^{n}\boldsymbol{F}_{s_\beta,U}\cdot\boldsymbol{v}_{s_\beta}\right)x_{s_\alpha} = \sum_{\alpha=1}^{n-1}\sum_{\beta=\alpha+1}^{n}(p_{s_\beta,U}\boldsymbol{F}_{s_\alpha,U}\cdot\boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U}\boldsymbol{F}_{s_\beta,U}\cdot\boldsymbol{v}_{s_\beta})(x_{s_\alpha} - x_{s_\beta}). \tag{7}$$

Thus, the heat flux J_x is finally

$$J_x V = \sum_{s_0=1}^{N} v_{x,s_0}E_{s_0} + \sum_{s_0=1}^{N}\frac{dE_{s_0}}{dt}x_{s_0}, \tag{8a}$$

$$= \sum_{s_0=1}^{N} v_{x,s_0}E_{s_0} + \sum_{\substack{\text{all }n\text{-body}\\\text{potentials}}}\sum_{s_0=1}^{N}\left(\frac{dE_{s_0}}{dt}\right)_n x_{s_0}, \tag{8b}$$

$$= \sum_{s} v_{x,s}E_s + \sum_{\substack{\text{all }n\text{-body}\\\text{potentials}}}\sum_{s_1}\sum_{s_2>s_1}\sum_{s_3>s_2}\cdots\sum_{s_n>s_{n-1}}\left[\sum_{\alpha=1}^{n}\left(\boldsymbol{F}_{s_\alpha,U}\cdot\boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U}\sum_{\beta=1}^{n}\boldsymbol{F}_{s_\beta,U}\cdot\boldsymbol{v}_{s_\beta}\right)x_{s_\alpha}\right]\quad[\because\text{Eq.(6d)}], \tag{8c}$$

$$= \sum_{s} v_{x,s}E_s + \sum_{\substack{\text{all }n\text{-body}\\\text{potentials}}}\sum_{s_1}\sum_{s_2>s_1}\cdots\sum_{s_n>s_{n-1}}\left[\sum_{\alpha=1}^{n-1}\sum_{\beta=\alpha+1}^{n}(p_{s_\beta,U}\boldsymbol{F}_{s_\alpha,U}\cdot\boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U}\boldsymbol{F}_{s_\beta,U}\cdot\boldsymbol{v}_{s_\beta})(x_{s_\alpha} - x_{s_\beta})\right]\quad[\because\text{Eq.(7)}], \tag{8d}$$

for $U=\{s_1, s_2, \ldots, s_n\}$. The second term in the final expression (8d) is the summation over all the sets of sites for which each n-body potential is defined, in each of which the summation is to be taken over all pairs of sites. When $n=2$ and $p_{s_i,U}=1/n$, Eq. (8d) reduces to Eq. (1) by the relation $\boldsymbol{F}_{s_1,U}=-\boldsymbol{F}_{s_2,U}$. Also, the second term of the expression (8d) is identical to what Marechal and Ryckaert have derived for a torsional potential,[2] when $n=4$ and $p_{s_i,U}=1/n$.

III. INTERMOLECULAR ENERGY TRANSFER BY MANY-BODY POTENTIAL

In a previous work, one of the authors has proposed that the molecular mechanism for heat conduction can be viewed as the exchange of internal energy between a pair of molecules and that the accumulated exchange makes up the macroscopic heat flux.[12,13] In this section, the concept of intermolecular energy transfer based on this view is extended to a set of sites which is governed by a many-body potential, and the mechanism of thermal energy transfer in a system with many-body potentials is discussed. The accumulation of this thermal energy transfer is also shown to yield Eq. (8d).

A. Energy transfer between two groups of sites due to a *n*-body potential

Given an arbitrary many-body potential that is defined for a set of sites $U=\{s_1, s_2, \ldots, s_n\}$, consider the energy transfer among the constituent sites due to the potential. Letting the force acting on a site $s_\alpha \in U$ due to the many-body potential be $\boldsymbol{F}_{s_\alpha,U}$, the rate of increase in the kinetic energy of the site s_α due to the potential is the scalar product of the force $\boldsymbol{F}_{s_\alpha,U}$ and the velocity vector of the site $\boldsymbol{v}_{s_\alpha}$,

$$\dot{E}_{s_\alpha,U}^{\text{kinetic}} = \boldsymbol{F}_{s_\alpha,U} \cdot \boldsymbol{v}_{s_\alpha}. \tag{9}$$

A dot on top of a character denotes the time derivative of the quantity.

By the energy conservation law, the rate of increase of the total kinetic energy of the sites due to the potential and that of the potential energy of the many-body potential $\dot{E}_U^{\text{pot}}$ should be balanced,

$$\sum_{\beta=1}^{n} \dot{E}_{s_\beta,U}^{\text{kinetic}} + \dot{E}_U^{\text{pot}} = 0. \tag{10}$$

By distributing the potential energy to each constituent site by the ratio $p_{s_1,U} : p_{s_2,U} : \cdots : p_{s_n,U}$, the rate of increase in the internal energy of a site s_α due to the potential would be

$$\dot{E}_{s_\alpha,U} = \dot{E}_{s_\alpha,U}^{\text{kinetic}} + p_{s_\alpha,U}\dot{E}_U^{\text{pot}}, \tag{11a}$$

$$= \dot{E}_{s_\alpha,U}^{\text{kinetic}} - p_{s_\alpha,U}\sum_{\beta=1}^{n} \dot{E}_{s_\beta,U}^{\text{kinetic}} \quad [\because \text{Eq.(10)}], \tag{11b}$$

$$= \boldsymbol{F}_{s_\alpha,U} \cdot \boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U}\sum_{\beta=1}^{n} \boldsymbol{F}_{s_\beta,U} \cdot \boldsymbol{v}_{s_\beta} \quad [\because \text{Eq.(9)}]. \tag{11c}$$

Here, we introduce a coordinate $x=x_{\text{cs}}$ to divide the sites belonging to U into two groups. The total rate of increase in the internal energy of all the constituent sites in the region $x_{\text{cs}} < x$ due to the many-body potential $\dot{q}_{U+}$ is

$$\dot{q}_{U+} = \sum_{\alpha=1}^{n} \dot{E}_{s_\alpha,U} \cdot H(x_{s_\alpha} - x_{\text{cs}}), \tag{12a}$$

$$= \sum_{\alpha=1}^{n} \left(\boldsymbol{F}_{s_\alpha,U} \cdot \boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U}\sum_{\beta=1}^{n} \boldsymbol{F}_{s_\beta,U} \cdot \boldsymbol{v}_{s_\beta} \right) \cdot H(x_{s_\alpha} - x_{\text{cs}}), \tag{12b}$$

where the flag function H is defined as follows:

$$H(x) = \begin{cases} 0 & (x < 0) \\ 1 & (x > 0). \end{cases} \tag{13}$$

On the other hand, the increase rate of the internal energy of the sites in the region $x < x_{\text{cs}}$ is

$$\dot{q}_{U-} = \sum_{\alpha=1}^{n} \dot{E}_{s_\alpha,U} \cdot H(x_{\text{cs}} - x_{s_\alpha}), \tag{14a}$$

$$= \sum_{\alpha=1}^{n} \dot{E}_{s_\alpha,U} \cdot \{1 - H(x_{s_\alpha} - x_{\text{cs}})\}, \tag{14b}$$

$$= \sum_{\alpha=1}^{n} \dot{E}_{s_\alpha,U} - \sum_{\alpha=1}^{n} \dot{E}_{s_\alpha,U} \cdot H(x_{s_\alpha} - x_{\text{cs}}), \tag{14c}$$

$$= \sum_{\alpha=1}^{n} (\dot{E}_{s_\alpha,U}^{\text{kinetic}} + p_{s_\alpha,U}\dot{E}_U^{\text{pot}}) - \sum_{\alpha=1}^{n} \dot{E}_{s_\alpha,U} \cdot H(x_{s_\alpha} - x_{\text{cs}}) \\ [\because \text{Eq.(11a)}], \tag{14d}$$

$$= \sum_{\alpha=1}^{n} \dot{E}_{s_\alpha,U}^{\text{kinetic}} + \dot{E}_U^{\text{pot}} - \dot{q}_{U+} \quad [\because \text{Eq.(4)}], \tag{14e}$$

$$= -\dot{q}_{U+} \quad [\because \text{Eq.(10)}], \tag{14f}$$

which represents the intuitive image of the energy transfer that the increase of internal energy in one of the two groups is identical to the decrease of the energy in the other group. In other words, $\dot{q}_{U+}$ is the energy transferred due to the many-body potential from one group of sites to the other across the boundary $x=x_{\text{cs}}$.

Equation (12b) can be transformed in the same manner as Eq. (7) to obtain the following expression (see Appendix A for details):

$$\sum_{\alpha=1}^{n} \left(\boldsymbol{F}_{s_\alpha,U} \cdot \boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U} \sum_{\beta=1}^{n} \boldsymbol{F}_{s_\beta,U} \cdot \boldsymbol{v}_{s_\beta} \right) \cdot H(x_{s_\alpha} - x_{\mathrm{cs}})$$

$$= \sum_{\alpha=1}^{n-1} \sum_{\beta=\alpha+1}^{n} (p_{s_\beta,U} \boldsymbol{F}_{s_\alpha,U} \cdot \boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U} \boldsymbol{F}_{s_\beta,U} \cdot \boldsymbol{v}_{s_\beta}) \cdot \{H(x_{s_\alpha} - x_{\mathrm{cs}}) - H(x_{s_\beta} - x_{\mathrm{cs}})\}. \quad (15)$$

The summation on the right hand side of Eq. (15) is to be taken over all the pairs of n sites. However, due to the term $\{H(x_{s_\alpha} - x_{\mathrm{cs}}) - H(x_{s_\beta} - x_{\mathrm{cs}})\}$, substantial contributions to the sum are made only by the pairs of sites chosen in such a manner that one of the sites is in a different group from the other—the contributions cancel each other for pairs of sites in an identical group. The direction of the energy transfer is also described by the term $\{H(x_{s_\alpha} - x_{\mathrm{cs}}) - H(x_{s_\beta} - x_{\mathrm{cs}})\}$.

B. Thermal energy flux across a control surface

Taking the summation over all groups of sites in the system where the n-body potential is defined, the right hand side of Eq. (15) becomes

$$\sum_{s_1} \sum_{s_2 > s_1} \cdots \sum_{s_n > s_{n-1}} \left[\sum_{\alpha=1}^{n-1} \sum_{\beta=\alpha+1}^{n} (p_{s_\beta,U} \boldsymbol{F}_{s_\alpha,U} \cdot \boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U} \boldsymbol{F}_{s_\beta,U} \cdot \boldsymbol{v}_{s_\beta}) \cdot \{H(x_{s_\alpha} - x_{\mathrm{cs}}) - H(x_{s_\beta} - x_{\mathrm{cs}})\} \right]. \quad (16)$$

Furthermore, by taking the summation over all n-body potentials in the system, expression (16) becomes

$$\sum_{\substack{\text{all } n\text{-body} \\ \text{potentials}}} \sum_{s_1} \sum_{s_2 > s_1} \cdots \sum_{s_n > s_{n-1}} \left[\sum_{\alpha=1}^{n-1} \sum_{\beta=\alpha+1}^{n} (p_{s_\beta,U} \boldsymbol{F}_{s_\alpha,U} \cdot \boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U} \boldsymbol{F}_{s_\beta,U} \cdot \boldsymbol{v}_{s_\beta}) \cdot \{H(x_{s_\alpha} - x_{\mathrm{cs}}) - H(x_{s_\beta} - x_{\mathrm{cs}})\} \right], \quad (17)$$

for $U = \{s_1, s_2, \ldots, s_n\}$.

The term (17) is the contribution of interactions by all the potentials in the system to the thermal energy flux that passes a control surface located at $x = x_{\mathrm{cs}}$. The conductive internal energy flux J_x across a control surface, whose area is S_{cs}, needs an additional term for the internal energy of sites that move across the control surface per unit time,

$$J_x S_{\mathrm{cs}} = \sum_s (E_s/1) \frac{v_{x,s}}{|v_{x,s}|} + \sum_{\substack{\text{all } n\text{-body} \\ \text{potentials}}} \sum_{s_1} \sum_{s_2 > s_1} \cdots \sum_{s_n > s_{n-1}} \left[\sum_{\alpha=1}^{n-1} \sum_{\beta=\alpha+1}^{n} (p_{s_\beta,U} \boldsymbol{F}_{s_\alpha,U} \cdot \boldsymbol{v}_{s_\alpha} - p_{s_\alpha,U} \boldsymbol{F}_{s_\beta,U} \cdot \boldsymbol{v}_{s_\beta}) \cdot \{H(x_{s_\alpha} - x_{\mathrm{cs}}) - H(x_{s_\beta} - x_{\mathrm{cs}})\} \right], \quad (18)$$

for $U = \{s_1, s_2, \ldots, s_n\}$, where the summation of the first term on the right hand side is to be taken only for the sites that traverse the control surface. The term "/1" indicates that the value is per unit time.

When one integrates Eq. (18) along the x axis, the first term is weighted by the traveling distance of each site, and the flag functions $\{H(x_{s_\alpha} - x_{\mathrm{cs}}) - H(x_{s_\beta} - x_{\mathrm{cs}})\}$ of the second term turn into the distance between the sites, to yield the expression of heat flux derived in the previous section [Eq. (8d)]. Equations (8d) and (18) are essentially the same, with the only difference that Eq. (8d) gives the heat flux averaged along the direction of the flux, whereas Eq. (18) allows the measurement of heat flux locally. Equation (18) is especially effective when the system is nonuniform, and this expression agrees with what Zhang and Todd have derived for two- and three-body potentials,[5] subject to the following conditions: (1) for our expression, which the many-body potential energy is distributed equally over the corresponding sites $(p_{s_i,U} = 1/n)$ to evaluate the internal energy of the sites and (2) for the expression of Zhang and Todd, which the macroscopic flow velocity $\mathbf{u}(y)$ is zero.

IV. MOLECULAR DYNAMICS SIMULATION

A MD simulation was performed to demonstrate the applicability of the formula derived in the previous sections. The simulation system shown in Fig. 1 consisted of pure saturated liquid n-octane with periodic boundary conditions in three directions. The temperature at both edges in the z direction was kept lower than the regions in the middle to produce a steady heat flux driven by the temperature gradient. The data were collected for 20 ns after the system had reached an equilibrium.
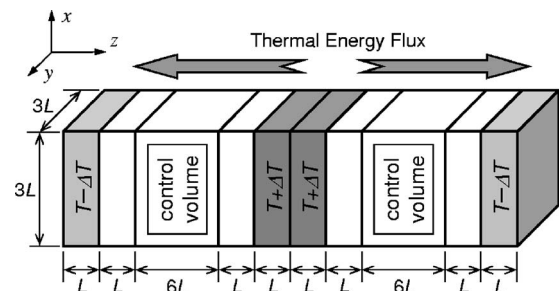

FIG. 1. Molecular dynamics simulation system, which is filled with liquid n-octane molecules. For the present study, $L = 13.1$ Å, $T = 402$ K, and $\Delta T = 21$ K.

The potential model employed in the present simulation was NERD,[14] one of the "united-atom" models, where the carbon atom and the hydrogen atoms covalently bonded to it are treated as one interaction site. The model included three intramolecular degrees of freedom: stretching between the adjacent two sites, bending among the adjacent three sites, and torsion among the adjacent four sites. A LJ (12-6) potential was defined for the interaction against sites in other molecules or those which were separated by more than four sites in the identical molecule.

The mean temperature of the system T was 402 K, selected to be equal to $0.7T_c$, where $T_c=574.1$ K is the critical temperature of the same fluid estimated from the saturated liquid and vapor densities.[14] A temperature difference $\Delta T = 21$ K was set to obtain a temperature gradient of approximately 0.4 K/Å.

Under the assumption that each potential energy is distributed evenly over all the constituent sites ($p_{s_i,U}=1/n$), the thermal energy flux was measured using Eq. (8d) in the control volumes defined in Fig. 1, and the time-averaged contribution of each term of the equation is shown in Fig. 2. The thermal conductivity calculated from the total amount of the heat flux was 2.98×10^2 MW/m² and the resulting temperature gradient of 0.372 K/Å was 8.01×10^{-2} W/(K m), which is in fairly good agreement with the correlated experimental value of 9.32×10^{-2} W/(K m) obtained by the empirical formula.[15] As is usually the case for liquids at low temperatures, the second term of Eq. (8d), i.e., the potential term, is accounted for almost 80% of the conductive internal energy flux. Within the second term, 48% of the thermal energy flux was contributed by the intermolecular LJ potential and 30% by the intramolecular potentials. Within the intramolecular potentials, stretching, bending, and torsional interactions contributed almost evenly, while the contribution of the intramolecular LJ potential remained as little as 2%.

V. CONCLUSION

The molecular dynamics expression of heat flux involving many-body potentials was derived. By extending the concept of intermolecular energy transfer, which had previously been proposed by one of the authors as the dominant element of heat conduction in dense liquids, the energy trans-
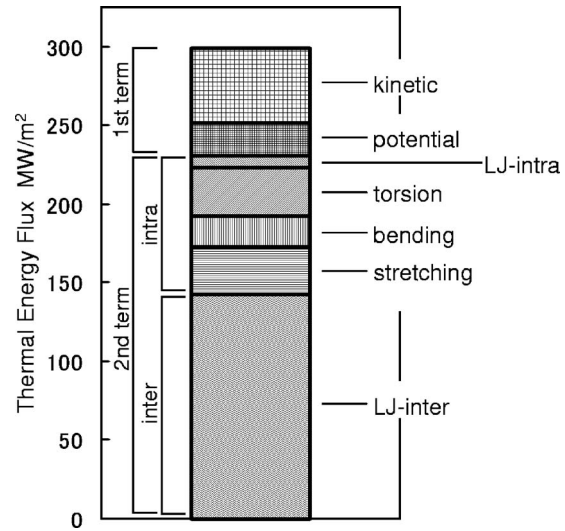

FIG. 2. Contributions of each term and each potential to thermal energy flux, calculated by Eq. (8d). The items labeled as "1st term" and "2nd term" refer to those of Eq. (8d).

fer among sites for which a many-body potential was defined was discussed, and it was shown that the potential term of the molecular dynamics expression of heat flux can be comprehended based on this extended concept. Molecular dynamics simulation for liquid n-octane was conducted to demonstrate the applicability of the expression, and the result showed that about 50% of the conductive internal energy flux was due to the thermal energy transfer between molecules and 30% to thermal energy transfer along each chain polymer molecule.

ACKNOWLEDGMENTS

APPENDIX A: TRANSFORMATION OF EQS. (7) and (15)

The transformation of Eqs. (7) and (15) is shown here. In the expressions below, $P_\alpha=\boldsymbol{F}_{s_\alpha,U}\cdot\boldsymbol{v}_{s_\alpha}$ and $p_\alpha=p_{s_\alpha,U}$, and Q_α is either x_{s_α} or $H(x_{s_\alpha}-x_{cs})$,

$$\sum_{\alpha=1}^{n}\left(P_\alpha-p_\alpha\sum_{\beta=1}^{n}P_\beta\right)Q_\alpha=\sum_{\alpha=1}^{n}\left(P_\alpha\sum_{\beta=1}^{n}p_\beta-p_\alpha\sum_{\beta=1}^{n}P_\beta\right)Q_\alpha \quad [\because \text{Eq.}(4)]$$

$$=\sum_{\alpha=1}^{n}\sum_{\beta=1}^{n}(p_\beta P_\alpha-p_\alpha P_\beta)Q_\alpha=\frac{1}{2}\sum_{\alpha=1}^{n}\sum_{\beta=1}^{n}\{(p_\beta P_\alpha-p_\alpha P_\beta)Q_\alpha+(p_\alpha P_\beta-p_\beta P_\alpha)Q_\beta\}$$

$$=\frac{1}{2}\sum_{\alpha=1}^{n}\sum_{\beta=1}^{n}(p_\beta P_\alpha-p_\alpha P_\beta)(Q_\alpha-Q_\beta)=\sum_{\alpha=1}^{n-1}\sum_{\beta=\alpha+1}^{n}(p_\beta P_\alpha-p_\alpha P_\beta)(Q_\alpha-Q_\beta).$$

APPENDIX B: EXAMPLES OF EQ. (8d) FOR THREE- AND FOUR-BODY POTENTIALS

As particular cases, the contribution of a three-body or a four-body potential to the second term of Eq. (8d) is shown here. In the expressions below, equal apportioning of potential energy between interaction sites $p_{s_i,U} = 1/n$ is assumed.

1. Contribution of a three-body potential

$$(J_x V)_{\text{2nd term},n=3} = \sum_{s_1} \sum_{s_2>s_1} \sum_{s_3>s_2} \left[\sum_{\alpha=1}^{2} \sum_{\beta=\alpha+1}^{3} \left(\frac{1}{3} \mathbf{F}_{s_\alpha,U} \cdot \mathbf{v}_{s_\alpha} - \frac{1}{3} \mathbf{F}_{s_\beta,U} \cdot \mathbf{v}_{s_\beta} \right) (x_{s_\alpha} - x_{s_\beta}) \right]$$

$$= \sum_{s_1} \sum_{s_2>s_1} \sum_{s_3>s_2} \frac{1}{3} [(\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2})(x_{s_1} - x_{s_2}) + (\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3})(x_{s_1} - x_{s_3})$$

$$+ (\mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2} - \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3})(x_{s_2} - x_{s_3})],$$

for $U = \{s_1, s_2, s_3\}$.

2. Contribution of a four-body potential

$$(J_x V)_{\text{2nd term},n=4} = \sum_{s_1} \sum_{s_2>s_1} \sum_{s_3>s_2} \sum_{s_4>s_3} \left[\sum_{\alpha=1}^{3} \sum_{\beta=\alpha+1}^{4} \left(\frac{1}{4} \mathbf{F}_{s_\alpha,U} \cdot \mathbf{v}_{s_\alpha} - \frac{1}{4} \mathbf{F}_{s_\beta,U} \cdot \mathbf{v}_{s_\beta} \right) (x_{s_\alpha} - x_{s_\beta}) \right]$$

$$= \sum_{s_1} \sum_{s_2>s_1} \sum_{s_3>s_2} \sum_{s_4>s_3} \frac{1}{4} [(\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2})(x_{s_1} - x_{s_2}) + (\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3})(x_{s_1} - x_{s_3})$$

$$+ (\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_4,U} \cdot \mathbf{v}_{s_4})(x_{s_1} - x_{s_4}) + (\mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2} - \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3})(x_{s_2} - x_{s_3})$$

$$+ (\mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2} - \mathbf{F}_{s_4,U} \cdot \mathbf{v}_{s_4})(x_{s_2} - x_{s_4}) + (\mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3} - \mathbf{F}_{s_4,U} \cdot \mathbf{v}_{s_4})(x_{s_3} - x_{s_4})],$$

for $U = \{s_1, s_2, s_3, s_4\}$.

APPENDIX C: EXAMPLES OF EQ. (18) FOR THREE- AND FOUR-BODY POTENTIALS

As examples, contribution of a three-body or a four-body potential to the second term of the right hand side of Eq. (18) is shown here. In the expressions below, equal apportioning of potential energy between interaction sites $p_{s_i,U} = 1/n$ is assumed.

1. Contribution of a three-body potential

We consider a set of sites $U = \{s_1, s_2, s_3\}$ among which a three-body potential is defined. Assuming that the sites are located across a control surface $x = x_{\text{cs}}$ in a manner that $x_{s_1} < x_{\text{cs}} < x_{s_2}, x_{s_3}$, the amount of energy transferred across the control surface due to this three-body potential is given as

$$\sum_{\alpha=1}^{2} \sum_{\beta=\alpha+1}^{3} \left(\frac{1}{3} \mathbf{F}_{s_\alpha,U} \cdot \mathbf{v}_{s_\alpha} - \frac{1}{3} \mathbf{F}_{s_\beta,U} \cdot \mathbf{v}_{s_\beta} \right) \cdot \{ H(x_{s_\alpha} - x_{\text{cs}}) - H(x_{s_\beta} - x_{\text{cs}}) \}$$

$$= \frac{1}{3} [(\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2}) \cdot \{ H(x_{s_1} - x_{\text{cs}}) - H(x_{s_2} - x_{\text{cs}}) \} + (\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3}) \cdot \{ H(x_{s_1} - x_{\text{cs}}) - H(x_{s_3} - x_{\text{cs}}) \}$$

$$+ (\mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2} - \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3}) \cdot \{ H(x_{s_2} - x_{\text{cs}}) - H(x_{s_3} - x_{\text{cs}}) \}]$$

$$= \frac{1}{3} [(\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2}) \cdot (-1) + (\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} - \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3}) \cdot (-1) + (\mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2} - \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3}) \cdot 0]$$

$$= \frac{1}{3} (-2\mathbf{F}_{s_1,U} \cdot \mathbf{v}_{s_1} + \mathbf{F}_{s_2,U} \cdot \mathbf{v}_{s_2} + \mathbf{F}_{s_3,U} \cdot \mathbf{v}_{s_3}).$$

2. Contribution of a four-body potential

We consider a set of sites $U = \{s_1, s_2, s_3, s_4\}$ among which a four-body potential is defined. Assuming that the sites are located across a control surface $x = x_{\text{cs}}$ in a manner that $x_{s_2} < x_{\text{cs}} < x_{s_1}, x_{s_3}, x_{s_4}$, the amount of energy transferred across the control surface due to this four-body potential is given as

$$\sum_{\alpha=1}^{3}\sum_{\beta=\alpha+1}^{4}\left(\frac{1}{4}\boldsymbol{F}_{s_\alpha,U}\cdot\boldsymbol{v}_{s_\alpha}-\frac{1}{4}\boldsymbol{F}_{s_\beta,U}\cdot\boldsymbol{v}_{s_\beta}\right)\cdot\{H(x_{s_\alpha}-x_{\mathrm{cs}})-H(x_{s_\beta}-x_{\mathrm{cs}})\}$$

$$=\frac{1}{4}[(\boldsymbol{F}_{s_1,U}\cdot\boldsymbol{v}_{s_1}-\boldsymbol{F}_{s_2,U}\cdot\boldsymbol{v}_{s_2})\cdot\{H(x_{s_1}-x_{\mathrm{cs}})-H(x_{s_2}-x_{\mathrm{cs}})\}+(\boldsymbol{F}_{s_1,U}\cdot\boldsymbol{v}_{s_1}-\boldsymbol{F}_{s_3,U}\cdot\boldsymbol{v}_{s_3})\cdot\{H(x_{s_1}-x_{\mathrm{cs}})-H(x_{s_3}-x_{\mathrm{cs}})\}$$

$$+(\boldsymbol{F}_{s_1,U}\cdot\boldsymbol{v}_{s_1}-\boldsymbol{F}_{s_4,U}\cdot\boldsymbol{v}_{s_4})\cdot\{H(x_{s_1}-x_{\mathrm{cs}})-H(x_{s_4}-x_{\mathrm{cs}})\}+(\boldsymbol{F}_{s_2,U}\cdot\boldsymbol{v}_{s_2}-\boldsymbol{F}_{s_3,U}\cdot\boldsymbol{v}_{s_3})\cdot\{H(x_{s_2}-x_{\mathrm{cs}})-H(x_{s_3}-x_{\mathrm{cs}})\}$$

$$+(\boldsymbol{F}_{s_2,U}\cdot\boldsymbol{v}_{s_2}-\boldsymbol{F}_{s_4,U}\cdot\boldsymbol{v}_{s_4})\cdot\{H(x_{s_2}-x_{\mathrm{cs}})-H(x_{s_4}-x_{\mathrm{cs}})\}+(\boldsymbol{F}_{s_3,U}\cdot\boldsymbol{v}_{s_3}-\boldsymbol{F}_{s_4,U}\cdot\boldsymbol{v}_{s_4})\cdot\{H(x_{s_3}-x_{\mathrm{cs}})-H(x_{s_4}-x_{\mathrm{cs}})\}]$$

$$=\frac{1}{4}[(\boldsymbol{F}_{s_1,U}\cdot\boldsymbol{v}_{s_1}-\boldsymbol{F}_{s_2,U}\cdot\boldsymbol{v}_{s_2})\cdot 1+(\boldsymbol{F}_{s_1,U}\cdot\boldsymbol{v}_{s_1}-\boldsymbol{F}_{s_3,U}\cdot\boldsymbol{v}_{s_3})\cdot 0+(\boldsymbol{F}_{s_1,U}\cdot\boldsymbol{v}_{s_1}-\boldsymbol{F}_{s_4,U}\cdot\boldsymbol{v}_{s_4})\cdot 0+(\boldsymbol{F}_{s_2,U}\cdot\boldsymbol{v}_{s_2}-\boldsymbol{F}_{s_3,U}\cdot\boldsymbol{v}_{s_3})\cdot(-1)$$

$$+(\boldsymbol{F}_{s_2,U}\cdot\boldsymbol{v}_{s_2}-\boldsymbol{F}_{s_4,U}\cdot\boldsymbol{v}_{s_4})\cdot(-1)+(\boldsymbol{F}_{s_3,U}\cdot\boldsymbol{v}_{s_3}-\boldsymbol{F}_{s_4,U}\cdot\boldsymbol{v}_{s_4})\cdot 0]$$

$$=\frac{1}{4}(\boldsymbol{F}_{s_1,U}\cdot\boldsymbol{v}_{s_1}-3\boldsymbol{F}_{s_2,U}\cdot\boldsymbol{v}_{s_2}+\boldsymbol{F}_{s_3,U}\cdot\boldsymbol{v}_{s_3}+\boldsymbol{F}_{s_4,U}\cdot\boldsymbol{v}_{s_4}).$$

[1] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**, 817 (1950).
[2] G. Marechal and J.-P. Ryckaert, Chem. Phys. Lett. **101**, 548 (1983).
[3] P. J. Daivis and D. J. Evans, Mol. Phys. **81**, 1289 (1994).
[4] P. J. Daivis and D. J. Evans, Chem. Phys. **198**, 25 (1995).
[5] J. Zhang and B. D. Todd, Phys. Rev. E **69**, 031111 (2004). The term $(1/(4A))\Sigma_{ij}\boldsymbol{v}_i\cdot\boldsymbol{F}_{ij}^{(2)}[\mathrm{sgn}(y-y_i)+\mathrm{sgn}(y-y_j)]$ is missed in Eq. (27).
[6] B. D. Todd, P. J. Daivis, and D. J. Evans, Phys. Rev. E **51**, 4362 (1995).
[7] Y. Chen, J. Chem. Phys. **124**, 054113 (2006).
[8] R. J. Hardy, J. Chem. Phys. **76**, 622 (1982).
[9] J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986).
[10] J. Tersoff, Phys. Rev. B **39**, 5566 (1989).
[11] F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).
[12] T. Ohara, J. Chem. Phys. **111**, 6492 (1999).
[13] T. Ohara, J. Chem. Phys. **111**, 9667 (1999).
[14] S. K. Nath, F. A. Escobedo, and J. J. de Pablo, J. Chem. Phys. **108**, 9905 (1998).
[15] M. J. Assael, J. H. Dymond, M. Papadaki, and P. M. Patterson, Int. J. Thermophys. **13**, 269 (1992).