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# Contribution of intermolecular energy transfer to heat conduction in a simple liquid

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Heat conduction in a low-temperature liquid is mainly caused by interaction between molecules. The intermolecular energy transfer (IET), which contributes to macroscopic heat conduction flux, is discussed in the present paper. Intermolecular energy transfer is examined using the results of molecular dynamics (MD) simulations for a simple liquid, which is modeled using the Lennard-Jones (LJ) (12-6) potential. The intermolecular energy exchange rate (IEER) is defined as the product of the intermolecular forces acting between two molecules and the velocities of the molecules. A probability distribution of the magnitude of the IEER was obtained in an ordinary equilibrium MD simulation; such a distribution was well correlated to the intermolecular distances. The substantial contribution of the IET to heat conduction flux, which is called the intermolecular energy transfer rate (IETR) here, is given by a time average of the IEER. A model is introduced to evaluate the contribution of the IET to heat conduction flux, based on an assumption that the IETR is proportional to the magnitude of the IEER itself. To verify this model, MD simulations of heat conduction in the LJ liquid under a constant temperature gradient were performed and the IETR was obtained directly. It was found that the IETR had a strong correlation with the IEER. The direct observation of the IETR by the simulation of heat conduction also showed that energy transfer in the direction opposite to the macroscopic heat flux appears in certain regions of intermolecular distances periodically. The negative energy transfer is observed between a center molecule and molecules in the inner half shell of the second and further neighbor shells. The appearance of negative energy transfer reduces the net contribution of energy transfer between molecules separated by longer distances, and consequently heat conduction in a liquid is effected only by the IET between first neighbor molecules. © 1999 American Institute of Physics. [S0021-9606(99)50145-1]

## I. INTRODUCTION

Heat conduction is a fundamental thermal phenomenon, and its importance is widely recognized in science and technology. Thermal conductivity is an essential parameter used to characterize heat conduction phenomena in continuum fluids, and a number of excellent studies have been reported<sup>1-8</sup> in which the thermal conductivity is determined by molecular dynamics (MD) simulations. These studies treat pure liquids<sup>1,2,4-7</sup> and binary mixtures<sup>2,3,8</sup> by using equilibrium MD with the Green-Kubo formula<sup>1-3</sup> or nonequilibrium MD simulations.<sup>4-8</sup> Most of these studies<sup>1-4,7,8</sup> are for simple liquids modeled by the Lennard-Jones intermolecular potential. There was good agreement among the studies, and the basic method to calculate the thermal conductivity by MD simulations appears to be well established.

Presently there is a need to clarify the molecular mechanism of heat conduction, particularly in the field of thermal engineering. One desired outcome of this effort is the ability to predict the influence of temperature, density, and impurities such as ions on thermal conductivity by understanding the underlying molecular mechanisms of the process. In the near future, attempts will be made to produce fluids that have a predetermined thermal conductivity by making specially structured molecules.

Understanding the molecular mechanism of heat conduction is also required as a basis for studying molecular-scale energy transfer in microscopic or nonequilibrium thermal phenomena, which are processes that do not take place in a macroscopic continuum fluid and cannot be characterized by a thermal conductivity. The energy transfer at a liquid-vapor interface is related to phase change phenomena such as condensation and evaporation. The energy transfer in micropores is governed by the energy transfer characteristics at the liquid-solid interface. Understanding the molecular mechanism of energy transfer in liquids will lead to new insights into these thermal phenomena and their practical applications where the continuum theory is no longer effective.

Thermal energy is transferred between molecules according to the interaction via intermolecular forces. The intermolecular energy transfer (IET) is a dominant factor in heat conduction in low-temperature liquids. The author has studied the characteristics of the IET in liquid water and discussed the role of hydrogen bonds in heat conduction, using a model to evaluate the rate and characteristics of the IET.<sup>9</sup> The model is based on an assumption that the contribution of IET to heat conduction flux is characterized by the intermolecular energy exchange. The present paper focuses on the IET in simple liquids; its contribution to heat conduction is directly obtained as a function of the intermolecular

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distances by MD simulations for Lennard-Jones liquids. The model utilized in the author's previous paper<sup>9</sup> is verified by the present results.

In the next section, the intermolecular energy exchange rate (IEER) is defined as power acting on the two molecules according to the intermolecular force and velocity of the molecules. An ordinary equilibrium MD simulation is applied to observe the magnitude of the IEER as a function of the intermolecular distances. In Sec. III, the contribution of IET to heat conduction is discussed in terms of a model utilizing the obtained characteristics of the IEER, which is essentially the same as that proposed in the author's previous paper.<sup>9</sup> In Sec. IV, the results of MD simulations of heat conduction in a liquid under a constant temperature gradient are presented, and the model defined in Sec. III is verified.

## II. CHARACTERISTICS OF ENERGY EXCHANGE BETWEEN MOLECULES

### A. The intermolecular energy exchange rate

Under a pair-potential approximation, the motion of a molecule is determined by the intermolecular forces between the molecule and surrounding molecules. Transfer of energy between molecules occurs during the process of molecular motion. The energy exchange between molecules is evaluated as follows.<sup>9</sup>

Let  $E_i^k$  be the kinetic energy of molecule  $i$ , i.e.,

$$E_i^k = \frac{1}{2} m |\mathbf{v}_i|^2, \quad (1)$$

where  $m$  and  $\mathbf{v}_i$  denote the mass and velocity vector of molecule  $i$ , respectively. The time rate of change in  $E_i^k$  (i.e., the power) due to the force acting on the molecule  $i$  is

$$\dot{E}_i^k = \frac{\partial E_i^k}{\partial t} = \mathbf{F}_i \cdot \mathbf{v}_i. \quad (2)$$

The force acting on the molecule  $i$ ,  $\mathbf{F}_i$ , is a resultant of the intermolecular forces between the molecule  $i$  and all the other molecules  $j$ ,  $\mathbf{F}_{ij}$ . Therefore,

$$\dot{E}_i^k = \sum_j \mathbf{F}_{ij} \cdot \mathbf{v}_i = \sum_j \dot{E}_{ij}^k. \quad (3)$$

$\dot{E}_{ij}^k = \mathbf{F}_{ij} \cdot \mathbf{v}_i$  is the contribution of molecule  $j$  to the increase in the kinetic energy of molecule  $i$ .

In addition to the increase in kinetic energy discussed above, changes in the intermolecular potential energy should also be considered. The increase in potential energy due to the motion of molecules  $i$  and  $j$ ,  $\dot{E}_{ij}^p$ , is given by the following equation:

$$\dot{E}_{ij}^k + \dot{E}_{ji}^k + \dot{E}_{ij}^p = 0. \quad (4)$$

Since  $E_{ij}^p$  is a symmetric pair potential, the sum of  $\dot{E}_{ij}^k$  and one half of  $\dot{E}_{ij}^p$  is regarded as the amount of energy transferred from molecule  $j$  to  $i$  in a unit period of time, which is denoted by  $\dot{q}_{ij}$ , i.e.,

$$\dot{q}_{ij} = \dot{E}_{ij}^k + \frac{1}{2} \dot{E}_{ij}^p = \frac{1}{2} (\dot{E}_{ij}^k - \dot{E}_{ji}^k). \quad (5)$$

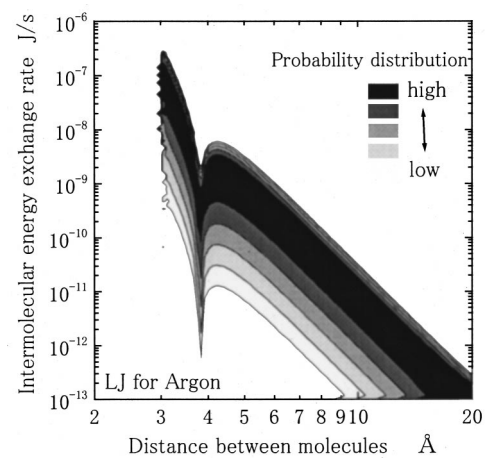


FIG. 1. Probability distribution of the intermolecular energy exchange rate as a function of intermolecular distances.

In the present paper,  $\dot{q}_{ij}$  is called the intermolecular energy exchange rate (IEER). The expression of Eq. (5) states that  $\dot{q}_{ij} = -\dot{q}_{ji}$ , which is consistent with the idea that during molecular interaction, a certain amount of energy transfers from one molecule to the other.

### B. The IEER observed in an equilibrium MD simulation

To observe the magnitude of the IEER, an equilibrium MD simulation of a simple fluid has been performed. A system of 1000 molecules in a cubic box with three-dimensional periodic boundary conditions was utilized. The Lennard-Jones (12-6) potential,

$$\phi(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right], \quad (6)$$

with  $\sigma = 3.405 \text{ \AA}$  and  $\epsilon = 1.774 \times 10^{-21} \text{ J}$  for argon, was applied for the intermolecular potential. Mass of the molecules was  $6.634 \times 10^{-26} \text{ kg}$ . The cutoff distance was  $6\sigma$ .

The system simulated was a saturated liquid at a low temperature. Guided by the saturation curves reported for a Lennard-Jones (LJ) fluid,<sup>10,11</sup> nondimensional temperature and density were selected to be  $T^* = k_B T / \epsilon = 0.7$  and  $\rho^* = N \sigma^3 / L^3 = 0.83$ , where  $k_B$ ,  $N$ , and  $L$  are the Boltzmann constant, number of molecules, and length of the simulation box, respectively. For argon, these nondimensional quantities correspond to a temperature of 90 K and a density of  $1395 \text{ kg/m}^3$ .

After aging of the system for 20 000 steps, the MD simulation was performed for 100 000 steps with constant total energy. The IEER was acquired for every pair of molecules at every step. Frequencies of the magnitude of the IEER and the intermolecular distances were counted. The time step was 2.5 fs.

The magnitude of the IEER observed in the MD simulation is shown in Fig. 1 as a function of intermolecular distance. The figure presents the probability distribution of IEER magnitude for a pair of molecules at a given intermolecular distance. The information of the radial distribution of molecules is eliminated. The probability distribution of ab-

solute values of the IEER is shown in the figure because the IEER shows the same distribution at positive and negative values.

A strong correlation is apparent between the IEER and the intermolecular distances. A steep drop of the IEER is clearly evident at  $r=3.8 \text{ \AA}$ , which corresponds to  $r=\sqrt[6]{2}\sigma$ , where the intermolecular forces given by the LJ potential are zero.

### III. MODELING OF THE CONTRIBUTION OF THE IET TO HEAT CONDUCTION

The IEER,  $\dot{q}_{ij}$ , indicated above, is an instantaneous rate of energy transfer between molecules. It does not lead directly to the macroscopic heat conduction flux under a temperature gradient. Hereafter, the rate of substantial IET which contributes directly to macroscopic heat conduction flux under a temperature gradient is called the intermolecular energy transfer rate (IETR) and denoted by  $\dot{Q}_{ij}$ . The IETR,  $\dot{Q}_{ij}$ , is given by a time average of the IEER,  $\dot{q}_{ij}$ . In a thermal equilibrium state such as simulated in Sec. II, the IETs among many pairs of molecules are isotropic. In this case, the IETR averaged over all the pairs of molecules is zero. On the other hand, in a state of heat conduction under a temperature gradient, the IETR in the opposite direction of the temperature gradient is slightly dominant; thus, nonzero heat flux results.

A model to evaluate the IET has been proposed in the author's previous report on the IET in water,<sup>9</sup> and is briefly described here. In the following, the averages of the absolute value of the IEER and the IETR are treated as functions of the intermolecular distance, i.e.,  $\overline{|\dot{q}_{ij}|} = \overline{|\dot{q}_{ij}|}(r_{ij})$  and  $\overline{\dot{Q}_{ij}} = \overline{\dot{Q}_{ij}}(r_{ij})$ . Here, the overstrike indicates an average over the molecular pairs. In order to evaluate heat conduction flux due to the IET which is caused by a temperature gradient, we should consider both the magnitude of energy transfer through a path of IET and the number of paths of IET in the liquid. The former is given by  $\overline{\dot{Q}_{ij}}(r_{ij})$ . For the latter, the radial distribution of molecules is utilized. These two factors give the contribution to heat conduction flux by IET between molecule  $i$  and all neighboring molecules within a distance  $r$ . These contributions, denoted as  $\overline{\dot{Q}_i}(r)$ , are given by

$$\overline{\dot{Q}_i}(r) = C \rho_{N,j} \int_{r_{ij}=0}^r r_{ij}^n g(r_{ij}) \overline{\dot{Q}_{ij}}(r_{ij}) dr_{ij}. \quad (7)$$

Here,  $g(r_{ij})$  is the radial distribution function,  $\rho_N$  is the number density of molecules, and  $C$  is a proportionality constant. The value of the exponent  $n$  will be discussed below. For the whole molecular system, the contribution of the IET between molecules whose distance is shorter than  $r$  to heat conduction flux, which is denoted by  $\overline{\dot{Q}}(r)$ , is expressed as

$$\overline{\dot{Q}}(r) = \rho_{N,i} \overline{\dot{Q}_i}(r) = C \rho_N^2 \int_{r_{ij}=0}^r r_{ij}^n g(r_{ij}) \overline{\dot{Q}_{ij}}(r_{ij}) dr_{ij}. \quad (8)$$

The possible factors that determine the index  $n$  in Eqs. (7) and (8) are as follows.<sup>9</sup> First, the contribution of the IET

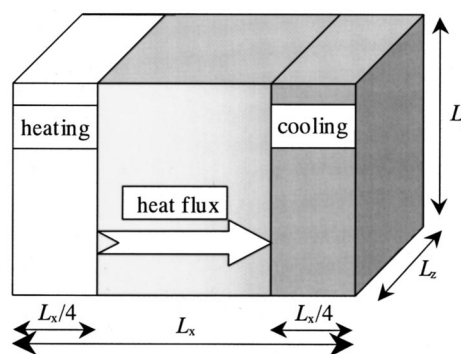


FIG. 2. Simulation system for the steady heat conduction.

between molecules  $i$  and  $j$  to macroscopic heat flux averaged over a volume should be weighted by  $r_{ij}$ , as will be described below [Eq. (11)]. Second, when the IET between molecule  $i$  and all the other surrounding molecules  $j$  is taken into account equally, the number of molecules  $j$  at  $r_{ij}$  is given by  $\rho_N g(r_{ij}) \cdot 4\pi r_{ij}^2 dr_{ij}$ ; therefore, this is proportional to  $r_{ij}^2$ . If these two factors are taken into account, the  $n$  is evaluated to be 3.

Concerning the IETR,  $\overline{\dot{Q}_{ij}}(r_{ij})$ , let us assume that it is proportional to the magnitude of the IEER, i.e.,

$$\overline{\dot{Q}_{ij}}(r_{ij}) = C' \overline{|\dot{q}_{ij}|}(r_{ij}), \quad (9)$$

where  $C'$  is a proportionality constant. Thus, we can evaluate the heat conduction flux due to the IET by Eqs. (8) and (9) with  $\overline{|\dot{q}_{ij}|}(r_{ij})$  given in Fig. 1. Results of the above evaluation of the  $\overline{\dot{Q}}(r)$  will be shown in Fig. 5 and verified by direct observation of  $\overline{\dot{Q}_{ij}}(r_{ij})$  and  $\overline{\dot{Q}}(r)$ , via a MD simulation of heat conduction under a temperature gradient.

### IV. MD SIMULATION OF HEAT CONDUCTION UNDER A TEMPERATURE GRADIENT

A MD simulation has been performed to obtain values for  $\overline{\dot{Q}_{ij}}(r)$  and  $\overline{\dot{Q}}(r)$  during macroscopic heat conduction under a temperature gradient for the purpose of verification of the model by Eqs. (8) and (9). The method of the simulation of heat conduction is essentially the same as that applied in the author's previous study on water.<sup>9</sup> The simulation system is shown in Fig. 2. Molecules modeled by the Lennard-Jones (12-6) intermolecular potential with parameters for argon were arranged in a rectangular basic cell having a square cross section. Simulation conditions for the system are shown in Table I. The cutoff distance for the intermolecular potential was  $5\sigma$ . In order to produce a temperature gradient in the  $x$  direction in the liquid, a cooling region was installed at one end of the cell and a heating region was at the other

TABLE I. Conditions for the simulations of steady heat conduction.

Case	Number of molecules	$L_x$ (Å)	$L_y=L_z$ (Å)	Number of steps
1	1000	58	29	6 000 000
2	3000	86	42	5 000 000

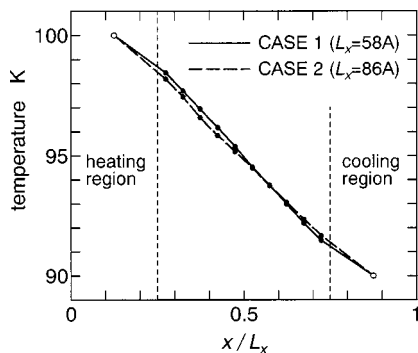


FIG. 3. Time-averaged temperature distribution given by the simulations.

end. Average temperatures of the liquid in these heating and cooling regions were kept at 100 K and 90 K, respectively, by scaling velocities of molecules in these regions. Periodic boundary conditions were applied to the  $y$  and  $z$  directions, which are perpendicular to the temperature gradient. At the end faces perpendicular to the  $x$  direction, the Lennard-Jones (12-6) potential was applied between the molecules and the end faces, which prevented the molecules from leaving the cell. The simulation was performed for the two conditions of different system sizes as shown in Table I. The applied time step was 2.5 fs.

The simulations yielded time-averaged temperature distributions which are shown in Fig. 3. Excellent linearity in the temperature distribution was realized in the center region of the cell owing to a large number of time steps applied in the simulations. The temperature gradients were  $2.7 \times 10^9$  for case 1 and  $1.7 \times 10^9$  K/m for case 2.

In many reports in which heat conduction flux is evaluated by MD simulations, the heat flux is calculated based on the following equation:

$$J_{Q,x} S_{yz} = \sum_i (E_i/1) \frac{v_{x,i}}{|v_{x,i}|} + \frac{1}{2} \sum_i \sum_j (\mathbf{v}_i \cdot \mathbf{F}_{ij}) \frac{x_{ij}}{|x_{ij}|}. \quad (10)$$

Here,  $J_{Q,x}$  and  $S_{yz}$  represent heat flux in the direction of  $x$  and the area of control surface in the  $y$ - $z$  plane, respectively.  $E_i$  represents energy held by a molecule  $i$ , which is given by the sum of the kinetic energy,  $E_i^k$ , and potential energy,  $E_i^p$ . The term  $v_{x,i}$  represents the velocity component of the molecule  $i$  in the direction of  $x$ . The first term on the right side of Eq. (10) represents the energy transport caused by the motion of the molecule itself. The  $\Sigma$  is the sum of the energy of all the molecules which pass through the control surface  $S_{yz}$  in a unit period of time. The term  $(/1)$  represents the dimension of  $\text{time}^{-1}$ . The second term represents the energy transferred through the control surface due to the interaction between molecules, which is equivalent to  $\sum_i \sum_{j>i} \dot{q}_{ij}$ . The  $\Sigma \Sigma$  is the sum of the IET between all pairs of molecules which interact across the control surface.

In most cases, the following equation is applied for practical use, which is derived by integrating Eq. (10) over a certain length in the direction of the heat flux,  $x$ .

TABLE II. Simulation results for thermal conductivity and energy transport according to molecular motion [the first and second terms of Eq. (11)] and intermolecular energy transfer [the third term of Eq. (11)].

	Case 1	Case 2
Thermal conductivity (W/mK)	0.157	0.162
Kinetic energy transport	5.6%	7.4%
Potential energy transport	3.9%	3.5%
Intermolecular energy transfer	90.5%	89.1%

$$\begin{aligned} J_{Q,x} V &= \sum_i E_i v_{x,i} + \frac{1}{2} \sum_i \sum_j x_{ij}^* (\mathbf{v}_i \cdot \mathbf{F}_{ij}) \\ &= \sum_i E_i^k v_{x,i} + \sum_i E_i^p v_{x,i} + \frac{1}{2} \sum_i \sum_j x_{ij}^* (\mathbf{v}_i \cdot \mathbf{F}_{ij}). \end{aligned} \quad (11)$$

Equation (11) gives the heat flux averaged over a control volume,  $V$ . In the present simulation, a control volume was located at the center of the cell in the  $x$  direction and the heat flux was evaluated by Eq. (11). The width of the control volume,  $x_{CV}$ , was 8 and 15 Å for cases 1 and 2, respectively. The  $\Sigma$  in the first and second terms on the right side of Eq. (11) is the sum of all molecules that are contained in the control volume. The third term is equivalent to  $\sum_i \sum_{j>i} x_{ij}^* \dot{q}_{ij}$  and the double summation is over all pairs of molecules with the condition that the line connecting the two molecules penetrates any  $yz$  plane included in the control volume. In cases where only part of the connecting line is contained in the control volume, i.e., one or both of the two molecules are located out of the control volume, then  $x_{ij}^*$  is the  $x$ -component of the portion of the connecting vector contained in the control volume.

Thermal conductivity obtained in the present simulations is shown in Table II. Contributions of the three terms in the right side of Eq. (11) to the total heat flux are also indicated. It is confirmed that the IET is a governing factor in heat conduction in liquid. Excellent agreement is observed between the two cases with different system sizes.

Thermal conductivity of a LJ liquid at a similar state point is reported by several researchers<sup>1,4,8</sup> to be 0.127–0.138 W/(mK). As compared with these values, the present simulation gives higher values by 20%. This discrepancy may be caused by some differences in simulation conditions, such as temperature gradient and cutoff distance for the intermolecular potential.

The IETR  $\bar{Q}_{ij}(r_{ij})$ , which is the substantial contribution of the IET to heat conduction flux as a function of intermolecular distance, is investigated here. The intermolecular distance  $r_{ij}$  ( $2 \leq r_{ij} \leq 20$  Å) was divided into 100 sections with an equal interval in log space  $\log r_{ij}$ , and  $\dot{q}_{ij}$  was summed in each section according to the intermolecular distance of the pair. The sign of the term was plus for the IET in the direction of macroscopic heat conduction flux and minus in the opposite direction. Thus, an average value of  $\dot{q}_{ij}$  was obtained as a function of intermolecular distance, which indicates the average contribution of the IET between a pair of

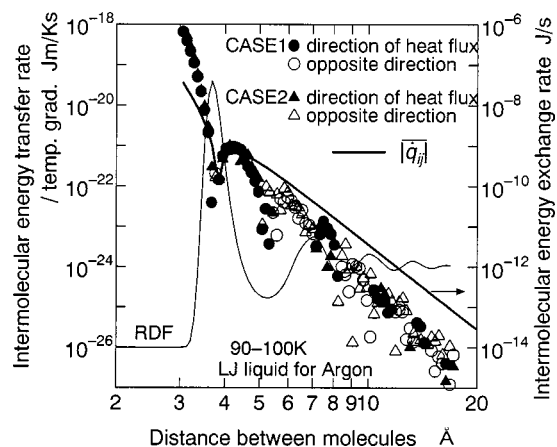


FIG. 4. The intermolecular energy transfer rate (IETR) under a temperature gradient as a function of intermolecular distances. The intermolecular energy exchange rate (IEER) and the radial distribution function (RDF) are also plotted.

molecules to heat conduction flux, which is equivalent to  $\bar{Q}_{ij}(r_{ij})$ .

The above average values of  $\bar{Q}_{ij}(r_{ij})$ , divided by the temperature gradient, are plotted in Fig. 4. The value was found negative at certain regions of intermolecular distance and was positive elsewhere. Absolute values of  $\bar{Q}_{ij}(r_{ij})$  are plotted in the figure with different marks indicating their signs. The results from two simulations having different system sizes agree well with each other.

The average magnitude of the IEER,  $|\bar{q}_{ij}|$ , is indicated in the figure to compare the dependency on  $r_{ij}$ . The IETR shows an apparent dependency on  $r_{ij}$  similar to that of the IEER. The dependency on  $r_{ij}$  of  $\bar{Q}_{ij}(r_{ij})$  is comparable to that of  $|\bar{q}_{ij}|/r_{ij}^2$  at  $r_{ij} > 3.8 \text{ \AA}$ .

One of the more interesting findings shown in Fig. 4 is that the simulations yielded negative IET, which is in the direction opposite to the macroscopic heat conduction flux, in a certain region at  $r_{ij} > 5 \text{ \AA}$ . The negative energy flow appeared periodically at the inner half of neighbor shells, where the radial distribution function inserted in the figure had positive gradient in the second and further neighbor shells. The appearance of the regions of negative IET was caused by the following mechanism. Molecules in the inner half shell of the second neighbor shell were influenced by weak attractive force from the center molecule and also by stronger repulsive force from the molecules in the first neighbor shell. Therefore, for molecules in the inner half shell of the second neighbor shell, the IET from the center molecule always had the opposite sign to the IET from molecules in the first neighbor shell. Motions of the second neighbor molecules were mainly influenced by the first neighbors rather than the center molecule. This caused the IET between a molecule in the first neighbor shell and a molecule in the second neighbor shell to be positive on average. Therefore, the IET between the center molecule and molecules in the inner half shell of the second neighbor shell was negative.

Contribution of the IET between molecules whose separation is shorter than  $r$  to macroscopic heat conduction flux,

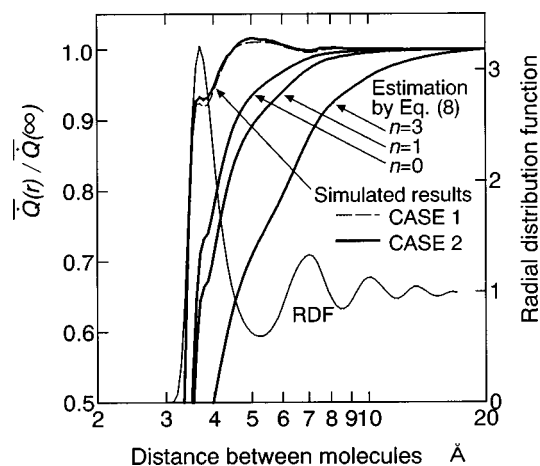


FIG. 5. Ratios of the IET between molecules whose distance is shorter than  $r$  to the total heat flux by IET. Simulation results and estimations by Eqs. (8) and (9) are shown. Radial distribution function (RDF) is also plotted.

$\bar{Q}(r)$ , was evaluated in Sec. III by a model represented by Eqs. (8) and (9). Now the real  $\bar{Q}(r)$  is derived by an integration of the product of  $\bar{Q}_{ij}$  plotted in Fig. 4 and  $r^3 g(r)$  from 0 to  $r$ . The ratio of  $\bar{Q}(r)$  to  $\bar{Q}(\infty)$  is plotted in Fig. 5, where the real values and those evaluated by Eqs. (8) and (9) are compared. Here,  $\bar{Q}(\infty)$  is evaluated at  $r=20 \text{ \AA}$ .

The real  $\bar{Q}(r)$  increases most rapidly and exceeds  $\bar{Q}(\infty)$  once, due only to the IET between first neighbor molecules. After that, the negative energy transfer from the inner half shell of the second neighbor shell reduces  $\bar{Q}(r)$ . At larger  $r$ , oscillations with a small amplitude appear in the outer half shell of the second neighbor shell and the inner half shell of the third neighbor shell. Good agreement is observed between the two cases for the simulations.

The ratio of  $\bar{Q}(r)$  to  $\bar{Q}(\infty)$  predicted by Eqs. (8) and (9) for the index  $n=0, 1$ , and  $3$  are plotted in the figure. The prediction by Eqs. (8) and (9) with  $n=0$  gives the best result that is closest to the real  $\bar{Q}(r)$ . However, even in this case, the contribution of the IET between molecules with long distances is overestimated.

The contributions of the IET among first neighbor molecules and second neighbor molecules, which are read from the figure, are listed in Table III. Only the IET between first neighbor molecules contributes to macroscopic heat conduction, and the IET between second neighbor molecules in total has a slightly negative contribution. The prediction by Eqs.

TABLE III. Ratios of the IET between the center molecule and molecules in the neighbor shells to the total IET.

	1st neighbor shell	2nd neighbor shell
Simulated result Case 1	101.1%	-1.0%
Simulated result Case 2	101.5%	-1.3%
Eq. (8) with $n=0$	94.4%	5.3%
Eq. (8) with $n=1$	90.4%	8.7%
Eq. (8) with $n=3$	72.8%	20.9%

(8) and (9), even with  $n=0$ , underestimates the contributions of the IET between first neighbor molecules by approximately 7%.

## V. CONCLUSION

In the present paper, the rate of energy exchange between molecules and the rate of the substantial energy transfer between molecules that contributes to macroscopic heat conduction flux under a temperature gradient have been discussed by using the concept of the IEER,  $|\dot{q}_{ij}|$ , and the IETR,  $\bar{Q}_{ij}$ . The IEER as a function of the intermolecular distance was examined by an equilibrium MD simulation. Based on an assumption that the IETR as a function of the intermolecular distance is proportional to the IEER, a model to evaluate the contribution of the IET to heat conduction was presented. The model was verified by a MD simulation of heat conduction under a temperature gradient.

One of the findings of the present study is that  $|\dot{Q}_{ij}|$  is strongly correlated to  $|\dot{q}_{ij}|$ , and both exhibit a similar functional dependence on intermolecular distance. As was discussed in Ref. 9, substantial IET in response to a temperature gradient is a result of heat dissipation owing to the equilibration process caused by energy exchange between molecules. Therefore, the magnitude of the intermolecular energy exchange determines the rate of the IET in heat conduction. In this respect, the assumption of Eq. (9) is justified, although some modifications are necessary for a more precise evaluation.

A second interesting finding is the energy transfer in the direction opposite to macroscopic heat conduction for certain intermolecular distances. This can be interpreted as the influence of liquid structure on the molecular mechanism of heat

conduction. The IET between the center molecule and molecules in the inner half shell of the second neighbor shell is canceled by the IET between the center molecules and molecules in the outer half shell of the second neighbor shell. Therefore, it appears that the IET only between first neighbor molecules contributes to macroscopic heat conduction. The IET between molecules that are outside the first neighbor shell does not contribute to heat conduction in spite of the fact that there are still large intermolecular interactions between them. It has been found in the author's previous study on water<sup>9</sup> that the  $n$  in the model by Eq. (8) is reduced to values less than 1. One of the reasons for this may be the cancellation of the IET from the second neighbor molecules.

## ACKNOWLEDGMENT

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