Analysis on Thermal Conductivity Definitions for Equilibrium Molecular Dynamics Simulation

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Abstract - *The Green-Kubo relation in equilibrium molecular dynamics (EMD) has been widely utilized for evaluation of the lattice thermal conductivity (TC) of condensed matters. In previous studies adopting the Green-Kubo relation, however, there exist three different expressions of TC by EMD. In the present study, by comparing these expressions in theory and MD simulations for binary systems, we identified the most accurate TC expression among the three different expressions. We found that the partial specific enthalpy and the reduced heat of transport affect the differences among the three TC expressions. Our approach was applied to Li_2O over a wide temperature range including both solid and liquid phases. It was confirmed that when the atoms in a system become mobile even if it is in a condensed phase, one of the three widely utilized TC expressions causes a larger error up to around +120 % in comparison with the value determine by the most accurate TC expression.*

I. INTRODUCTION

Thermal conductivity (TC) is the fundamental material property needed to design nuclear engineering devices such as the nuclear fuel in fission reactors and the blanket in fusion reactors. Due to its importance, various experimental and computational methods were proposed and applied to evaluate TC. In computational methods, equilibrium molecular dynamics (EMD) simulation using the Green-Kubo (GK) relations is carefully investigated and regarded as a confidential method [1] compared to the non-equilibrium molecular dynamics method (NEMD). Also, it have been widely utilized to determine TC in condensed matters including rare gas liquids, covalent crystals, ionic crystals and liquids, and plasmas.

The GK relation enables us to derive a phenomenological coefficient, which can be determined in experiments such as self-diffusion coefficient and viscosity, from the integral of corresponding correlation function. TC is expressed with several phenomenological coefficients. Among those phenomenological coefficients related to TC, the phenomenological coefficient for the heat flux autocorrelation function (HACF) is the main component, which is described as

$$L_{QQ} = \frac{1}{3k_B V} \int_0^\infty \langle \mathbf{j}_Q(0)\mathbf{j}_Q(t)\rangle dt, \qquad (1)$$

where L_{QQ} is the PC for HACF, $\mathbf{j}_Q(t)$ the heat flux, k_B the Boltzmann constant, and V the volume of system. The angled bracket inside the integral denotes the ensemble average of correlation function.

In previous studies of TC in binary systems, however, various expressions are considered as the expression of TC, which are different either in (i) the way how TC is expressed with PCs, or (ii) the way how the heat flux is defined.

On the difference in (i) the TC expression itself, some studies express TC only with L_{QQ} as [2]–[6]

$$\kappa_1 = \frac{L_{QQ}}{T^2}, \qquad (2)$$

while others involve another combination of PCs as [7]–[12]

$$\kappa_2 = \frac{1}{T^2}\left(L_{QQ} - \frac{L_{Q1}L_{1Q}}{L_{11}} \right), \qquad (3)$$

where L_{1Q} and L_{Q1} are PCs on the correlation between heat flux and mass flux. In the present paper, we denote the former one as single-term expression of TC, and the latter as double-terms expression. While the single-term expression is often utilized for solids, the usage of double-terms expression concerns mostly to fluids like plasma [12] or liquids [7]–[9], [11], albeit the application to solids [10], [11] also sparsely exist. As the double-term expression considers cross-coupling phenomenon of the heat flux with mass flux, the strength of such cross effect is expected to make distinct the double-term expression from the single-term expression.

On the difference in (ii) the definition of the heat flux, which is calculated by the time derivative of atomic energy moment in MD, some studies subtract partial specific enthalpy (PSE) from the atomic energy, [2]–[6] while others do not. [13]–[16] This difference introduces two distinct heat flux expressions as (for zero barycentric velocity **u**)

$$\mathbf{j}_Q^*(t) = \frac{d}{dt} \sum_{i=1}^N \mathbf{r}_i(t) e_i(t)$$

$$= \sum_{i=1}^N \mathbf{v}_i(t) e_i(t) + \sum_{i=1}^N \left[\sum_{j=1,\neq i}^N \mathbf{F}_{ij}(t) \cdot \mathbf{v}_j(t) \right] \mathbf{r}_{ij}(t), \quad (4)$$

for PSE non-subtracted form, and

$$\mathbf{j}_Q(t) = \mathbf{j}_Q^*(t) - \sum_{k=1}^2 \bar{h}_k \mathbf{j}_k(t),$$

$$\mathbf{j}_k(t) = \sum_{i=1}^{N_k} m_i \mathbf{v}_i(t), \quad (5)$$

for PSE subtracted form, where $\mathbf{r}_i$ is the position vector ($\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$), m_i the mass, e_i the total energy (kinetic + potential) atom i, $\mathbf{F}_{ij}$ the force on atom i due to atom j, and $\bar{h}_k$ the partial specific enthalpy of component k ($\bar{h}_k = h_k / m_k$), where h_k is the partial molar enthalpy). This specific quantity is for the use of mass flux instead of molar flux in equations. Upper asterisk is used for expressions related to the non-subtracted heat flux throughout the present paper in order to clearly distinguish between PSE subtracted and non-subtracted expressions, e.g. $\mathbf{j}_Q^*$ for PSE non-subtracted heat flux and $\mathbf{j}_Q$ for PSE subtracted one.

Using the notations mentioned above, TC expressions of Eqs. (2) and (3) with PSE non-subtracted heat flux are written as

$$\kappa_1^* = \frac{L_{Q^*Q^*}}{T^2}, \quad (6)$$

and

$$\kappa_2^* = \frac{1}{T^2} \left(L_{Q^*Q^*} - \frac{L_{Q^*1} L_{1Q^*}}{L_{11}} \right), \quad (7)$$

Various works stated that the double-term expressions (both κ_2^* and κ_2) are equivalent under the sensible linear transformation of heat flux, [7] such as the relation between $\mathbf{j}_Q^*$ and $\mathbf{j}_Q$ in this study. Thus the double-term expression liberates the choice of any heat flux for TC calculation. For a single-component system, Hoheisel [17] pointed out that the subtraction of PSE does not change the value of TC when center of mass is fixed, thus $\kappa_1^* = \kappa_1$. These confirmed equivalences are under the assumption of fixed total center of mass during the MD simulation. For multi-component systems with limited dimension, however, non-subtraction of PSE term induces some difference in the resultant TC because the center of mass of each element cannot be fixed completely.

In summary, there are 3 independently different versions of TC expression in EMD with the GK relation for binary systems: κ_1^*, κ_1, and κ_2. However, no study analyzed the difference between these TC formalisms systematically. In this study, we compare TC values determined by those 3 TC expressions to clarify the differences among them for binary ionic systems. As a model system, Li_2O is chosen to emphasize the influence of mobility of atoms on TC. Li_2O is known as a superionic conductor where Li diffuses like in a liquid even in the solid phase. Li_2O is also a candidate breeding material of fusion reactors, and is of an anti-fluorite crystal structure, which is similar to UO_2, which is of a fluorite crystal structure.

Reference of classification		Type of heat flux	
		PSE subtracted heat flux	PSE non-subtracted heat flux
Number of phenomenological coefficients	1	$\dfrac{L_{Q^*Q^*}}{T^2}$	$\dfrac{L_{Q^*Q^*}}{T^2}$
	2	$\dfrac{1}{T^2}\left(L_{QQ} - \dfrac{L_{Q1}L_{1Q}}{L_{11}}\right)$	$\dfrac{1}{T^2}\left(L_{Q^*Q^*} - \dfrac{L_{Q^*1}L_{1Q^*}}{L_{11}}\right)$

Table I. Summary of different thermal conductivity expressions in equilibrium molecular dynamics using Green-Kubo relation, for the binary systems. Note that the equivalence of both double term expressions is already reported [7] and confirmed.

II. DESCRIPTION OF THE ACTUAL WORK

A. Difference analysis between TC expressions

The differences among definition in EMD with the GK relation for binary systems: κ_1^*, κ_1, and κ_2 are shown in Fig. 1.
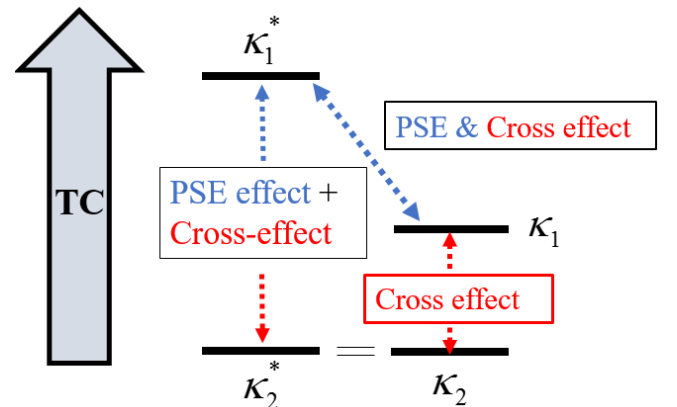
Fig. 1. Summary of the difference between thermal conductivity expressions in equilibrium molecular dynamics using Green-Kubo relation, for the binary systems.

There are two main effect that comprises the difference between TC expressions; namely PSE and Cross effect. PSE effect is called when the difference between TC is triggered by $\Delta \bar{h} = \bar{h}_1 - \bar{h}_2$, which is the difference of PSE between two components. Meanwhile, Cross effect is called when the reduced heat of transport $\bar{Q}_1 = L_{1Q}/L_{11}$ triggers the difference. Thus we can consider $\Delta \bar{h}$ and $\bar{Q}_1$ as the characteristic energy of certain material system, because both of them play the similar role in the difference of TC expressions. The explicit difference among TC expressions can be summarized as below equations.

$$\kappa_1^* - \kappa_1 = (2\Delta \bar{h} \cdot \bar{Q}_1 + \Delta \bar{h}^2) \cdot L_{11} / T^2 \qquad (8)$$

$$\kappa_1 - \kappa_2 = \bar{Q}_1^2 \cdot L_{11} / T^2 \qquad (9)$$

In Eq. (8) and (9), both energy-related terms are multiplied by PC of mass flux autocorrelation, L_{11}. As the L_{QQ} closely related to TC, we can expect for L_{11} be closely related to the diffusion coefficient.

From above equations and Fig. 1, it can be seen that the difference between κ_1^* and κ_1 is due to the PSE and Cross effect, and between κ_1 and κ_2 is due to the Cross effect. Conceptually, **$\Delta \bar{h}$** denotes the resultant energy difference due to the exchange of particles of species 1 and 2. And the reduced heat of transport represents the excessive energy that is conveyed by diffusing particle by its definition. Therefore, these two kinds of characteristic energy reflect the energy transport due to the mass diffusion. Considering the purely conducing process, these effects should be subtracted properly. Thus κ_2 can be considered as the most appropriate TC expression. The deviation from κ_2 of other TC expressions can be considered as an error.

B. Details of MD simulation

Based on theoretical work, EMD simulations are conducted on Li_2O model system using LAMMPS MD simulator. The potential parameters are used from Ref. [18]. To avoid the overlapping of pairwise interaction, the dimension of supercell size is set to supersede the twice of cutoff radius (10 Å) of pairwise Buckingham potential. Thereby we used 6x6x9 supercell for the anti-fluorite Li_2O crystal (2592 atoms).

To obtain the TC result, equilibration and production run is conducted for one single MD simulation. The former is to assure our system of equilibrium state, and the latter is to obtain TC by GK relation. Every simulation is done by 1 fs timestep. For equilibration run, we conducted two different types of simulation: increasing and decreasing the temperature, namely upward and downward simulations. These are to equilibrate the system in ordered and disordered phase, respectively. The lattice constant is determined during equilibration run via 200 ps NPT simulation. By the determined lattice constant, the supercell of model systems having equilibrium volume is created.

During the production run, 200~400 ps NVT simulation is conducted to relax the atomic position in the supercell of fixed volume for upward simulations. After that, 3~9 ns simulation is followed to extract the correlation function of currents of interest in this study. For downward simulations, the initial configuration is heated at 3000~5000 K for 50 ps in NVT ensemble, to fully melt the system. After that, the system was thermally equilibrated during 200 ps with the target temperatures. Finally, the GK production run is followed with the disordered and stabilized system for 9 ns. The value of correlation functions is sampled by 5 fs interval, and the length of correlation is set to 20 ~ 50 ps depending on the TC value; the bigger the TC value is, the longer correlation length is needed.

III. RESULTS

As we do simulations over the wide temperature range beyond the melting point, several phases of material can appear. The information of phase status can be inferred by the change of supercell volume and diffusion coefficients with regard to the temperature.

A. Phase status of Li₂O system

Figure 2 shows the change of supercell volume for Li_2O as the temperature increases. For Li_2O upward, sudden increase of supercell volume occurs between 1000 K and 1200 K. We can consider the melting point of Li_2O with this potential model resides between these two temperatures, which is far below the experimental melting point of 1711 K. By constructing a system which contains solid-liquid interface, [19] melting point of Li_2O with current potential model is estimated around 1100 K. Therefore, deviation of supercell volume in Fig. 2 in Li_2O upward at 800 ~ 1000 K from Li_2O downward is due to the metastable super-cooled liquid phase.
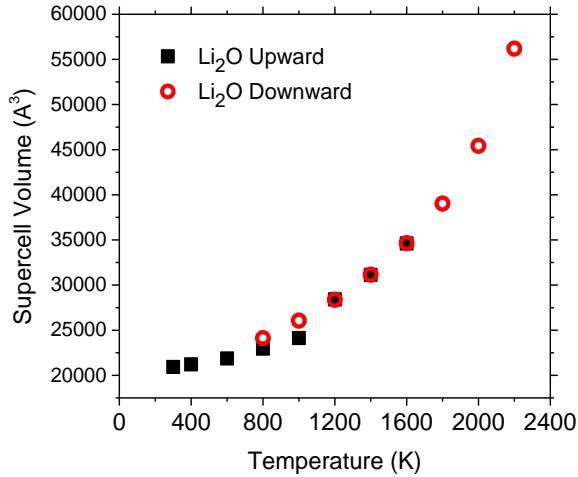
Fig. 2. The change of supercell volume following the temperature increase, Li_2O upward and downward systems. For Li_2O upward, sudden increase of supercell volume between 1000 and 1200 K is observed, which is an evidence of melting. As the temperature decreases for Li_2O downward, there exists difference in volume at 800 ~ 1000 K for both cases. It suggests the Li_2O downward is in a supercooled liquid state for that temperature range.

To investigate more about the phase status of systems, self-diffusion coefficient for Li_2O system is calculated as shown in Fig. 3. This result suggests that Li_2O system undergoes the superionic transition at 800 K, where only Li atom partially melts and diffuses like a liquid. Again, there is difference in the self-diffusion coefficient result between Li_2O and TiO_2 between 800 and 1000 K. This supports the idea that supercooled liquid state appears below 1000 K for Li_2O downward case. Because this metastable phase has higher diffusion coefficient than Li_2O upward, it is possible to observe the effect of self-diffusion coefficient on the value of TC expressions.
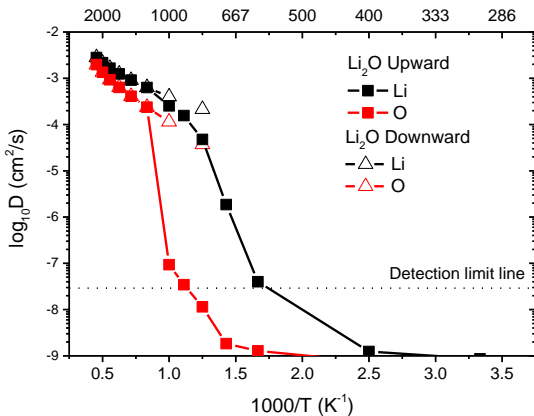

Fig. 3. Change of self-diffusion coefficients following the temperature change, Li_2O upward and downward systems.

For Li_2O upward, more than 3 orders of magnitude difference in the diffusion coefficient of Li and O supports the superionic state. Also, the difference in the diffusion coefficient between Li_2O upward and downward suggests the existence of supercooled liquid state.

B. Thermal conductivity result

TC results of Li_2O is shown in Fig. 4. The result of Li_2O downward is neglected other than of 800 and 900 K, for it shows redundant TC result with Li_2O upward near and after the melting point.
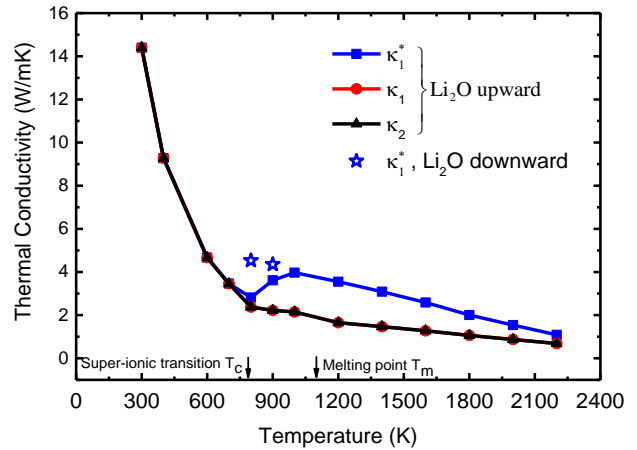

Fig. 4. The change of three thermal conductivity expressions, for Li_2O upward and downward systems. Data points of Li_2O downward is omitted other than 800 and 900 K because they give a redundant result with Li_2O upward. For the overall temperature range, κ_1 and κ_2 matched exactly with each other, which suggests that there is no cross effect at all. Meanwhile, κ_1^* result in different value starting from 800 K, showing at most 1.9 W/mK difference compared to other expressions. This corresponds to more than twice of κ_1 and κ_2.

For Li_2O upward, κ_1 and κ_2 shows 1/T decreasing trend having the same value with each other. It is an ordinary temperature dependence of the ceramic compounds, which is well-explained by umklapp scattering of phonon. Meanwhile, κ_1^* deviates from the others. This difference starts to emerge at 800 K, which is around superionic transition temperature and below the melting point. It is an erroneous result of κ_1^* according to discussions in previous sections. The result of Li_2O downward shows even more error than the upward case. It suggests that systems with higher atomic mobility phase, κ_1^* result in more error than with static environment phase.
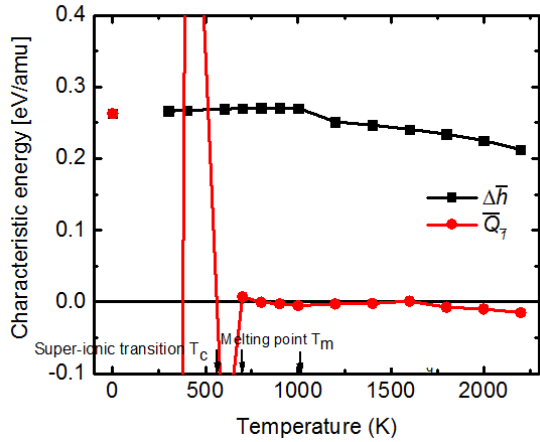
Fig. 5. The temperature response of the difference of partial specific enthalpy of species 1 and 2, $\Delta\bar{h}$, and the reduced heat of transport, $\bar{Q}_1$, for Li_2O upward system. While $\Delta\bar{h}$ is around 0.3 ev/amu, $\bar{Q}_1$ is almost zero for the high temperature range. Below the melting point, $\bar{Q}_1$ shows highly fluctuating value. This is thought to be caused by the poor statistics because the ordinary diffusion event rarely occurred at such low temperatures.

The result of two kinds of characteristic energy is summarized in Fig. 5; $\Delta\bar{h}$ and $\bar{Q}_1$. Due to the difficulty in achieving decent statistics for the L_{1Q}, $\bar{Q}_1$ shows fluctuating value at low temperatures. By comparing $\Delta\bar{h}$ and $\bar{Q}_1$, we can know that the Cross effect is negligible compared to the PSE effect. Indeed, it is turned out that the Cross effect is negligible for all the temperature range (details not given here). This result suggests the cause of decent agreement between different TC expressions is not these characteristic energy, but other terms involved in Eq. (8) and (9). As the L_{11} is the PC of mass flux auto-correlation, we consider the emergence of κ_1^* error is due to the activation of mass flux inside the system. Even though mass flux is a diffusive one, it triggers error of κ_1^* as a result.

Furthermore, it can be expected that κ_1 can also be an erroneous TC expressions for the systems with high value of $\bar{Q}_1$. For example, $\bar{Q}_1$ for hydrogen in palladium lattice is reported as 0.25 eV/amu, [5] which is comparable to the current $\Delta\bar{h}$ value of Li_2O system. As $\bar{Q}_1$ is a mass-specific quantity, high value of $\bar{Q}_1$ is thought to originate from the small mass of hydrogen. It would result in comparable error of κ_1 to κ_1^*. Therefore, special consideration will be needed for the calculation of TC in systems containing light element.

IV. CONCLUSIONS

In summary, we reviewed the concurrent existing TC expressions which vary with each other. The difference between these expressions are investigated in terms of material's properties which can be microscopically defined. Consequently, it is suggested that κ_2 is the most accurate TC expression for binary systems. We referred to the value of κ_2 for the discussion of the accuracy of other TC expressions. With Li_2O model systems, effects of atomic mobility, which is represented by the self-diffusion coefficient, on the value of each TC expression is confirmed. It is turned out that as the atoms in a system becomes mobile, κ_1^* starts to show an erroneous value. The error of κ_1^* is mostly originated from the "PSE effect". In numerical result, κ_1^* showed more than 120% value of κ_2.

With comparison to other two expressions (κ_1 and κ_1^*), it is revealed that κ_2 is obtained by subtracting the contribution of energy transport via mass diffusion from the overall energy transport. Thus the remaining part of κ_2 represents the purely conductive process of excess energy, which is heat. The subtracted energy is composed of two kinds of characteristic energy of a material; difference of PSE and reduced heat of transport. While these two energies are of innate material's property, the effect of them can be hidden at low temperatures due to negligible atomic motion. However, as the temperature increases even below the melting point, their effect is triggered by the high value of diffusion coefficient, resulting in the error of certain TC expressions.

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