

Thermal conductivity of simple liquids: Temperature and packing-fraction dependenceNorikazu Ohtori,^{1,*} Yoshiki Ishii,² Yoshinori Togawa,² Takuya Oono,² and Keiichi Takase²¹*Faculty of Science, Niigata University, 8050 Ikarashi 2-no cho, Nishi-ku, Niigata 950-2181, Japan*²*Graduate School of Science and Technology, Niigata University, 8050 Ikarashi 2-no cho, Nishi-ku, Niigata 950-2181, Japan*

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The thermal conductivity of rare gases in liquid and dense fluid states has been evaluated using molecular dynamics simulation with the Lennard-Jones (LJ) potentials and the Green-Kubo (GK) formula. All the calculated thermal conductivities are in very good agreement with experimental results for a wide range of temperature and density. Special attention was paid to temperature and packing-fraction dependence which is nontrivial from dimensional analysis on the LJ potentials and the GK formula. First, the temperature dependence of $T^{1/4}$ was determined from the calculations at constant densities. Secondly, in order to obtain the dependence on packing fraction from that on number density separately, a scaling method of particle and/or cell size was introduced. The number density dependence of $(N/V)^{2/3}$ which is expected from the dimensional analysis of the GK formulas was confirmed and the packing-fraction dependence of $\eta^{3/2}$ was determined by using the scaling method. It turned out that the summarized functional form of $m^{-1/2}(N/V)^{2/3}\eta^{3/2}T^{1/4}$ can well express both the calculated and experimental thermal conductivities for Ar, Kr, and Xe, where m is the atomic mass. The scaling method has also been applied to molten NaCl and KCl so that it has been found that the thermal conductivity has the packing-fraction dependence of $\eta^{2/3}$ which is much weaker than that of the simple LJ liquids.

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I. INTRODUCTION

Among the transport properties of liquids, thermal conduction has less extensively been studied theoretically compared with diffusion and viscous flow [1–3], although several theoretical equations of thermal conductivity of liquids have been proposed for simple and polyatomic liquids [4–10]. The Bridgman equation [4] is based on the simple model that heat can be transferred between atoms which are arranged on a cubic lattice along the temperature gradient with the sound velocity:

$$\lambda = \frac{3kU}{l^2}, \quad (1)$$

where k is the Boltzmann constant, U the sound velocity, and l the mean neighbor interatomic distance. The l equals to $(V/N)^{1/3}$, where V is the system volume and N the particles number included in the V . Using the expression for sound velocity [5] of

$$U = \left(\frac{v_l}{v_f}\right)^{1/3} \left(\frac{\gamma kT}{m}\right)^{1/2}, \quad (2)$$

where v_l and v_f mean V/N and the free volume per particle, respectively, γ the ratio of specific heats for ideal gas, T the temperature, and m the atomic mass, Eq. (1) can be rewritten as

$$\lambda = 3k \left(\frac{v_l}{v_f}\right)^{1/3} \left(\frac{\gamma kT}{m}\right)^{1/2} (N/V)^{2/3}. \quad (3)$$

For simple liquids, the Enskog formulas, proposed for transport coefficients for the hard-sphere fluids, have been extended to the smooth hard-sphere and the rough hard-sphere models [11,12]. A useful equation based on the formulas with

the Carnahan-Starling approximation has been given for the thermal conductivity as

$$\lambda = 4\eta_{\text{HS}} \left[\frac{1.02513}{y} + 1.23016 + 0.776483y \right] \lambda^{\text{B}}, \quad (4)$$

$$\lambda^{\text{B}} = \left(\frac{75k}{64\sigma_{\text{HS}}^2} \right) \left(\frac{kT}{m\pi} \right)^{1/2}, \quad (5)$$

$$y \approx 4\eta_{\text{HS}} \left(1 - \frac{1}{2}\eta_{\text{HS}} \right) / (1 - \eta_{\text{HS}})^3, \quad (6)$$

where η_{HS} is the packing fraction with hard-sphere diameter, σ_{HS} , and λ^{B} the Boltzmann equation of thermal conductivity for dilute gas [13].

In these representative equations, there are two common and characteristic points. One is that the terms of mass and temperature are directly taken from the kinetic theory, as $(kT/m)^{1/2}$. The other is that free volume or packing fraction is included explicitly in them. Although both density, mN/V , and packing fraction, $\pi\sigma_{\text{HS}}^3 N/(6V)$, have number density term, N/V , and they all change in the same way when thermal expansion or contraction occurs, we think here that packing fraction has different physical meaning from that of number density. That is, whereas number density has the literal sense, packing fraction may represent the scale of the amount of void rather than particle volume in liquids. In the other theoretical equations [6–10], both atomic mass and number density dependencies of $m^{-1/2}(N/V)^{2/3}$ can be seen explicitly or implicitly and some of them also assume the temperature dependence of $T^{1/2}$, while free volume or packing-fraction dependence is widely divergent. In the semiempirical equations obtained using the principle of corresponding states [14], temperature is usually used as a single variable for the reduced thermal conductivity which should include both dependencies.

For liquid and fluid states of Ar, whereas experimental results are available as a function of both wide ranges of

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temperature and pressure or density [15], there is no verification for these equations. Since density is not only a product of atomic mass and number density but includes also the information of packing fraction, any assumptions are necessary for deriving each dependence of number density and packing fraction from the density dependence. Primarily, it is unexamined whether it is possible to divorce the packing-fraction dependence from the density dependence. Therefore, even in simple liquids, dependence on thermodynamic variables has not theoretically been established for thermal conductivity.

In this work, using computer experiments, we directly derive the dependence not only on temperature and density but also on mass, number density, and packing fraction of thermal conductivity for simple liquids and give a decisive expression with these variables. Molecular dynamics (MD) simulation is useful as a tool of computer experiments for this purpose. We have evaluated the thermal conductivity of simple molten alkali halides by MD simulation with the Green-Kubo (GK) formula [16–19] and shown that it follows the equation of $m^{-1/2} (N/V)^{2/3}$, where m means the geometric average mass of cation and anion, and has practically no temperature dependence. It is a natural way to think that any collective excitation can carry heat in liquids as phonon in solids so that void or vacancy in liquids might have any effect on propagation of the collective wave. Therefore, it is an original question why the above equation without packing fraction and temperature works so well in the molten salt systems, which has led us to this more fundamental work.

In the framework of the Lennard-Jones (LJ) potentials,

$$\phi(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right], \quad (7)$$

used in this work, dimensional analysis for the GK formula is useful for deriving the dependence on some variables, before the MD simulation. First, we express the thermal conductivity as a dimensionless quantity by using appropriate units, i.e., σ for length, m for mass, ϵ/k for temperature, and $(m\sigma^2/48\epsilon)^{1/2}$ for time, where the σ and ϵ are the parameters of particle size and interaction energy used in the above LJ potentials, respectively. Then, by inserting these into the GK formula,

$$\lambda = \frac{1}{3kVT^2} \int_0^\infty \langle J^e(t)J^e(0) \rangle dt, \quad (8)$$

where J^e is the energy current [1], we obtain a result as

$$\lambda(\sigma, \epsilon, m, N, V, E) = a\sigma^{-2}\epsilon^{1/2}m^{-1/2}\lambda^*(N, V^*, E^*), \quad (9)$$

where a is the proportional coefficient, E the internal energy, $V^* = V/\sigma^3$, $E^* = E/\epsilon$, and λ^* the dimensionless thermal conductivity. This shows directly the mass dependence of $m^{-1/2}$. Since, with change of density, both number density and packing fraction change simultaneously, we introduce a simple scaling method for particle size σ and/or cell size $L = V^{1/3}$, in order to discuss these separately. A diagrammatic explanation for the method is given in Fig. 1, where we assume that the particle can be scaled as if it is hard sphere. Therefore, the packing fraction η is defined as $\pi\sigma^3 N/6V$. Scaling only the particle size changes packing fraction, keeping number density at a constant. On the other hand, scaling both the particle size and cell size changes number density, keeping packing

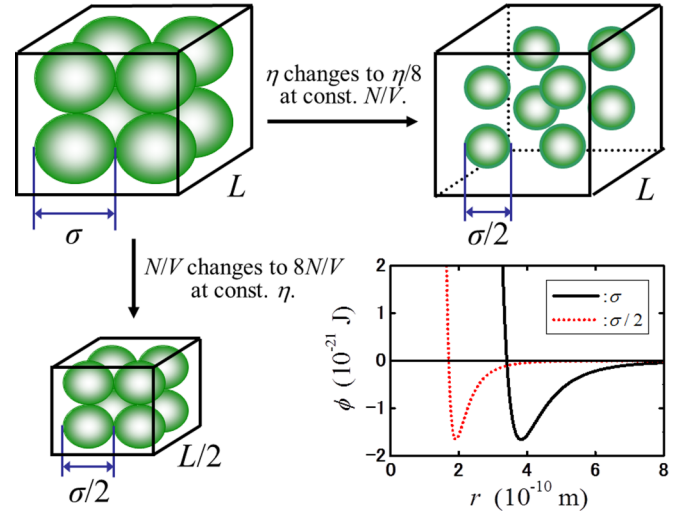


FIG. 1. (Color online) Schematic illustration for number density change at a constant packing fraction and packing fraction change at a constant number density by scaling particle size σ , and/or cell size L . The plot of potential energy ϕ shows the position change of repulsive barrier (r at $\phi = 0$) which corresponds to the change of particle size by scaling σ .

fraction at constant. Under constant packing fraction, since $V^* = (L/\sigma)^3$ is constant and $(N/V)^{2/3} = (N/V^*\sigma^3)^{2/3} = (N/V^*)\sigma^{-2}$, σ^{-2} means $(N/V)^{2/3}$, which suggests the number density dependence of $(N/V)^{2/3}$ in Eq. (9). In summary, for the simple LJ liquids, the thermal conductivity can be expressed as

$$\lambda(m, N/V, T, \eta) = m^{-1/2}(N/V)^{2/3} f(T, \eta). \quad (10)$$

MD simulations are necessary for further discussions regarding the functional form of temperature and packing-fraction dependence, $f(T, \eta)$.

II. CALCULATION

MD calculations were carried out for Ar, Kr, and Xe using NVE conditions. The particle number N was 864 and the cell volume V was determined from the experimental density [20] at each temperature. The parameters for the LJ potentials are given in Table I [21]. The equations of motion were integrated using the velocity Verlet algorithm [22] with a time step of 10 fs. The initial configuration of the atoms had an fcc structure. The kinetic energy was kept at each temperature by scaling the velocities of all atoms during the initial 10 ps, and then without scaling them, the calculation was carried out for up to 10 ps to equilibrate each system. The velocities of all atoms were corrected every 5000 steps in order to keep the total

TABLE I. Parameters for LJ potentials, σ and ϵ , in rare gases system [21].

Atom	σ (nm)	ϵk^{-1} (K)
Ar	0.3405	119.8
Kr	0.3670	167.0
Xe	0.3924	257.4

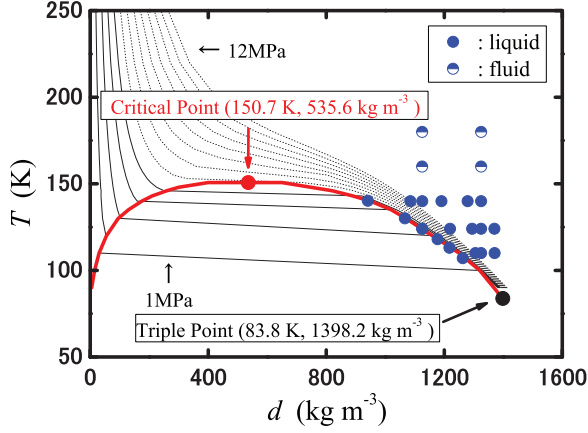


FIG. 2. (Color online) Thermodynamic states studied in this work on the phase diagram of Ar [20].

momentum of the system negligible. The atomic coordinates and velocities obtained for the subsequent 50 ns were used for the calculation of thermal conductivity using Eq. (8). MD calculations for molten NaCl and KCl are also performed in order to determine precise temperature and packing-fraction dependence of the thermal conductivity. A detailed description of calculations for them is given in Ref. [16].

III. RESULTS AND DISCUSSION

Figure 2 shows the thermodynamic states calculated on the phase diagram of Ar which is based on the results of Ref. [20]. In order to compare with the experimental results, a wide range of the conditions was sampled. In particular, from the viewpoint of examining packing-fraction dependence, it ranged up to the fluid region. Figure 3 shows representative comparisons between the calculated and the experimental results. They are in very good agreement with each other. The upper figure shows calculated λ as a function of T at densities which correspond to the saturated vapor line shown in Fig. 2. The lower figure shows calculated λ as a function of T at a constant density. We can see the apparent temperature dependence is caused by density change and the net temperature dependence is very weak.

Figure 4(a) shows the definitive evaluation of the temperature dependence and clearly tells that it follows $T^{1/4}$ rather than $T^{1/2}$ which is plotted in the inset. We have confirmed the same temperature dependence at all the densities. As stated above, in the case of molten alkali halides, we observed practically no temperature dependence. The reason why the temperature dependence in the LJ and the molten salt systems is weaker than that in the hard-sphere system, $T^{1/2}$, will be discussed in the subsequent paper by using the Weeks-Chandler-Anderson potentials. Figures 4(b) and 4(c) show the results of the number density dependence at a constant packing fraction and the packing-fraction dependence at a constant number density, obtained using the scaling method, respectively. The number density dependence of $(N/V)^{2/3}$ is the same as expected from the dimensional analysis. This supports the assumption used in the analysis. Packing-fraction dependence at a constant number density was determined as $\eta^{3/2}$ in the figure. We have

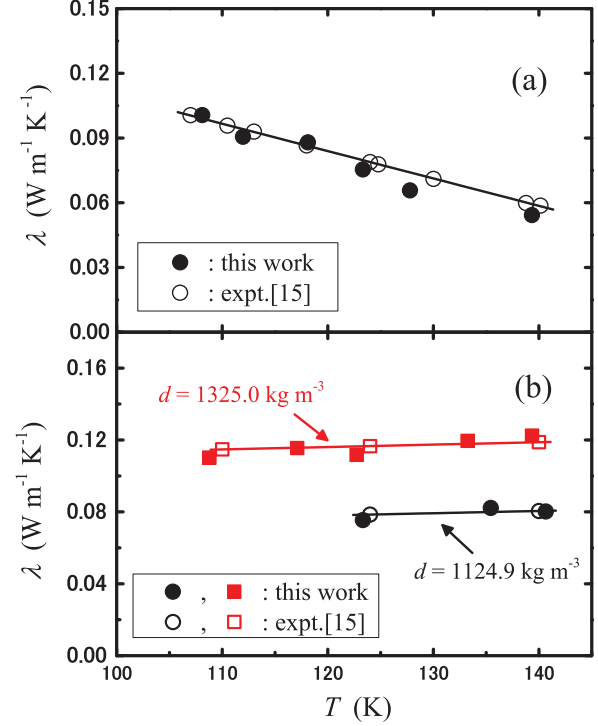


FIG. 3. (Color online) Temperature dependence of the thermal conductivity of Ar (a) with density change which corresponds to the saturated vapor line and (b) under constant densities of 1125 and 1325 kg m^{-3} .

confirmed the same dependence on η at all the states shown in Fig. 2.

The present result of packing-fraction dependence is significantly different from those which Eqs. (3) and (4) give. In Eq. (3), $(v_l/v_f)^{1/3}$ equals to $(1-\eta)^{-1/3}$ and can be approximated as $\eta^{1/6}$ in the range of η discussed in this work. Obviously, the dependence is excessively underestimated, compared with this result and, in addition, the experimental results shown in Fig. 5. In Eq. (4), the term σ_{HS}^{-2} can be converted to the term of number density via the definition of packing fraction, $\eta_{\text{HS}} = \pi \sigma_{\text{HS}}^3 N / (6V)$, as $\eta_{\text{HS}}^{2/3} \sigma_{\text{HS}}^{-2} (\pi/6)^{-2/3} = (N/V)^{2/3}$. Using this relation, in Eq. (4) the net packing-fraction dependence can be approximated as $\eta^{1.9}$. The reason why the packing-fraction dependence in the LJ systems, $\eta^{1.5}$, is weaker than that in the hard-sphere system, $\eta^{1.9}$, will also be discussed in the subsequent paper.

The mass dependence of $m^{-1/2}$ was also confirmed by artificial change of mass in MD simulation. In summary, the thermal conductivity of simple LJ liquids should follow the function of $m^{-1/2} (N/V)^{2/3} \eta^{3/2} T^{1/4}$, if they are not coupled among them. Figure 5 shows plots of all the calculated results and the experimental results [15,23] in the states with temperatures and densities on each saturated vapor line for Ar, Kr, and Xe as a function of $m^{-1/2} (N/V)^{2/3} T^{1/4}$ and $m^{-1/2} (N/V)^{2/3} \eta^{3/2} T^{1/4}$.

In the states shown in Fig. 5, since temperature and density change on the saturated vapor lines, both N/V and η change simultaneously with the density through volume expansion or contraction even in each material. However, the plot shows that the parameters in the abscissa are practically independent

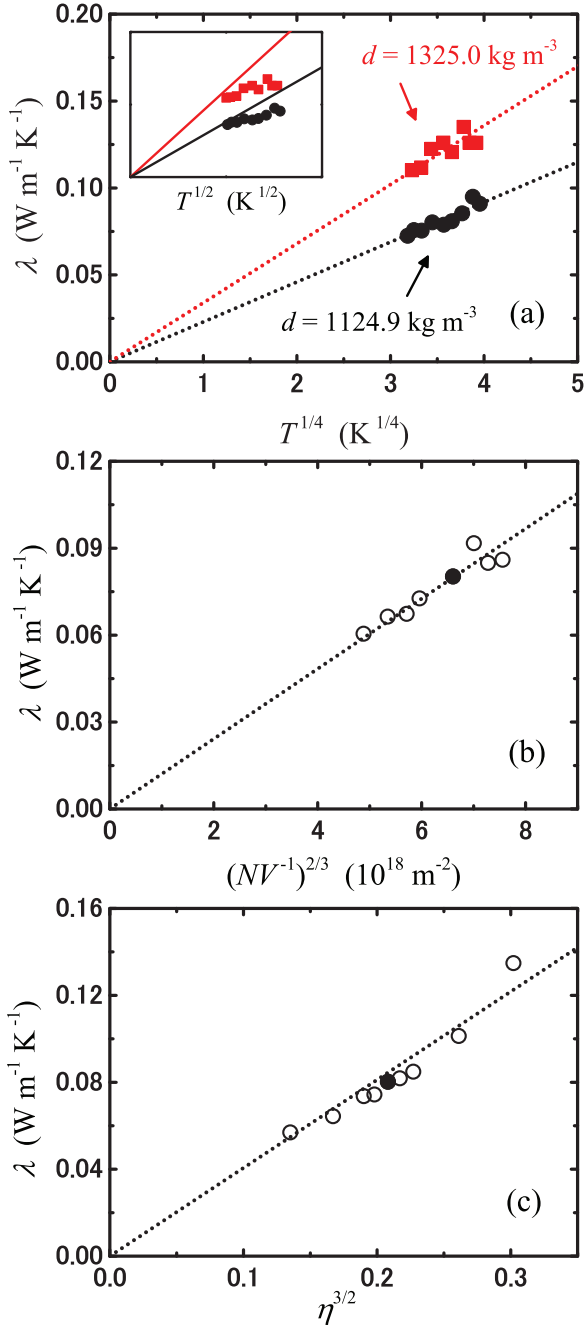


FIG. 4. (Color online) The calculated thermal conductivity of Ar as a function of (a) temperature at constant densities, (b) number density at a constant packing fraction, and (c) packing fraction at a constant number density.

of one another or there is no significant coupling among them. Therefore, Fig. 5 shows also each dependence on N/V and η in each material with a constant σ . On the other hand, Figs. 4(b) and 4(c) show each dependence on N/V and η in the LJ liquids with varying σ , since the material is changed by scaled σ from Ar as a reference. Therefore, the fact that the dependence shown in Figs. 4(b) and 4(c) is valid also under all the states shown in Fig. 5 means that σ expressing originally individuality of materials such as Ar, Kr, and Xe has effect on the thermal conductivity simply as a common

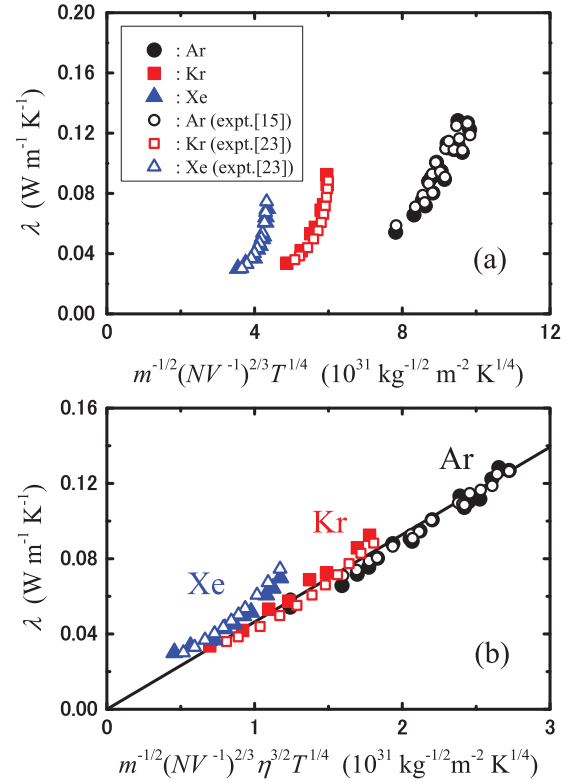


FIG. 5. (Color online) The calculated and experimental thermal conductivity in the states with temperatures and densities on each saturated vapor line for Ar, Kr, and Xe as a function of (a) mass and number density and (b) mass, number density, and packing fraction.

parameter to the LJ liquids, taking a form of packing fraction of $\pi\sigma^3 N/6V$. If we regard packing fraction as a measure of the amount of void rather than entity in liquid, it is natural that it is a common parameter to the LJ liquids as a group. In the expression of $m^{-1/2}(N/V)^{2/3}\eta^{3/2}T^{1/4}$ for the thermal conductivity, only the mass term is an explicit parameter showing individuality of material. However, implicitly, at a given temperature, density including number density and packing fraction is determined through potential parameters, σ and ϵ , which express individuality of the materials. We can see the explicit individuality of materials through packing fraction as the difference between groups such as the LJ liquids and molten alkali halides. In fact, using the method of scaling particle size, we have obtained the packing-fraction dependence of $\eta^{2/3}$ for molten NaCl and KCl which is very different from that for the LJ liquids.

These results show the validity of both the obtained functional form and the present method. The most important finding is a strong packing-fraction dependence in simple liquids, which is different from that in molten NaCl and KCl. The dependence on temperature and packing fraction in the molten salts are much weaker than those in the simple liquids. Therefore, it turned out that, in the previous work [16], the thermal conductivity was practically well expressed by $m^{-1/2}(N/V)^{2/3}$ without considering both temperature and packing-fraction dependence. The origin of these behaviors based on the interaction potentials, i.e., the softness of repulsive part, will be reported in the subsequent paper.

Once one has known the results obtained in this work, one might think that he could derive similar results from the experimental data. First, he might carefully examine the temperature dependence for the data under constant density. Then, he might obtain the packing-fraction dependence simply by dividing the data by both the temperature and number density dependence. However, no one has ever done that. Without the present results, one must first assume that the thermal conductivity can be expressed simply by temperature, number density, and packing fraction, and that they are independent of one another. In addition, one must assume the explicit expression of number density dependence. Although we have first assumed the independence between number density and packing fraction, we have validated the assumption by the present MD simulation. By using the present method of scaling particle size, we have successfully obtained the single variable dependence on number density or packing fraction. Furthermore, as a result, the plot shown in Fig. 5 has validated the practical independence among temperature, number density, and packing fraction.

IV. CONCLUSIONS

We have performed MD simulation of simple LJ liquids and fluids in a wide range of temperature and density, and

calculated the thermal conductivity using the Green-Kubo formula. The calculated thermal conductivities were in very good agreement with experimental results. The temperature dependence of $T^{1/4}$ has been determined from the calculations under constant density, and has been confirmed in all the states calculated. The number density dependence of $(N/V)^{2/3}$ and the packing-fraction dependence of $\eta^{3/2}$ have been obtained from the calculations by using the scaled particle size. It has turned out that the combination of each dependence can well reproduce the thermal conductivities in the states of temperatures and densities on the saturated vapor lines of Ar, Kr, and Xe. These results show that there is no significant coupling among temperature, number density, and packing fraction which are variables of the thermal conductivity. The same scaling method has been applied to molten NaCl and KCl so that we have obtained the same number density dependence but the different packing-fraction dependence of $\eta^{2/3}$.

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