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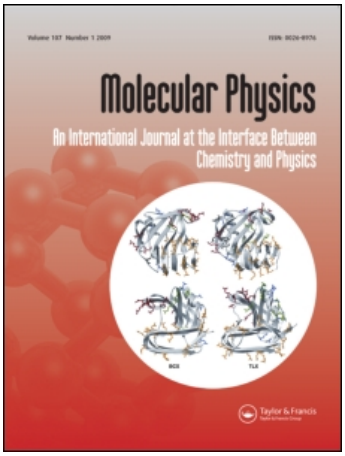

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The vibrational contribution to the thermal conductivity of a polyatomic fluid

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RESEARCH ARTICLE

The vibrational contribution to the thermal conductivity of a polyatomic fluid

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A simple analytical expression is proposed in this article to calculate the vibrational contribution to the thermal conductivity of a polyatomic fluid. The analytic expression was obtained based on the assumption that the self-diffusion process is the major mechanism in the transport of vibrational energy. The proposed expression is validated by comparing the thermal conductivity of CO_2 calculated by molecular dynamics (MD) simulations to experimental data over a wide range of temperature and pressure. It is also demonstrated that the proposed analytic expression greatly increases the accuracy of calculated thermal conductivity for CO_2 at the supercritical state.

Keywords: thermal conductivity; vibrational contribution; molecular dynamics

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1. Introduction

The thermal conductivities of polyatomic fluids have been calculated using equilibrium or non-equilibrium MD simulations for decades [1–7]. Since thermal conductivity measures the transport of energy through the fluid, the inclusion of vibrational energy of the molecule into the calculation is important. No matter which MD simulation is used, however, there always exists a problem of how to treat molecular vibrations properly. As the number of atom in a molecule increases, more vibrational modes need to be considered in the calculation. The characteristic vibrational temperature normally varies from a few hundred K for vibrational modes, such as torsional vibrations, to several thousand K for vibrational modes, such as stretching vibrations. Generally, two approaches are frequently used to treat different vibrational motions. The first one is to treat the vibrational motion classically with a potential in which the parameters are often determined from infrared spectroscopy data or quantum chemistry results [1,2,4,6,7]. This classical approximation is appropriate if the characteristic temperature of the vibrational mode is considerably lower than the simulation temperature. The other approach is to apply constraints to the bond lengths or bond bending angles, and the stretching or bending energy is accordingly neglected [1,3–5]. The second approach is normally used when the characteristic temperature of the vibrational mode is much higher than the simulation temperature. However, there exist many vibrational modes of which the characteristic temperature is higher but not too much higher than the simulation temperature. In these cases, the vibration motion is strongly affected by quantum effects. The classical treatment of vibrational modes may lead to wrong vibrational energies and hence wrong vibrational contributions to the thermal conductivity. On the other hand, a simple neglect of vibrational energies is also not appropriate, because a non-negligible population of molecules may have been excited to the corresponding vibrational modes at the simulation temperature. As an example, Nieto-Draghi *et al.* [1] have shown that both the classical treatment and the neglect of vibrational motions of CO_2 lead to a significant underestimate of thermal conductivity at the supercritical state. This problem was resolved recently by using a Monte Carlo (MC) method to treat the quantum effects of the vibrational motion [8,9]. The proposed MC method is based on the assumption that the exchange of energy between the constrained vibrational motion, which is strongly affected by quantum effects, and all other modes of motion is negligible. In implementation, the vibrational energies of constrained vibrational modes are considered to be constant during the simulation after they are initialized by the Metropolis algorithm [10] at the simulation temperature. Meanwhile, the molecule (in the case when all vibrational modes are constrained) or a part of the molecule (in the case when a part of the molecule is constrained)

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is considered rigid in the simulation, and the structure of the constrained part of the molecule is considered unaffected by the initial vibrational energies. This MC method used for quantum treatments of constrained vibrational motion has been applied to accurately determine the thermal conductivity of CO_2 gas in a wide range of temperature and pressure [8,9]. It was found [9] that the vibrational contribution to the thermal conductivity of CO_2 gas has reached about 20% of the total thermal conductivity at 300 K. This temperature is much lower than all characteristic vibrational temperatures of CO_2, but a significant vibrational contribution has been observed.

In the aforementioned studies [8,9], it was found that the vibrational energies of all constrained modes can be considered constant and, hence, independent of time during the simulation. Hence, it may be possible to find an analytic expression that can be used to calculate the vibrational contribution to the thermal conductivity. This work aims to develop such an analytic expression for a polyatomic fluid. In order to test the validity of the proposed analytic expression, it is necessary to ensure that an accurate intermolecular potential is used in the simulation and all other parameters in the MD simulation such as cut-off radius, simulation time step, and total simulation length do not significantly influence the calculation results of thermal conductivity. It has been shown that an *ab initio* intermolecular potential for CO_2 dimer proposed by Bukowski *et al.* (BUK) [11] can be used to accurately reproduce the thermophysical property of CO_2 gas in a wide range of temperature and pressure [8,9,12,13]. Therefore, in this study the MD calculation of the thermal conductivity of CO_2 gas based on BUK potential is used to test the validity of the proposed analytic expression in the temperature range of 300−1000 K and pressure range of 1−40 atm. In addition to CO_2 gas, the analytic expression is applied to the calculation of thermal conductivity of supercritical CO_2 [1].

2. Theoretical background

In this work, the computations of thermal conductivity are carried out by the equilibrium MD simulation in a microcanonical ensemble. To study the vibrational contribution to the thermal conductivity, we start with the well-known Green–Kubo (GK) formula for the calculation of thermal conductivity λ [14,15]:

$$\lambda = \frac{V}{3k_B T^2}\int_0^\infty \mathrm{d}t\langle \vec{J}(t)\cdot\vec{J}(0)\rangle \tag{1}$$

where $\vec{J}$ represents the energy current, t is the time, $\langle\cdots\rangle$ denotes the ensemble average, k_B is the Boltzmann constant, V is the volume of the system and T is the average temperature of the system. The general expression for the energy current $\vec{J}$ in pure fluids which contain flexible, multicentre molecules can be expressed as [6,16,17]

$$\vec{J} = \frac{1}{V}\sum_i \left[E_i\vec{v}_i + \frac{1}{2}\sum_{a\in i}\sum_{i\neq j}\sum_{b\in j}\vec{r}_{ij}\cdot(\vec{f}_{ab}\cdot\vec{v}_a)\right], \tag{2}$$

where i and j are molecular indices, and a and b are atomic indices. $\vec{v}$ is the velocity vector (all velocities are barycentric), $\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ is the centre–centre intermolecular distance vector and $\vec{f}_{ab}$ is the intermolecular force. The internal energy E_i of molecule i in Equation (2) includes the translational, rotational, intermolecular potential energies and energies of vibrational modes that can be treated classically in the MD simulation. All these energies vary continuously with time in the simulation. For the constrained vibrational motion of which quantum effects cannot be neglected, however, the energies do not vary continuously with time and hence were normally not considered in the MD simulation. This is a defect in most MD simulations of thermal conductivity of polyatomic fluids in the past.

Previous work [8,9] has shown that the quantum effects of the constrained vibrational motion can be included in MD simulation by a MC method. Our simulation results indicate that the exchange of energy between the constrained vibrational motion and all other modes of motion is negligible for a dilute and moderate dense polyatomic fluid. This conclusion is similar to the assumption made by Chapman and Cowling [18] when they derived the modified Eucken formula for a dilute polyatomic gas. Based on the assumption that there is no exchange of energy between translational and internal modes (rotational and vibrational) of motion, Chapman and Cowling argued that the transport of internal energy would take place by the diffusion of molecules. Hence, Chapman and Cowling divided the thermal conductivity λ_{all} which includes all modes of motions into two parts in the following equation [18]:

$$\lambda_{\mathrm{all}} = \lambda_{\mathrm{tr}} + \rho D C_{V,\mathrm{int}} \tag{3}$$

where λ_{tr} represents the thermal conductivity due to the transport of translational energy, ρ is the density of the system, D is the self-diffusion coefficient and $C_{V,\mathrm{int}}$ is the contribution to the isochoric heat capacity from internal modes of motion. $\rho D C_{V,\mathrm{int}}$ represents

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the thermal conductivity due to the transport of internal energy.

However, neglecting the exchange of energy between the translational and internal modes of motion (especially the rotational motion) is generally a crude approximation. Instead, it is more appropriate to use the approximation made in our previous work which only neglects the exchange of energy between the constrained vibrational motion and all other modes of motion. In this study, we propose that the thermal conductivity λ_{all} can be divided into two parts as in the following equation:

$$\lambda_{all} = \lambda + \rho D C_{V,vib} \tag{4}$$

where λ is the thermal conductivity due to the transport of intermolecular potential energy and energies of all modes of motion which can be treated classically. Here, λ is identical to the thermal conductivity in Equation (1) and, hence, can be obtained from MD simulations. If the simulation temperature is higher than the characteristic temperature of some vibrational mode, a classical treatment of this vibrational motion should be performed in the MD simulation with an intramolecular potential for the corresponding vibrational mode. But all other vibrational modes should still be constrained in the molecule. $\rho D C_{V,vib}$ represents the thermal conductivity due to the energy transport of constrained vibrational modes through the self-diffusion process. In Equation (4), $\rho D C_{V,vib}$ can be considered as the 'correction' term to the original thermal conductivity λ. The quantum effects of constrained vibrational motions are taken into account by the isochoric vibrational heat capacity $C_{V,vib}$ which can be calculated by the harmonic assumption using [19]:

$$C_{V,vib} = k_B \sum_{j=1}^{n} \left[\left(\frac{E_{vj}}{k_B T} \right)^2 \frac{e^{-E_{vj}/k_B T}}{\left(1 - e^{-E_{vj}/k_B T}\right)^2} \right], \tag{5}$$

where E_{vj} is the fundamental vibrational transition energy of jth constrained vibrational mode of the molecule and n is the total number of constrained vibrational modes. The self-diffusion coefficient D in Equation (4) can be readily obtained from the MD simulation by [20]

$$D = \frac{1}{3} \int_0^\infty \mathrm{d}t \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle. \tag{6}$$

The validity of Equation (4) is to be tested in this work by calculating the thermal conductivity of CO_2 fluid. The CO_2 molecule has four vibrational modes, among which the bending mode has the lowest characteristic temperature of about 960 K. Hence, quantum effects of all vibrational modes of the CO_2 molecule cannot be neglected unless the simulation temperature is higher than 1000 K. All MD simulations in this work are carried out at a temperature lower than 1000 K. According to the assumption made in this work, therefore, all vibrational modes are constrained in the simulation so that the CO_2 molecule is modelled as a linear rigid rotor. For a linear rigid molecule, the energy current $\vec{J}$ which does not include the contribution from the vibrational energy can be simplified to [8]:

$$\vec{J} = \frac{1}{V} \sum_i \left[\frac{1}{2} \vec{v}_i \left(m \vec{v}_i^{\,2} + I \vec{u}_i^{\,2} + \sum_{j \neq i} U_{ij} \right) + \frac{1}{2} \sum_{j>i} \vec{r}_{ij} \cdot \left((\vec{v}_i + \vec{v}_j) \cdot \vec{F}_{ij} + (\vec{u}_i \cdot \vec{G}_{ij} - \vec{u}_j \cdot \vec{G}_{ji}) \right) \right], \tag{7}$$

where m and I represent, respectively, the mass and the moment of inertia of the CO_2 molecule, $\vec{u}_i$ is the rotational velocity of molecule i which is defined as the time derivative of the unit vector along the molecular axis, $\vec{F}_{ij}$ is the intermolecular force acting on molecule i due to the interaction between the molecule i and the molecule j, and U_{ij} represents the intermolecular potential. In Equation (7), $\vec{G}_{ij}$ can be determined from the intermolecular forces by

$$\vec{G}_{ij} = \sum_a d_{ia} \vec{f}_{ija} \tag{8}$$

where d_{ia} is the distance of the site a in molecule i relative to the centre of mass and $\vec{f}_{ija}$ is the force acting on the site a in molecule i due to the interaction between molecule i and molecule j.

3. Simulation details

The BUK potential employed in this work uses a site–site representation of the intermolecular potential for CO_2 dimer as shown in the following equation:

$$U_{BUK} = \sum_{a \in i} \sum_{b \in j} \left[\exp(\alpha_{ab} - \beta_{ab} r_{ab}) + f_1(\delta_1^{ab} r_{ab}) \frac{q_a q_b}{r_{ab}} - f_6(\delta_6^{ab} r_{ab}) \frac{C_6^{ab}}{r_{ab}^6} - f_8(\delta_8^{ab} r_{ab}) \frac{C_8^{ab}}{r_{ab}^8} \right], \tag{9}$$

where

$$f_n[x] = 1 - e^{-x} \sum_{k=0}^{n} \frac{x^k}{k!}. \tag{10}$$

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Here, sites a belong to molecule i, sites b belong to molecule j and r_{ab} is the distance between a and b. Each molecule contains five sites, with three corresponding to the centres of the atoms in CO_2 and the remaining two on the C–O bonds 0.8456 Å away from the C atom. The C–O distance is fixed at 1.162047 Å. Parameters α_{ab}, β_{ab}, δ_n^{ab}, q_a, and C_n^{ab} are given in [11]. Since the CO_2 molecule is modelled as a linear rigid rotor in this work, the dipole moment of the CO_2 molecule is zero at every time step of the simulation. Hence, it is not necessary to use the reaction field method [21] to account for the long-range electrostatic interactions. In fact, the first non-vanishing electrostatic interaction for CO_2 dimer is the quadrupolar interaction, which decays as r^{-5} at a large intermolecular separation. On the other hand, the quadrupolar interaction also depends on the relative orientations between molecules. It is assumed that there are no preferential relative orientations beyond the cut-off sphere. Therefore, the long-range correction for the quadrupolar interaction is negligible. In the application of BUK potential, the cut-off radius, within which all pair interactions are calculated, is chosen to be 14 Å. The long range correction to the pressure is calculated by orientational averaging of the virial beyond the cut-off radius.

The equilibrium MD simulations are all carried out in a constant NVE ensemble with $N = 4096$ for dilute CO_2 gas at 1 atm and 300−1000 K, and $N = 1024$ for moderate dense CO_2 gas at 300 K and 10−40 atm. The volume V (or density ρ) and the total energy E of the constant NVE ensemble corresponding to each simulation temperature and pressure are obtained by the method described in [9]. The coordinates of the molecular centre of mass and the molecular orientations are all initialized randomly in a cubic box. The translational and rotational velocities are both initialized by the Maxwell–Boltzmann relation at the simulation temperature. The equations of molecular translational motions and molecular rotational motions are integrated by, respectively, the Verlet leap-frog algorithm and the Singer leap-frog algorithm [22]. The molecules in the system are equilibrated for 500 ps using the Berendsen's velocity scaling method [23] with a time constant of 100 ps for dilute gases and 25 ps for moderate dense gases before the calculation of the time-correlation function starts. The time step size, total simulation length of each simulation and the calculated density of the fluid at each simulated state point are given in Table 1. The time step size is chosen so that the total energy of the system remains constant within a relative accuracy of 10^{-4}. As shown in Table 1, a very long total simulation length is used at each simulated state point to ensure the statistical error of the calculated thermal conductivity is lower than or around 1%. The statistical error is calculated by Fincham's block averaging method [23]. Each long simulation shown in Table 1 is divided into 100 shorter parallel runs which are independently initialized and equilibrated at the given temperature and pressure.

Table 1. The time step size Δt, total simulation length t_{total} and calculated density of fluid ρ at each simulated state point. The statistical error of ρ is less than 0.2%.

P (atm)	T (K)	ρ (kg/m^3)	Δt (fs)	t_{total} (μs)
1	300	1.805	12.5	6.24
1	400	1.347	12.5	7.41
1	500	1.075	12.5	8.58
1	600	0.900	10.5	9.76
1	700	0.767	10.5	10.9
1	800	0.671	10.5	12.1
1	900	0.597	8.5	13.3
1	1000	0.537	8.5	14.4
10	300	18.85	8.5	1.56
20	300	40.10	8.5	0.78
30	300	64.57	8.5	0.51
40	300	95.09	8.5	0.39

The self-diffusion coefficient and vibrational heat capacity at a given temperature and pressure must be accurately determined before the calculation of vibrational contribution to the thermal conductivity is carried out. The velocity autocorrelation function used for the calculation of self-diffusion coefficient is averaged over the autocorrelation functions of all molecules in the system so that the statistical error of the calculated self-diffusion coefficient is less than 0.1%. In order to study the validity of Equation (4), the values of all variables used in the calculation should be as accurate as possible. Since very accurate experimental data (uncertainty ± 0.15%) of the heat capacity of CO_2 at zero density are available [25] at every simulation temperature, the vibrational heat capacity used in the calculation is obtained by Equation (10) instead of Equation (5).

$$C_{V,vib} = C_{V,\rho=0} - 2.5R \tag{10}$$

where $C_{V,\rho=0}$ represents the experimental data of isochoric heat capacity of CO_2 at zero density, R is the gas constant. Equation (5) is less accurate than Equation (10) because the Fermi resonance among different vibrational energy states of CO_2 makes the harmonic approximation more inaccurate.

4. Results and discussion

The first set of calculation is carried out at 1 atm and 300−1000 K. The calculated results are shown

Table 2. The simulated self-diffusion coefficient and thermal conductivity at 1 atm. The statistical error of the self-diffusion coefficient is less than 0.1%. The vibrational heat capacity is calculated by Equation (10) using the experimental data in [25]. The statistical error of the thermal conductivity λ_{MD} is less than 1.0%. The deviations are determined by $|\lambda_{all,MD} - \lambda_{all,exp.}|/\lambda_{all,exp.} \times 100\%$.

	ρD (mg/m · s)				Conductivity (mW/m · K)			
T (K)	*MD*	Exp. [26]	Dev (%)	$C_{V,vib}$(J/mol · K)	λ_{MD}	$\lambda_{all,MD}$	$\lambda_{all,exp.}$ [27]	Dev (%)
300	20.61	21.52	4.19	8.126	12.7	16.5	16.8	1.79
400	27.32	27.79	1.70	12.24	17.0	24.6	25.1	1.99
500	33.50	33.36	0.42	15.53	20.7	32.6	33.5	2.69
600	39.22	38.69	1.37	18.23	24.4	40.6	41.6	2.40
700	44.26	43.26	2.32	20.47	28.2	48.8	49.3	1.01
800	49.05	47.80	2.63	22.34	30.8	55.7	56.7	1.76
900	53.59	52.09	2.87	23.91	33.1	62.2	63.8	2.51
1000	57.83	56.11	3.08	25.22	37.6	70.7	70.6	0.14

in Table 2. The uncertainty of the experimental data of the self-diffusion coefficient at 1 atm was estimated to be ±5% [26]. It can be seen from Table 2 that the deviations between the calculated and experimental self-diffusion coefficients are within the experimental uncertainty. The error caused by decoupling the vibrations from other degrees of freedom is assumed negligible and Equation (10) is applied to calculate the vibrational heat capacity. The uncertainty of the experimental data of the heat capacity was estimated to be ±0.15% [25]. In Table 2, λ_{MD} the thermal conductivity which does not include the vibrational contribution is obtained directly from the MD simulation with the statistical error of less than 1.0%. It is evident that λ_{MD} significantly underestimates $\lambda_{all,exp.}$ the experimental thermal conductivity at all simulation temperatures. The uncertainty of $\lambda_{all,exp}$ was estimated to be ±1% near room temperature and ±2% at the higher temperatures. As shown in Table 2, the density-diffusion product, ρD and vibrational heat capacity both increase with tempeature. As a result, the magnitude of $\rho D C_{V,vib}$, i.e., the vibrational contribution to the thermal conductivity also increases with temperature. When the vibrational contribution is included, the corrected thermal conductivity $\lambda_{all,MD}$ shows good agreement with the experimental data, as shown in Table 2. The significance of the vibrational contribution to the thermal conductivity for CO_2 gas at 1 atm is calculated by $\rho D C_{V,vib}/\lambda_{all,MD} \times 100\%$. The results are shown in Figure 1. The vibrational contribution increases with temperature from 24% at 300 K to 46% at 1000 K.

If the simulation temperature is higher than 1000 K, it may not be appropriate to assume the CO_2 molecule is a linear rigid rotor because the quantum effects of bending motions becomes negligible. In this case, it is more appropriate to treat the bend mode

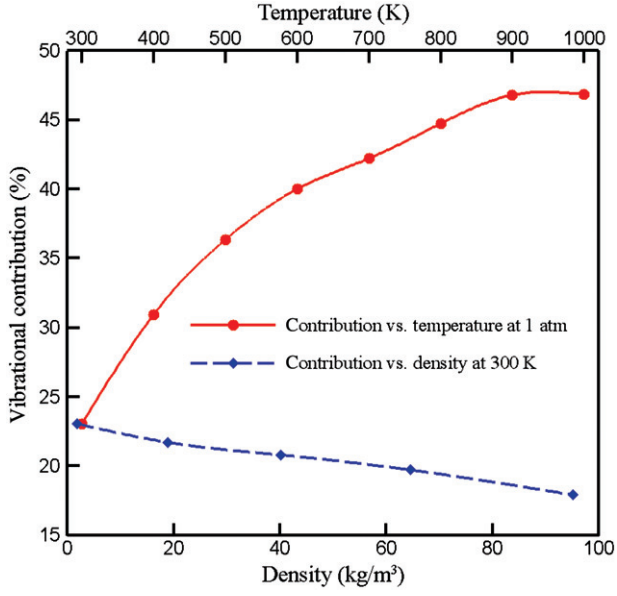

Figure 1. The vibrational contribution to the thermal conductivity as a function of temperature at 1 atm and as a function of density at 300 K.

of CO_2 classically and an intramolecular potential for bending motions should be included in the MD model. On the other hand, the other two vibrational modes of the CO_2 molecule should still be constrained because their characteristic temperatures are much higher than 1000 K. In these high temperature cases, the vibrational heat capacity $C_{V,vib}$ in Equation (4) only includes the contribution from the two constrained vibrational modes. The intermolecular potential employed in this work is based on a rigid geometry. Hence, it might not be appropriate to use it for the interaction between flexible CO_2 molecules at high temperatures.

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Table 3. The simulated self-diffusion coefficient and thermal conductivity at 300 K. The statistical error of the self-diffusion coefficient is less than 0.1%. The statistical error of the thermal conductivity λ_{MD} is less than 1.2%. The deviations are determined by $|\lambda_{\mathrm{all},MD} - \lambda_{\mathrm{all,exp.}}|/\lambda_{\mathrm{all,exp.}} \times 100\ \%$.

			Conductivity (mW/m · K)			
P (atm)	ρD (mg/m · s) MD results	Dev (%)	λ_{MD}	$\lambda_{\mathrm{all},MD}$	$\lambda_{\mathrm{all,exp.}}$ [25]	Dev (%)
10	20.28	1.46	13.5	17.2	17.3	0.58
20	20.17	1.99	14.2	17.9	18.0	0.56
30	19.93	3.16	15.0	18.7	19.0	1.58
40	19.85	3.55	16.8	20.5	20.7	0.97

Table 4. The correction term $\rho DC_{V,vib}$ of the calculated thermal conductivity of supercritical CO_2 in [1]. λ_{ND} denotes the thermal conductivity calculated by Nieto-Draghi *et al.* based on the rigid-rotor assumption. $\lambda_{all,exp.}$ denotes the experimental data of the thermal conductivity shown in TABLE III of [1]. The self-diffusion coefficient is obtained from [31].

ρ (kg/m^3)	λ_{ND} (mW/m · K)	$\lambda_{\mathrm{all,exp.}}$ (mW/m · K)	Dev. (%)	D (m^2/s)	$\rho DC_{V,vib}$ (mW/m · K)	$\lambda_{\mathrm{all,corrected}}$ (mW/m · K)	Dev. (%) (corrected)
300	30.0	42.6	30	113×10^{-9}	11.3	41.3	3.3
800	86.3	94.4	9	28.5×10^{-9}	7.56	93.9	0.5

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The second set of calculation is performed at 300 K and 10–40 atm. Similar to the 1 atm case, the calculated self-diffusion coefficient is firstly compared with the experimental data. Stiel *et al.* [28] established a relationship between the self-diffusion coefficients and temperature for gases at moderate pressures. The relationship as shown in Equation (11) was found to reproduce the experimental data of the self-diffusion coefficient of CO_2 gas with an average deviation of 1.99%.

$$\rho D = \frac{0.464}{\xi}\left[1.391\frac{T}{T_c} - 0.381\right]^{2/3} \qquad (11)$$

where $T_c = 304.2$ K is the critical temperature of CO_2, $\xi = 0.0224$ is constant for CO_2. According to Equation (11) at $T = 300$ K, $\rho D = 20.58$ mg/m · s is constant for CO_2 gas at moderate pressures. The calculated self-diffusion coefficient compared to the experimental value obtained from Equation (11) is shown in Table 3. It can be seen the calculated results generally agree well with the experimental data. However, a slightly decrease of the calculated ρD with density (or pressure) is observed. The decreasing trend agrees with the density dependence of ρD for a fluid at the subcritical gaseous states calculated by Meier *et al.* [29] using the Lennard–Jones potential model. Liang and Tsai [9] have shown that the decoupling between vibrations and other degrees of freedom is appropriate for moderate dense CO_2 gas. Hence, the vibrational heat capacity used in this set of calculation is the same as that of dilute CO_2 at 300 K in Table 2. When the vibrational contribution is not included, the calculated thermal conductivity λ_{MD} significantly underestimates the experimental thermal conductivity $\lambda_{\mathrm{all,exp}}$ [27] at all simulation pressures as shown in Table 3. After the vibrational contribution $\rho DC_{V,vib}$ is included, very good agreement is achieved.

The statistical error of λ_{MD} is about 1.2%. The uncertainty of the experimental data was estimated to be ±2% [27]. Since the vibrational heat capacity is constant and the density-diffusion product decreases with density, the magnitude of $\rho DC_{V,vib}$ slightly decreases with density. On the other hand, λ_{MD} increases with density due to the increasing contribution from the intermolecular potential. Therefore, the vibrational contribution to the thermal conductivity decreases with density from 21.7% at 18.9 kg/m^3 to 17.9% at 95.1 kg/m^3 as shown in Figure 1. As the density or pressure is further increased, the vibrational contribution to the thermal conductivity will be even lower. In very high density fluids where the potential contribution to the thermal conductivity dominates, the vibrational contribution to the thermal conductivity becomes smaller or negligible.

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To test validity of the proposed correction for the vibrational contribution to the thermal conductivity in high density fluid, the MD simulation should be extended to higher density range. However, the BUK intermolecular potential employed in this work has been proved unsuitable for high density CO_2 fluids. As an example, Bratschi *et al.* [30] showed that BUK potential predicts too large critical temperature and pressure compared to the experimental results. To test the validity of Equation (4) in high density fluids, therefore, a more appropriate intermolecular potential should be employed.

Nieto-Draghi *et al.* [1] calculated the thermal conductivity of CO_2 along the supercritical isotherm at 470 K using EPM2 potential. EPM2 model is a well know potential model for carbon dioxide which reproduces accurately the critical properties. Using the rigid-rotor assumption, Nieto-Draghi *et al.* calculated the thermal conductivity of CO_2 by MD simulations. An underestimation of 30% and 9% were found at 300 kg/m^3 and 800 kg/m^3, respectively. With the classical treatment of the vibrational motions in the simulation, they obtained an underestimation of 23% at 300 kg/m^3. Nieto-Draghi *et al.* discussed in their paper that 'an increase in the accuracy of the thermal conductivity might require a quantum treatment of the atomic vibration inside the molecule'. Since 470 K is much lower than the characteristic vibrational temperature of bending mode of CO_2, all vibrational modes should be constrained in the simulation based on the assumption made in this work. According to the analysis shown in this work, the deviations in their calculations can be corrected by $\rho DC_{V,vib}$. The vibrational quantum effects is taken into account by $C_{V,vib}$. We compare our corrected results with Draghi *et al.*'s results based on the rigid-rotor assumption and the experimental results in Table 4. The self-diffusion coefficient data are taken from the correlation provided by [31]. The vibrational heat capacity at 470 K is 14.62 J/mol K [25]. It can be seen from Table 4 that the deviations between Nieto-Draghi *et al.*'s results and the experimental data can be corrected by the proposed vibrational correction very well. The deviation is reduced from 30% to 3.3% at 300 kg/m^3, and from 9% to 0.5% at 800 kg/m^3. From this calculation we can see the vibrational contribution to the thermal conductivity might be non-negligible even at a density close to the liquid density. At 470 K, both diffusion coefficient D and vibrational heat capacity $C_{V,vib}$ are higher than those at 300 K at the same density. For dilute CO_2 gas at 470 K, the vibrational contribution is about 36% according to Figure 1. Hence, the vibrational contribution of about 30% and 9%, respectively, at 300 kg/m^3 and 800 kg/m^3 is reasonable.

5. Conclusions

A simple correction term $\rho DC_{V,vib}$ is proposed to account for the vibrational contribution to the thermal conductivity. The proposed correction term is based on the assumption that, depending on the simulation temperature, the molecular vibrational modes with relatively higher characteristic temperatures can be considered constrained in the MD simulation. It is proved that the energy of constrained vibrations mainly contribute to the thermal conductivity through the self-diffusion process. Base on the proposed expression, the calculated thermal conductivities of CO_2 fluid at gaseous and supercritical states agree well with experimental data.

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