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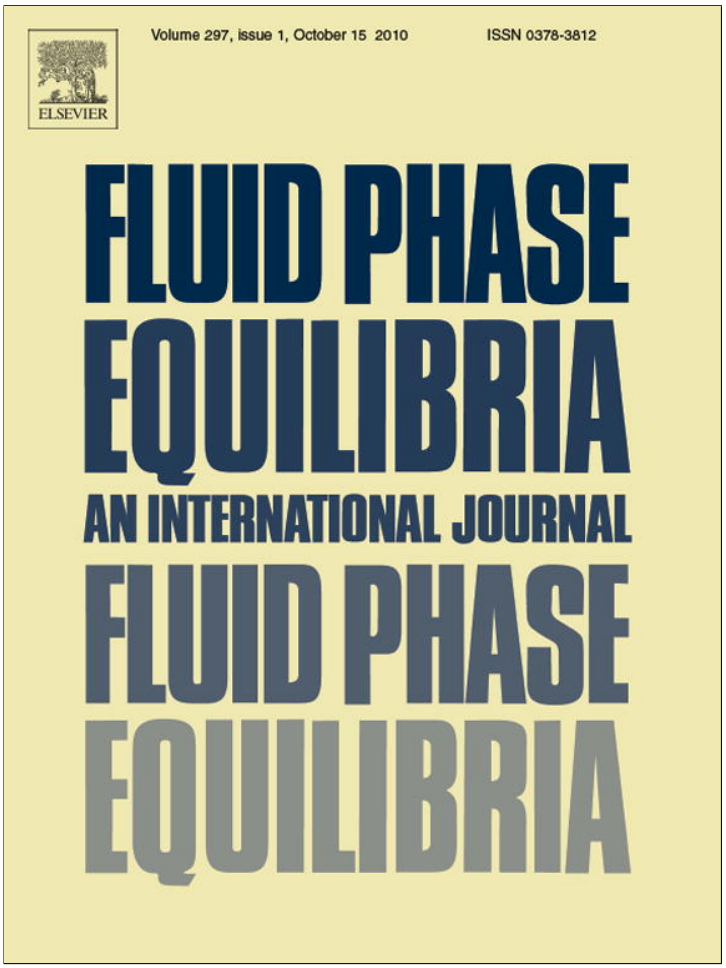

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Molecular dynamics simulations of self-diffusion coefficient and thermal conductivity of methane at low and moderate densities

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ABSTRACT

This article demonstrates a highly accurate molecular dynamics (MD) simulation of thermal conductivity of methane using an *ab initio* intermolecular potential. The quantum effects of the vibrational contribution to thermal conductivity are more efficiently accounted for in the present MD model by an analytical correction term as compared to by the Monte Carlo method. The average deviations between the calculated thermal conductivity and the experimental data are 0.92% for dilute methane and 1.29% for methane at moderate densities, as compared to approximately 20% or more in existing MD calculations. The results demonstrate the importance of considering vibrational contribution to the thermal conductivity which is mainly through the self-diffusion process.

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1. Introduction

Methane is of specific importance in different fields ranging from its industrial application as a feed-gas for ultra-smooth diamond coating to its environmental impact as an important greenhouse gas. Moreover, it is the principal component of natural gas which is often described as the cleanest fossil fuel. Accurate knowledge of the transport properties of methane is therefore essential for the engineering design of chemical process and fluid transportation. Although the experimental data for transport properties of methane are available, they, especially the self-diffusion coefficient and thermal conductivity data, are of acceptable accuracy only around room temperature [1]. This work attempts to calculate the self-diffusion coefficient and thermal conductivity of methane in a wide range of temperature at dilute phase and in an intermediate dense phase by equilibrium MD simulations using an *ab initio* potential energy surface (PES) which was recently proposed by Hellmann et al. [2]. A quantum mechanical treatment of vibrational motions is employed in the MD model to improve the accuracy of the calculated thermal conductivity.

In addition to MD simulations, there also exist several other approaches for the calculation of transport properties from a known intermolecular potential. For example, the classical-trajectory (CT) method has been shown to be highly accurate in reproducing the transport and relaxation properties of simple molecular gases in a wide range of temperatures [1,3–5]. However, this method is restricted to the computation of transport properties in the dilute gas limit. For the calculation of transport properties at moderate and high densities, Rainwater–Friend [6,7] and modified Enskog theories [8,9] need to be used. The application of these theories must rely on the existence and accuracy of the experimental transport property data because some scaling parameters used in these calculations are obtained by the best fit of the available experimental data [10,11]. On the other hand, MD simulations do not have such restrictions and are applicable at any arbitrary density and temperature. If an accurate intermolecular PES is available and the simulation length is long enough, MD simulations have been demonstrated to be able to reproduce the thermophysical properties of a polyatomic fluid in a wide range of temperatures and densities with high accuracy [12–14].

In MD simulations of methane fluids, the potential was often approximated by an isotropic Lennard–Jones (LJ) type function in which the two adjustable parameters were fitted to experimental data [15,16]. The spherical approximation of the methane molecule is an oversimplification for the calculation of transport properties, especially thermal conductivity. Using the approximation, it is not surprising that the deviations of the calculated thermal conductivity from the experimental data reached 20% in dense phase [15] and up to 55% in more dilute ones [16]. In order to calculate the thermal conductivity of methane accurately, therefore, an anisotropic PES should be employed to take into account the exchange of energy between translational and internal modes of motion. In MD simulations, a classical treatment of translational and rotational motions is normally valid, which, however, may not be true for vibrational

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motions. The methane molecule has nine vibrational modes with the lowest vibrational frequency of 1306 cm^{-1} [17]. The high vibrational frequency implies that the classical treatment of methane vibrations is not only inefficient, but also inappropriate due to the strong quantum effects at simulation temperatures. On the other hand, the negligence of vibrational motions in the MD simulation could cause a significant underestimate of thermal conductivity [14,18]. Therefore, a quantum treatment of molecular vibrations is necessary in the MD model. Since the exchange of vibrational and other kinetic energy caused by collisions is rare, it is assumed in this work that there is no exchange of energy between vibrational and other modes of motion. Accordingly, the methane molecule is considered as a rigid rotor and the molecular structure is assumed to be unaffected by the vibrational state of the molecule and the interaction between molecules. Hence, the influence of molecular vibrations on the transport of mass is neglected in this work. The transport of energy by vibrational excited molecules, on the contrary, cannot be neglected and is accounted for by a recently proposed correction term [14] based on the assumption that the vibrational energy mainly contributes to the thermal conductivity through self-diffusion processes. Therefore, the calculation of the self-diffusion coefficient is correlated with that of the thermal conductivity in this work. The calculation method is more efficient than the previously proposed Monte Carlo method [12,13] which involves the average of autocorrelation functions corresponding to thousands of initial vibrational energy distributions. The accuracy of the calculation method is examined by comparing the simulation results with experimental data whenever possible.

2. Intermolecular potential

As methane is the simplest alkane and suitable for very accurate *ab initio* calculations, it has attracted many theoretical studies on the interaction potential for methane pair in the past decades. The two most recent *ab initio* PES for the methane dimer are proposed by Hellmann et al. [2] and Chao et al. [19]. Both these groups calculated the PES by the counterpoise-corrected supermolecular approach at the CCSD(T) level of theory with the basis sets of aug-cc-pVTZ and aug-cc-pVQZ qualities. The calculated PES's were both extrapolated to the complete basis set. The major difference between the two PES's is that Hellmann et al. introduced an isotropic correction term to include the effects of zero-point vibrations so that a more accurate PES is obtained. Compared with Chao et al.'s potential, the global minimum of Hellmann et al.'s potential is deeper by about 50 K. Hellmann et al. used a nine-site potential function to fit the *ab initio* potential data. The potential function was validated against the experimental second pressure virial coefficient data. Chao et al. used a four-site Lennard–Jones (LJ) potential function to fit the calculated potential data. Although the expression of Chao et al.'s potential is much simpler, the fitting errors are relatively large. In MD simulations, we use the PES proposed by Hellmann et al.

Hellmann et al.'s potential assumes the methane molecule as a rigid rotor with the C-H bonds fixed at the experimental zero-point vibrationally averaged value of 1.099 Å. The bond angles of CH_4 were established to give a regular tetrahedron and each molecule contains 9 sites. Hence, each pair interaction contains 81 site–site contributions. The partial charges were assigned to the denoted C and H sites to reproduce the octupole moment of the methane monomer obtained from *ab initio* calculations. The total potential which includes a correction for zero-point vibrational effects is given by Eq. (1).

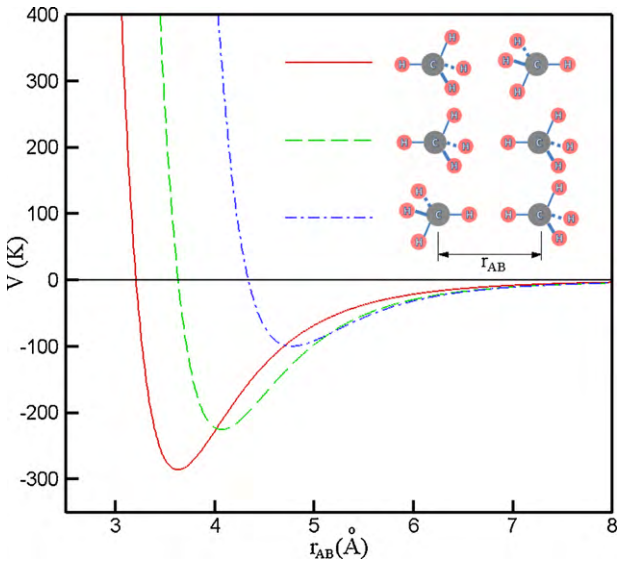

Fig. 1. Hellmann et al.'s potential as a function of the center of mass separation for different angular orientations.

$$U_{ij} = \sum_{a\in i}\sum_{b\in j}\left[A_{ab}\ \exp(-\alpha_{ab}r_{ab}) + \frac{q_a q_b}{r_{ab}} - f_6(\beta_{ab}r_{ab})\frac{C_{6ab}}{r_{ab}^6} - f_8(\beta_{ab}r_{ab})\frac{C_{8ab}}{r_{ab}^8}\right] - f_6(\beta_{corr}r_{ab})\frac{\Delta C_6}{r_{ij}^6} - f_8(\beta_{corr}r_{ab})\frac{\Delta C_{8,iso}}{r_{ij}^8}, \quad (1)$$

where

$$f_n(x) = 1 - e^{-x}\sum_{k=0}^{n}\frac{x^k}{k!}. \quad (2)$$

Here, sites a belong to molecule i, sites b belong to molecule j, r_{ab} is the distance between a and b, and r_{ij} is the distance between centers of mass of two molecules. Parameters A_{ab}, α_{ab}, β_{ab}, q_a, C_n^{ab}, β_{corr}, ΔC_6 and $\Delta C_{8,iso}$ are given in Ref. [2]. Fig. 1 depicts the anisotropy of Hellmann et al.'s potential. Since the methane molecule is modeled as a rigid rotor, the dipole moment of methane is exactly zero at each time step in the simulation. Therefore, it is not necessary to use the reaction field method [20] to account for the long-range electrostatic interactions. In fact, the first nonvanishing electrostatic interaction for a methane dimer is the octupole–octupole interaction, which decays as r^{-7} at a large intermolecular separation. In the application, the cut-off radius, within which all pair interactions are calculated, is chosen to be 14 Å.

3. Theory

The influence of vibrational motions is neglected in the calculation of self-diffusion coefficient. Hence, the self-diffusion coefficient is calculated directly from the Green–Kubo (GK) formulas [21,22]. The accurate determination of self-diffusion coefficient is important in this work because it will be used in calculating the vibrational contribution to the thermal conductivity. The self-diffusion coefficient D is given by [23]

$$D = \frac{1}{3}\int_0^\infty dt\,\left\langle \vec{v}_i(t)\cdot\vec{v}_i(0)\right\rangle, \quad (3)$$

where $\vec{v}_i$ is the translational velocity of molecule i, t is the time, and $\langle\cdots\rangle$ denotes the ensemble average.

Due to the strong quantum effects, vibrational motions are not directly taken into account in classical MD simulations. As a

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result, the vibrational energy is not included in the GK formula. The thermal conductivity $\lambda_{T,0}$ which does not include the vibrational contribution is calculated by [24]

$$\lambda_{T,0} = \frac{V}{k_B T^2} \int_0^\infty dt \left\langle J_\alpha(t) J_\alpha(0) \right\rangle . \quad (4)$$

Here, J_α is a component of the energy current which does not take into account the quantized vibrational energies, V is the volume of the system, k_B is the Boltzmann constant and T is the average temperature of the system. Using the rigid-rotor assumption, the expression for the energy current J_α which contains the contributions from translational energy, rotational energy and molecular interactions is given by [25]

$$J_\alpha = \frac{1}{V}\sum_i v_{i\alpha}\left(\frac{1}{2}m\vec{v}_i^2 + \frac{1}{2}\vec{\omega}_i \mathbf{I}_i \vec{\omega}_i + \frac{1}{2}\sum_{j\neq i} U_{ij}\right) + \frac{1}{V}\sum_i\sum_{j>i} r_{ij\alpha}\left(\frac{1}{2}\left(\vec{v}_i + \vec{v}_j\right)\cdot \vec{f}_{ij} + \frac{1}{2}(\vec{\omega}_i \cdot \vec{\Gamma}_{ij} - \vec{\omega}_j \cdot \vec{\Gamma}_{ji})\right), \quad (5)$$

where $\vec{\omega}_i$ and $\mathbf{I}_i$ are, respectively, the angular velocity and the matrix of moments of inertia for molecule i, m represents the mass of the methane molecule. r_{ij} and f_{ij} denote, respectively, the intermolecular distance and force. U_{ij} and $\vec{\Gamma}_{ij}$ are, respectively, the intermolecular potential energy between molecule i and molecule j and the torque acting on molecule i due to the interaction between molecule i and molecule j.

The energy current varies with time due to the interaction between molecules. Since collisions resulting in the exchange of vibrational and other kinetic energy are rare, the quantized vibrational energy is considered as frozen in the molecule and only contributes to the thermal conductivity by diffusion. Hence, the vibrational contribution to thermal conductivity is calculated separately in this work. Accordingly, the thermal conductivity λ_T which includes the vibrational contribution is given by [14]

$$\lambda_T = \lambda_{T,0} + \rho D C_{V,vib}, \quad (6)$$

where ρ is the density of the system and $C_{V,vib}$ is the isochoric vibrational heat capacity. The quantum effects of the molecular vibrations are included by $C_{V,vib}$ which can be normally calculated using the quantum harmonic approximation [24]. It is notable that Eq. (6) is similar to the modified Eucken formula [11] which is used for the estimation of thermal conductivity of dilute gas:

$$\lambda_T = \frac{15 k_B}{4m}\eta + \rho D C_{V,\mathrm{int}}. \quad (7)$$

In Eq. (7), the first term on the right side represents the translational contribution to thermal conductivity, and the second term represents the contribution from the internal modes of motion, $C_{V,\mathrm{int}}$ is the contribution to the isochoric heat capacity from internal modes of motion. In this work, $C_{V,\mathrm{int}} = C_{V,vib} + 1.5R$ where R is the gas constant. The major difference between the modified Eucken formula and Eq. (6) is that the modified Eucken formula assumes that there is no exchange of energy between the translational and internal modes of motion, whereas energy exchange between translational and rotational motion is included in Eq. (6) by MD simulations. In the case of dilute methane gas, the self-diffusion coefficient D is available through MD calculations and very accurate experimental shear viscosity η data exist. Therefore, the accuracy of the modified Eucken formula, i.e., Eqs. (7) and (6) for the calculation of thermal conductivity of dilute methane gas can be both examined by comparing the calculated results with the experimental thermal conductivity data. As the fluid density increases, it is unlikely to neglect the exchange of energy between translational and rotational energies. Hence, the modified Eucken formula, Eq. (7), is not applicable to dense fluids. In this case, the thermal conductivity is calculated by Eq. (6) and compared with experimental data to examine if the decoupling between vibrations and other degrees of freedom is also valid for a moderately dense methane fluid.

4. Simulation details and results

4.1. Simulation details

Two sets of simulations of the self-diffusion coefficient and thermal conductivity of methane are carried out in the microcanonical ensemble. In the first set of simulations, the pressure of methane gas is fixed at 1 atm and the temperature varies from 200 to 900 K. The density of the methane is determined from the ideal gas law. In the second set of simulations, the temperature is fixed at 200 or 300 K and the density varies from 0.04 to 5 mol/L. For any given temperature and density, the number of molecules included in a cubic simulation box is always 1024. The coordinates of the center of mass and the orientations of the molecules are both initialized randomly inside the simulation box with periodic boundary conditions. The minimum distance between any two molecules is set to be greater than 6 Å to avoid unrealistic large potentials and forces. The translational and angular velocities are both initialized by the Maxwell–Boltzmann relation at the given temperature. The equations of molecular translational and rotational motions are integrated by the Verlet leap-frog algorithm and the quaternion algorithm [23], respectively. Berendsen et al.'s algorithm [26] is applied to equilibrate the system to the desired temperature with a time constant of 2.0 ps. Using these settings, the system can be well equilibrated within 50 ps at all simulated state points. After the system is equilibrated and reaches the desired total energy corresponding to the given temperature and density, the thermostat is turned off and the transport properties are calculated in the constant-NVE ensemble. A step size of 2.5 fs is chosen for dilute gases of which the temperature is lower than 600 K. For moderately dense methane fluids and dilute methane gases with higher temperatures, the step size is chosen as 2 fs. The time step size is chosen such that the total energy of the system is always kept constant within 2 parts in 10^4.

In order to obtain the thermal conductivity with a low statistical error (~1%) from the MD simulation, it is necessary to carry out a long simulation length. For dilute gases at 1 atm, the total simulation length is increased from 3 μs at 200 K to 6 μs at 900 K. For moderately dense fluids, the total simulation length is decreased from 240 ns at 1 mol/L to 40 ns at 5 mol/L. With such long simulation lengths, the statistical error of the calculated self-diffusion coefficient can be reduced to less than 0.1% by additional averaging all the molecules in the system. Since the *ab initio* potential employed in this work is a nine-site potential model with a complex analytical expression for each site–site interaction, the total computational cost is very high. To save the computational time, the long simulation is divided into hundreds of shorter parallel runs which are independently initialized and equilibrated at the given temperature and density. The statistical error is estimated by Fincham's block averaging method [27].

4.2. Simulation results of dilute methane gases

The calculated self-diffusion coefficients comparing with the values extrapolated to the dilute gas limit [1] from the density-dependent experimental data measured by Dawson et al. [28] and Oosting and Trappeniers [29] are shown in Table 1. The uncertainties of the experimental data were estimated to be ±6% [28] and ±2% [29]. Due to difficulties of the measurements, the experimen-

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Table 1
Thermophysical properties of methane at 1 atm. The statistical error of self-diffusion coefficient is less than 0.1%. The statistical error of thermal conductivity is less than 1%.

T (K)	ρD (mg/m s)			η (μPa s)	$C_{V,vib}$ (J/mol K)	λ_T (mW/m K)				
	MD	Exp.	CT	Exp. [32,34]	Exp. [32]	MD $\lambda_{T,0}$	MD λ_T	Exp. [32,33]	CT	Modified Eucken
200	10.50	10.48 [28] 10.16 [29]	10.53	7.81	0.257	21.62	21.79	21.94	21.75	23.50
300	15.25	14.99 [28] 15.29 [29]	15.25	11.25	2.521	32.35	34.75	34.55	34.36	36.14
400	19.37	–	19.36	14.27	7.351	41.16	50.03	50.13	50.04	51.70
500	23.07	–	23.04	16.98	13.25	49.83	68.90	68.56	68.45	70.04
600	26.45	–	26.42	19.43	19.24	56.38	88.13	88.92	88.62	90.11
700	29.58	–	29.56	21.63	25.35	67.12	113.9	112.1	109.9	112.1
800	32.61	–	32.52	23.71	30.83	73.74	136.5	134.3	131.8	134.6
900	35.45	–	35.35	25.71	35.89	79.55	158.9	156.6	154.1	157.5

tal self-diffusion coefficient data at temperatures higher than 350 K are scarce or nonexistent. Comparing with the available experimental data at 200 and 300 K, the deviations of MD simulation results are generally within the experimental uncertainties. However, the deviation between the simulated self-diffusion coefficient and Oosting and Trappeniers' data [29] at 200 K is greater than the experimental uncertainty. As was pointed out by Hellmann et al. [1], the experimental uncertainties may be overoptimistic and the calculated self-diffusion coefficients from CT method are more reliable than the experimental data. Hence, we compared our MD simulation results with those calculated from CT method [1] in which the same intermolecular PES was used and the methane molecule was also treated as a rigid rotor. As shown in Table 1, very good agreement is found at all simulation temperatures. The CT method has been proved to be very accurate in reproducing transport properties of dilute gases [4,5,30,31]. Therefore, the deviations found in Table 1 should not be attributed to the MD simulation method or the GK formula used in the calculation of self-diffusion coefficient. A critical test of the accuracy of the potential energy surface and the proposed calculation method requires more accurate experimental data.

In Table 1, the MD simulation results of the thermal conductivity of dilute methane gases are compared with the experimental data [32,33], results from CT method [3] and modified Eucken formula. For temperatures lower than 600 K, the experimental thermal conductivity data of methane at 1 atm are obtained from the correlation provided by NIST [32] with the uncertainty estimated to be ±2.5%. At higher temperatures, however, there are no estimates of uncertainty of NIST correlation at 1 atm. Therefore, the experimental data at 700–900 K are from a theoretically based correlation for the zero-density thermal conductivity provided by Assael et al. [33] with the uncertainty estimated to be ±4%. In Table 1, $\lambda_{T,0}$ is obtained directly from the integral of the time correlation function of energy current which does not include the vibrational energy. The statistical errors are less than 1%. It is evident that $\lambda_{T,0}$ significantly underestimates the thermal conductivity except at a very low temperature. The vibrational contribution $\rho D C_{V,vib}$ is then included to obtain λ_T according to Eq. (6). In the calculation, the vibrational heat capacity $C_{V,vib}$ shown in Table 1 is calculated by Eq. (8).

$$C_{V,vib} = C_{V,\rho=0} - 3R, \tag{8}$$

where $C_{V,\rho=0}$ represents the isochoric heat capacity at zero density. Since experimental data of $C_{V,\rho=0}$ at each simulation temperature are all available [32] and the uncertainty is within ±1%, $C_{V,vib}$ calculated from Eq. (8) is supposed to be more accurate than that calculated from quantum harmonic approximation since the Fermi resonance in the methane vibrational modes makes the harmonic approximation inaccurate. It can be seen from Table 1 that the calculated thermal conductivity λ_T which includes the vibrational contribution agrees well with the experimental data. The ratio of the vibrational contribution to the total thermal conductivity increases from 0.8% at 200 K to 50% at 900 K. Hence, the vibrational contribution to the thermal conductivity of the dilute methane gas is non-negligible even at a temperature much lower than the lowest characteristic vibrational temperature (~1870 K) of methane.

To compare the accuracy of different calculation methods, the thermal conductivities calculated from CT method and the modified Eucken formula are also shown in Table 1. The shear viscosity used in the modified Eucken formula is obtained directly from the accurate experimental data [32,34]. The uncertainty of the experimental shear viscosity is estimated to be ±0.2% around room temperature and ±1% at low and high temperatures. The thermal conductivity calculated from CT method is provided by Hellmann et al. [3]. As was pointed out by Hellmann et al. [3], the CT calculation results are expected to be more reliable than the currently available correlations at low and high temperatures. For the aforementioned three calculation methods, the deviations between the calculated thermal conductivity and the experimental data [32,33] at each simulation temperature are shown in Fig. 2. It can be seen that both the MD calculation employed in the work and the CT method employed by Hellmann et al. predict the thermal conductivity within the experimental uncertainty. Using the following Eq. (9), the averaged absolute deviations (AAD) of the results from MD method and CT method are calculated to be 0.92% and 0.94%,

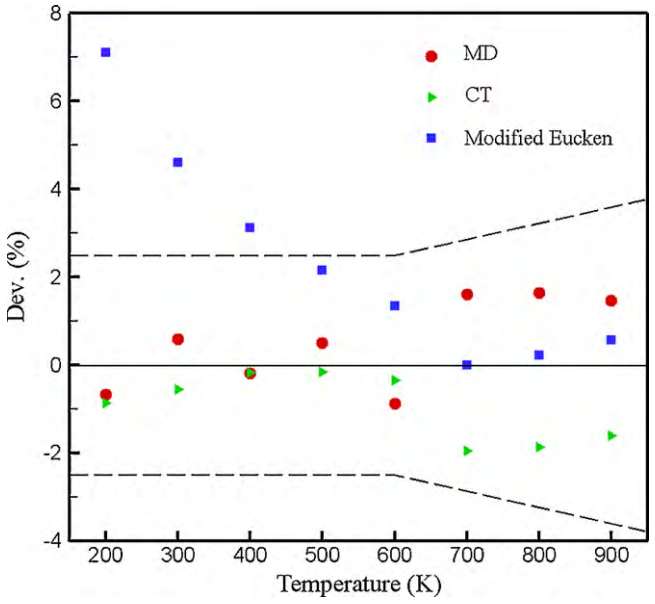

Fig. 2. The deviations between the calculated thermal conductivity and experimental data of dilute methane gases. The dashed lines show the uncertainties of the experimental data. Dev. % = $(\lambda_{T,cal}/\lambda_{T,exp} - 1) \times 100\%$.

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respectively.

$$\mathrm{AAD} = \frac{1}{N_{data}} \sum_{i=1}^{N_{data}} \left| \frac{\text{calculated result at state point } i}{\text{experimental data at state point } i} - 1 \right| \times 100\%, \quad (9)$$

where N_{data} means the number of data points. Therefore, the MD method is as accurate as the CT method in calculating thermal conductivities. The good agreement with experimental data indicates the assumption that the vibrations mainly contribute to thermal conductivity through self-diffusion processes is valid in a dilute gas.

As shown in the above discussion, the vibrational contribution to the thermal conductivity $\rho D C_{V,vib}$ could reach 50% of the total thermal conductivity at the highest temperature of our calculation. Hence, the accuracy of the calculated thermal conductivity strongly depends on the accuracy of the heat capacity $C_{V,vib}$ used in the calculation. It is noted in Fig. 2 that MD results at temperatures higher than 700 K are greater than CT results by 3–3.5% which is much greater than the statistical error (±1%) of the MD result. Since both the MD and CT calculations use the same intermolecular potential and the rigid-rotor approximation, the deviation between the two calculation results might be caused by different heat capacity reference data used in the calculation.

As shown in Fig. 2, the modified Eucken formula is not able to predict the thermal conductivity within the experimental uncertainty if the temperature is lower than 500 K. At relatively low temperatures, the vibrational contribution to the thermal conductivity is small. The large deviations are, therefore, mainly caused by neglecting the exchange of energy between translational and rotational motions. The MD calculation with an anisotropic intermolecular potential takes into account this kind of energy exchange, hence gives much better results. Nevertheless, the modified Eucken formula predicts reasonable thermal conductivities if the temperature is higher than 600 K. The results indicate that the exchange of energy between translational and internal modes of motion might become negligible for dilute gases at high temperatures so that both the rotational and vibrational motions contribute to thermal conductivities mainly through self-diffusion processes. This result agrees with Mason and Monchick's prediction of the temperature dependence of internal contribution to the thermal conductivity by making use of the energy-sudden and centrifugal-sudden approximations [35,36].

4.3. Simulation results at moderate densities

The MD simulation results of self-diffusion coefficients of moderately dense methane at 200 and 300 K are shown in Fig. 3. The experimental data are obtained from Dawson [37] who measured the density dependence of the self-diffusion coefficient of methane from 154 to 354 K. The uncertainty was estimated to be ±4.5% and is depicted by dashed lines in Fig. 3. The statistical error of the calculated self-diffusion coefficient is about 0.1% which is less than the size of the symbols in Fig. 3. At 300 K, the deviations between the calculated and experimental results are within the experimental uncertainty. The AAD between the MD results and experimental data is 1.21%. At 200 K, however, the calculated results only agree with the experimental data at densities lower than 3 mol/L. At higher densities, the deviations reached 4.55% and 5.25% which are higher than the experimental uncertainty. The vibrational energies of methane are rarely excited at 200 K. Hence, the disagreement should not be attributed to the decoupling between the vibrations and other degrees of freedom in the MD model. The relative large deviations at higher densities may come from the neglect of three-body effects in the pair potential employed in the calculation. On the other hand, the self-diffusion coefficients are notoriously difficult to measure accurately. The claimed experimental uncertainty may be optimistic [1]. Furthermore, the relatively large deviation at densities higher than 3 mol/L is not observed at 300 K. To investigate the deviation caused by the negligence of three-body effects, therefore, more accurate experimental data of self-diffusion coefficient should be used for comparison.

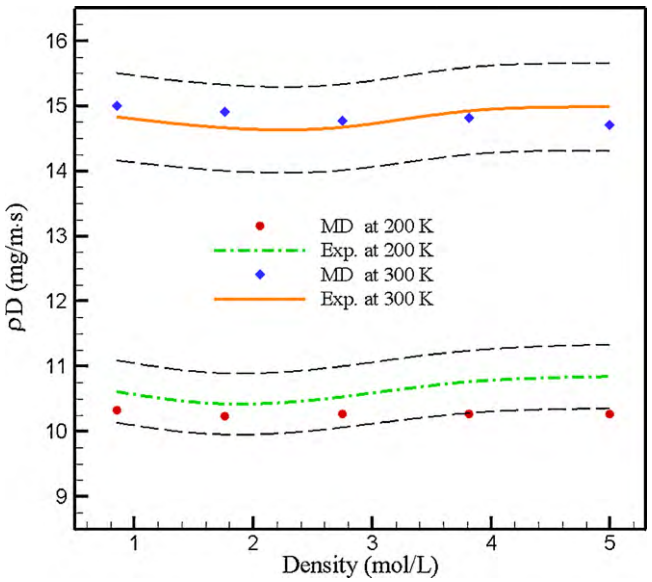

Fig. 3. The product ρD as a function of density at 200 or 300 K. The dashed lines show the uncertainties of the experimental data. The statistical errors are smaller than the size of the symbols.

Fig. 4 depicts the calculated thermal conductivity and the experimental data [32] as a function of density at 200 and 300 K. The uncertainty of the experimental data provided by NIST [32] was estimated to be ±2% and is depicted by dashed lines in Fig. 4. The statistical error of the calculated thermal conductivity is about 1.2% which is smaller than the size of the symbol shown in Fig. 4. Without the vibrational correction term, the MD results underestimate the thermal conductivity at both temperatures. The AADs between the calculated thermal conductivity without the vibrational correction term and the experimental data at 200 and 300 K are 1.54% and 7.36%, respectively. It is evident, especially at 300 K, that the

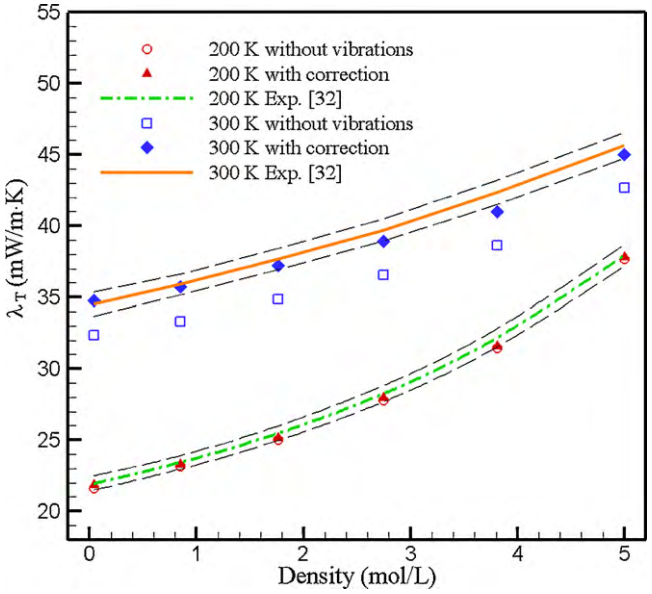

Fig. 4. The thermal conductivity as a function of density at 200 or 300 K. The dashed lines show the uncertainties of the experimental data. The statistical errors are smaller than the size of the symbols.

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accuracy of the calculation results is greatly improved when the vibrational correction term $\rho DC_{V,vib}$ is included. With the correction term, the AADs at 200 and 300 K are 1.05% and 1.53%, respectively. The calculated thermal conductivity at both temperatures has generally a good agreement with the experimental data. Although the MD results underestimate the self-diffusion coefficient of methane at relative high densities at 200 K, the underestimation has little effects on the calculated thermal conductivity because the vibrational contribution to thermal conductivity at 200 K is negligible. Nevertheless, it is found at both temperatures the calculated thermal conductivity always slightly underestimates the experimental data at moderate densities even when the vibrational contribution is included. The small deviations might come from the neglect of the exchange of energy between vibrations and other modes of motions. As is discussed in the self-diffusion results, however, the vibrational energy of methane at 200 K is negligible. It is possible that the underestimations are caused by the neglect of three-body effects in the pair potential. Therefore, in order to extend the calculation to more dense methane fluids or test the accuracy of the MD calculation method in calculating self-diffusion coefficient and thermal conductivity of methane at high densities, Hellmann et al.'s potential should be employed with a correction term to account for the three-body effects. The determination of an accurate potential that includes the three-body effects needs further investigations.

5. Conclusions

MD simulations of the self-diffusion coefficient and thermal conductivity of methane are performed in a wide range of temperature at dilute phase and in an intermediate dense phase. At the simulated state points, the experimental data of the two transport properties of interest are of relatively low accuracy or nonexistent. By comparing the MD simulation results with the available experimental data, it is found that the decoupling between vibrations and other degrees of freedom of methane is appropriate in a dilute or intermediate dense phase. On the other hand, the exchange of energy between translational and rotational motions cannot be neglected even in a dilute gas. The vibrational energies are proved to contribute to the thermal conductivity mainly through self-diffusion processes. The correction term $\rho DC_{V,vib}$ is able to nicely account for the vibrational contribution which is shown to be significant in the total thermal conductivity of methane at both low and intermediate densities. In order to obtain better results or extend the MD simulation to methane fluids at higher densities, the *ab initio* pair potential employed in this work needs some improvement to incorporate the three-body effects.

List of symbols

a	interaction site index
AAD	averaged absolute deviations
b	interaction site index
$C_{V,vib}$	vibrational heat capacity
$C_{V,\mathrm{int}}$	the contribution to the isochoric heat capacity from internal modes of motion
$C_{V,\rho=0}$	the isochoric heat capacity at zero density
D	self-diffusion coefficient
I	the matrix of moments of inertia
J_α	a component of the energy current
k_B	Boltzmann constant
m	the mass of molecule
N_{data}	the number of data points
q_a	partial charge on interaction site a
q_b	partial charge on interaction site b
r_{ab}	distance between interaction site a and b
$r_{ij\alpha}$	a component of the distance vector from the molecule j to i
R	gas constant
t	time
T	temperature
U_{ij}	intermolecular potential
$\vec{v}_i$	translational velocity of molecule i
$v_{i\alpha}$	a component of translational velocity of molecule i
V	volume

Greek letters

$\vec{\Gamma}_{ij}$	torque acting on molecule i due to the interaction between molecule i and molecule j
η	shear viscosity
$\lambda_{T,0}$	thermal conductivity that does not include the vibrational contribution
λ_T	thermal conductivity that includes the vibrational contribution
ρ	density
$\vec{\omega}_i$	angular velocity of molecule

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