

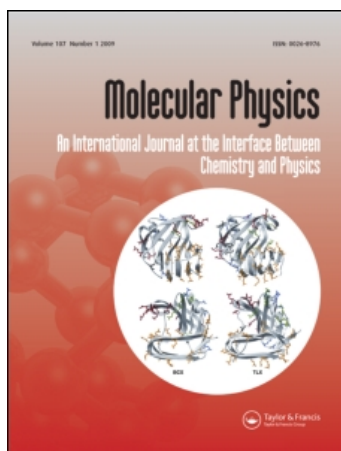
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RESEARCH ARTICLE

Calculation of thermophysical properties for CO₂ gas using an *ab initio* potential model

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The density, isochoric heat capacity, shear viscosity and thermal conductivity of CO₂ gas in the pressure range of 1–50 atm and 300 K are calculated based on a five-centre potential model obtained from *ab initio* calculations of the intermolecular potential of a CO₂ dimer. The quantum effects of the intramolecular motion are included in a model by the Monte Carlo (MC) Method. Without using any experimental data, the present model achieves excellent agreements between the calculated thermophysical properties and experimental data for all simulated CO₂ densities except the highest one at 135 kg/m³ (3 mol/L). The contributions of potential to the thermophysical properties of the moderate dense CO₂ gas and their dependence on density are investigated in detail.

Keywords: thermophysical properties; molecular dynamics; *ab initio*; CO₂ gas

1. Introduction

In general, as long as the structure of the molecule in a fluid and the intermolecular potentials which describe the interactions between molecules are known, all thermodynamic and transport properties of the fluid at any given temperature and pressure can be calculated by theoretical approaches such as the formal kinetic theory and time-correlation function theory. CO₂ is a moderate size molecule and is suitable for very accurate *ab initio* calculations. Based on different molecular potential models, a number of calculations for the CO₂ thermophysical properties were carried out in the last decade [1–6]. Bock *et al.* [1–3] calculated accurately the transport properties of CO₂ at the zero density limit by evaluating the relevant collision cross sections by means of classical-trajectory calculations directly from *ab initio* potentials. However, their calculation method so far cannot be extended to the calculation of transport properties for dense fluids. The determination of density-dependent thermophysical properties of real fluids based on the formal kinetic theory still strongly relies on experimental data [7]. On the other hand, many calculations [4–6] used molecular dynamics (MD) simulations and the Green and Kubo (GK) formulas [8–10] to calculate the CO₂ transport properties because the GK formulas do not depend upon the details of any particular molecular model and are not limited to any density condition [11]. Coelho *et al.* [4] and Ludemann *et al.* [5] used, respectively,

a LJ 6–12 potential and a rough hard sphere model to calculate the self-diffusion coefficient of CO₂. Both of the molecular models considered the molecule as a structureless spherical particle, and the parameters in the potentials were extracted from experimental data. It is well known that an isotropic potential is inadequate to describe the interactions between polyatomic molecules. Moreover, the parameters used to calculate the self-diffusion coefficient in these models cannot be used to reliably predict other transport properties such as viscosity and thermal conductivity. Hence, an anisotropic potential is required for quantitative calculations. Fernandez *et al.* [10] used a two-centre LJ plus point quadruple pair potential to calculate the shear viscosity and thermal conductivity of low temperature, high density CO₂ fluids. In their model, the parameters in the potential were adjusted exclusively to fit the experimental pure substance vapour–liquid equilibrium data. The calculated shear viscosities and thermal conductivities have an average deviation of 5% and 10%, respectively, as compared to experimental data. The deviations are mainly caused by inaccurate intermolecular potential since the experimental data can indicate only a limited region of the potential energy surface [12]. Therefore, one of the difficulties in the calculations of thermophysical properties of real fluids is to obtain an accurate intermolecular potential function. It is impossible to use a single intermolecular potential for the calculations of thermophysical

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properties at all fluid states. For dilute gases such as the low pressure high temperature CO₂ gas, it is possible to obtain an accurate pair potential directly from *ab initio* calculations of the intermolecular potential of a CO₂ dimer without adjusting to any experimental data. For instance, Bukowski *et al.* (BUK) [13] accurately computed a four-dimensional intermolecular potential energy surface for the CO₂ dimer using the many-body symmetry-adapted perturbation theory and a large *5s3p2d1f* basis set. With the increase of fluid density, the three-body contribution to the potential becomes important and the potential calculated from the molecular dimer would be inaccurate for dense fluids. However, in moderate dense gases, such as moderate dense CO₂ gas, in which the contributions of the potential to thermophysical properties would become important, it is still possible to use the potential for a CO₂ dimer to accurately reproduce the thermophysical properties without considering the three-body effects. In this study, we use MD simulations and a five-center *ab initio* intermolecular potential (BUK potential) to study the dependence of thermophysical properties on density for moderate dense CO₂ gas without relying on any experimental data. This study also shows the upper limit of the gas density where the molecular interactions can be well represented by the pair-additive potential obtained from the molecular dimer. Additionally, the potential contributions to thermophysical properties and their dependence on density are studied in details at each simulated state point.

In the present work, the density, isochoric heat capacity, shear viscosity and thermal conductivity of CO₂ gas at 300 K and in the pressure range of 1–50 atm (which corresponds to the density range 2–140 kg/m³) are calculated by the equilibrium MD simulations using the BUK potential. The simulation conditions are chosen in order to compare against experimental data. Different from a fluid at low temperatures in which the vibrational degrees of freedom can be neglected [6,14], for a polyatomic gas like CO₂, which has low-lying vibrational states, the vibrational energy contributions to the heat capacity and thermal conductivity are important even at room temperature. In this case, it is inappropriate to either neglect the vibrational degrees of freedom or treat the molecular vibration classically. The vibrational heat capacity can be easily calculated independently. However, it is hard to include the variation of vibrational energies directly into the GK formula for the calculation of thermal conductivities because the vibrational energy is not allowed to change continuously. The traditional Eucken formula [15] which accounts for internal degrees of freedom of molecules by Eucken correction

factor cannot reliably predict thermal conductivities over a large range of pressure and temperature. In this work, the quantum effects of molecular vibrational energies are taken into account by the MC method [16]. Using this method, thermal conductivities can be obtained much more accurately than those obtained from a classical treatment of vibrational motions or by the neglect of vibrational energies [17]. The present molecular model can accurately reproduce the thermophysical properties of moderate dense CO₂ gas totally based on *ab initio* calculation results.

2. The molecular structure and inter-molecular potential

In order to include the rotational and vibrational motions of molecules in the MD model, the moment of inertia and the vibrational energy eigen values are both calculated from the intramolecular potential. Two *ab initio* intramolecular potential surfaces have recently been proposed for the CO₂ molecule; one is based on the Coupled-Cluster Singles and the Doubles excitation with perturbative treatment of the Triple excitations [CCSD(T)] method [18] and the other is the Density Functional Theory (DFT) method [19]. The CCSD(T) method is generally more accurate than the DFT method, but is computationally more expensive. Both the intramolecular potentials predicted the linear symmetric equilibrium structure of CO₂. Our previous *ab initio* results [19] show the C-O bond length $r_0 = 1.162 \text{ \AA}$ which is consistent with the experimental data [20]. In this work, we assume the CO₂ molecules to be linear rigid rotors. Hence, the moment of inertia, I , of CO₂ is a constant in the simulation and can be computed via $I = 2m_O r_0^2$, where m_O is the mass of the oxygen atom. Using the *ab initio* intramolecular potential, the vibrational energy eigen values are obtained by solving the vibrational Schrödinger equation. The energy eigen values calculated from the intramolecular potential obtained by the CCSD(T) method normally gives more accurate results. Therefore, the corresponding results of CO₂ vibrational states are used in this work. The CO₂ molecule has four vibrational modes. The vibrational energy eigen values of the first excited states of the symmetric stretching mode, the asymmetric stretching mode, and the doubly degenerated bending modes are, respectively, 1387.9 cm^{-1} , 2348.8 cm^{-1} and 667 cm^{-1} [18]. In the calculation, we assume the energy differences between any two neighbouring energy states of each vibrational mode are constant. Due to the strong quantum effects, the classical MD simulation of molecular vibrational motions is inappropriate.

We use the MC calculations to take into account the quantum effects in the work.

The most important issue in a MD simulation is to use an appropriate intermolecular potential. The BUK potential employed in this work used a site-site representation of the intermolecular potential and was validated by comparing to the experimental second virial coefficients. The site-site fit BUK potential reads

$$U_{BUK} = \sum_{a \in A} \sum_{b \in B} \left[\exp(\alpha_{ab} - \beta_{ab} r_{ab}) + f_1(\delta_1^{ab} r_{ab}) \frac{q_a q_b}{r_{ab}} - f_6(\delta_6^{ab} r_{ab}) \frac{C_6^{ab}}{r_{ab}^6} - f_8(\delta_8^{ab} r_{ab}) \frac{C_8^{ab}}{r_{ab}^8} \right], \quad (1)$$

where

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

In Equation (1), the parameters α_{ab} , β_{ab} , δ_n^{ab} , q_a , and C_n^{ab} are given in [13].

Figure 1 shows the radial dependence of the intermolecular potential for different CO₂ dimer configurations. To ensure the continuity of the potential and force near the cut-off radius, the original BUK potential U_{BUK} is employed with a small modification as follows

$$U_{\text{mod}} = \begin{cases} U_{BUK} \cdot \left[1 - e^{\frac{(r_{AB}-r_{cut})^2}{-2.0}} \right] & r_{AB} \leq r_{cut} \\ 0 & r_{AB} > r_{cut} \end{cases}, \quad (3)$$

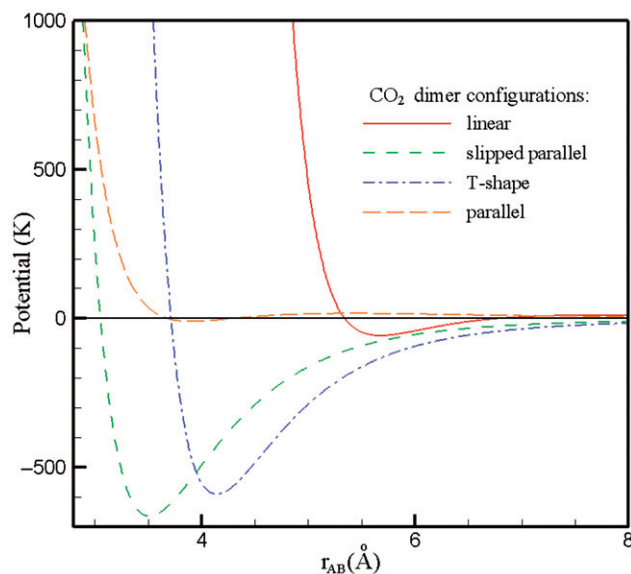


Figure 1. Radial dependence of BUK intermolecular potential for different CO₂ dimer configurations.

where r_{cut} is the cut-off radius and r_{AB} is the distance between the centre of mass for each of the two CO₂ monomers. Both the r_{AB} and r_{cut} are in atomic units. The modification only takes effects in the weak interaction region which is close to the cut-off radius. In this work, we set $r_{cut} = 14 \text{ \AA}$. Tests showed that with such a large cut-off radius, the use of an Ewald sum to treat long range Coulomb interactions was not necessary [21]. The modified potential makes the intermolecular potential, the intermolecular force, and the torque acting on the molecule all tend smoothly to zero at the cutoff radius so that possible problems associated with the energy conservation and numerical instability in the equations of motion are eliminated.

3. Theoretical background

The computations of thermophysical properties are all carried out by the equilibrium MD simulations in a microcanonical ensemble. The time-correlation function theory is employed for the calculations of shear viscosity and thermal conductivity. The heat capacity can be simply obtained from the energy fluctuations. The density is determined directly from the equilibration process described next.

3.1. Shear viscosity

The GK formula for shear viscosity η can be expressed as [22]

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \langle P_{\alpha\beta}(t) \cdot P_{\alpha\beta}(0) \rangle, \quad (4)$$

where

$$P_{\alpha\beta} = \underbrace{\frac{1}{V} \sum_i m v_{i\alpha} v_{i\beta}}_{P_{\alpha\beta,k}} + \underbrace{\frac{1}{V} \sum_i \sum_{j>i} r_{ij\alpha} f_{ij\beta}}_{P_{\alpha\beta,p}}. \quad (5)$$

In Equations (4) and (5), $P_{\alpha\beta}$ are the off-diagonal ($\alpha \neq \beta$) elements of the pressure tensor, $\langle \dots \rangle$ denotes the ensemble average which can be determined from MD simulations. The variations of translational velocities, v_i , intermolecular distances, r_{ij} , and forces, f_{ij} , in Equation (5) are all caused by the interactions between molecules and are assumed to be unaffected by molecular vibrational motions. To study the potential contribution to the shear viscosity as a function of gas density, Equation (5) is separated into two parts as suggested by Meier *et al.* [23]; one is the kinetic contribution $P_{\alpha\beta,k}$ and the other is the potential contribution $P_{\alpha\beta,p}$. When this separation is inserted into Equation (4), the viscosity is divided into

three different contributions, i.e. the kinetic-kinetic contribution η_{kk} , kinetic-potential contribution η_{kp} and potential-potential contribution η_{pp} . The three contributions as a function of gas density are all calculated in this work.

3.2. Thermal conductivity

The GK formula relates the thermal conductivity λ_T to the time autocorrelation function of the energy current [11].

$$J_\alpha = \underbrace{\frac{1}{V} \sum_i v_{i\alpha} \left(\frac{1}{2} m v_i^2 + \frac{1}{2} I u_i^2 + E_{Vi} \right)}_{J_{\alpha,k}} + \underbrace{\frac{1}{V} \left[\sum_i v_{i\alpha} \left(\frac{1}{2} \sum_{j \neq i} U_{ij} \right) + \sum_i \sum_{j > i} r_{ij\alpha} \left(\frac{1}{2} (\vec{v}_i + \vec{v}_j) \cdot \vec{F}_{ij} + \frac{1}{2} (\vec{u}_i \cdot \vec{G}_{ij} - \vec{u}_j \cdot \vec{G}_{ji}) \right) \right]}_{J_{\alpha,p}}. \quad (9)$$

$$\lambda_T = \frac{V}{k_B T^2} \int_0^\infty dt \langle J_\alpha(t) J_\alpha(0) \rangle. \quad (6)$$

Here, J_α is a component of the energy current. For a linear molecule like CO₂, J_α can be expressed as Equation (7) based on the frozen vibrational energy assumption [16]

$$J_\alpha = \frac{1}{V} \sum_i v_{i\alpha} \left(\frac{1}{2} m v_i^2 + \frac{1}{2} I u_i^2 + E_{Vi} + \frac{1}{2} \sum_{j \neq i} U_{ij} \right) + \frac{1}{V} \sum_i \sum_{j > i} r_{ij\alpha} \left(\frac{1}{2} (\vec{v}_i + \vec{v}_j) \cdot \vec{F}_{ij} + \frac{1}{2} (\vec{u}_i \cdot \vec{G}_{ij} - \vec{u}_j \cdot \vec{G}_{ji}) \right), \quad (7)$$

where \vec{u}_i is the rotational velocity of molecule i which is defined as \vec{e}_i , the time derivative of the unit vector along the molecular axis, and U_{ij} represents the intermolecular potential. In Equation (7), \vec{G}_{ij} can be determined from the intermolecular forces by

$$\vec{G}_{ij} = \sum_a d_{ia} \vec{f}_{ija}, \quad (8)$$

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

Most of the papers which calculated the thermal conductivity of the molecular fluids from the GK formula either removed the vibrational energy E_{Vi} [6,14,17,24] or treated the vibrational motions classically [17,25,26]. However, neither of the methods is appropriate for polyatomic gases. In this work, the quantized vibrational energy of each molecule is

initialized by MC method at the desired temperature. Due to the interactions among molecules in the system, the translational, rotational, and intermolecular potential energies all vary with time. However, the vibrational energies are assumed to be frozen in the molecules so that they have no influence on the molecular interactions.

To study the potential contribution to the thermal conductivity as a function of the gas density, the energy current expression is also separated into the kinetic contribution $J_{\alpha,k}$ and the potential contribution $J_{\alpha,p}$ as follows:

Similarly, the thermal conductivity is divided into three different contributions, i.e. kinetic-kinetic contribution $\lambda_{T,kk}$, kinetic-potential contribution $\lambda_{T,kp}$ and potential-potential contribution $\lambda_{T,pp}$. The density dependence of the three contributions is studied in details in this work.

3.3. Heat capacity

The calculation of isochoric heat capacity is much easier than the transport properties such as shear viscosity and thermal conductivity. In a constant NVE ensemble, the heat capacity can be calculated by [27]

$$\langle E_P^2 \rangle - \langle E_P \rangle^2 = \frac{d}{2} N k_B^2 T^2 \left(1 - \frac{d N k_B}{2 C_V} \right), \quad (10)$$

where E_P is the total potential energy of the system, C_V is the isochoric heat capacity excluding the vibrational contributions, and d is the degree of freedom. Since the vibrational energies are assumed frozen in the molecules during the simulation, the C_V in Equation (10) does not include the contribution from the vibrational degree of freedom. Hence, $d=5$ for CO₂ molecules which include three degrees of freedom of translational motion and two degrees of freedom of rotational motion. The vibrational heat capacity is calculated independently at the desired temperature. Since we assume the vibrational energies of each mode are equally spaced, the vibrational heat capacity can be calculated as the sum of four independent harmonic oscillators:

$$C_{V,vib} = N k_B \sum_{j=1}^4 \left[\left(\frac{E_{vj}}{k_B T} \right)^2 \frac{e^{-E_{vj}/k_B T}}{(1 - e^{-E_{vj}/k_B T})^2} \right], \quad (11)$$

where E_{vj} means the fundamental vibrational transition energy of mode j whose value is given in Section 2.1. The sum of the calculated C_V from Equation (10) and the vibrational heat capacity from Equation (11) is the isochoric heat capacity of CO₂ gas. The potential contribution $C_{V,p}$ to the isochoric heat capacity is obtained directly from the difference between the heat capacity of a real gas and the heat capacity of the ideal polyatomic gas at the corresponding temperature.

4. Initialization and equilibration

The MD simulations in this work are all carried out in a constant NVE ensemble with $N = 1024$. This number was chosen since no systematic dependence on the system size was found for the calculated thermophysical property when the number of molecules is greater than 1024. The pressure and temperature of the system each fluctuates around a desired value during the simulations. In order to be able to compare the calculated results with experimental data at the given temperature and pressure, the corresponding volume and energy of the constant NVE ensemble must be evaluated at the desired temperature and pressure. The two values are obtained by an equilibration process described in this section. To save the simulation time for the equilibration process, the configuration of molecules and the distribution of energies should all be initialized at the desired temperature and pressure so that they can relax quickly to the appropriate distributions.

4.1. Initialization

The coordinates of the molecular center of mass are initialized randomly inside the cubic simulation box and its volume can be initialized by the ideal gas law. The minimum distance between any two molecules is controlled to be greater than 6 Å to avoid unrealistic large potentials and forces. The molecular orientations are initialized as random vectors uniform in solid angle.

The distributions of translational, rotational and vibrational energies all fulfil the Boltzmann distribution at the given temperature. The translational velocities are initialized directly by the Maxwell–Boltzmann distribution. Theoretically, the rotational and vibrational energies are both quantized. The rotational energy levels of a CO₂ molecule which is modelled as a rigid rotor are determined by the following equation:

$$E_{rot}[J] = J(J+1) \frac{\hbar^2}{2I} \quad \text{with } J = 0, 1, 2, \dots, \infty \quad (12)$$

where the degeneracy of level J equals $2J+1$. The rotational energy level of each molecule in the system can be initialized by the Metropolis MC method [27]. Initially, we set all molecules on the ground rotational energy state, i.e. $J=0$. Then, a trial transition from the current energy level o to the new level n is carried out. The probability of accepting such a trial transition is $acc(o \rightarrow n)$ which can be determined by

$$acc(o \rightarrow n) = 0.5 \cdot \min \left(1, \frac{g(n)}{g(o)} \exp \left\{ -\frac{E_{rot}[n] - E_{rot}[o]}{k_B T} \right\} \right), \quad (13)$$

where $n = o \pm 1$ and $n \geq 0$. In Equation (13), $g(n)$ and $g(o)$ are, respectively, the degeneracy of level n and level o , and $E_{rot}[n]$ and $E_{rot}[o]$ are, respectively, the rotational energy on level n and level o . After several thousand trial transitions, the average rotational energy per molecule starts to fluctuate around a constant value. The fluctuating rotational energies correspond to different distributions of rotational energies in the molecule. Any one of these distributions can be used to initialize the rotational energy distribution at the given temperature. After the rotational energy is initialized, the energy is allowed to change continuously in the simulation since the rotational quantum effects can be neglected. Hence, the rotational velocity is also allowed to change continuously. The magnitude of rotational velocity, \bar{u} , is determined by

$$E_{rot} = \frac{1}{2} I \bar{u}^2 \quad (14)$$

where the directions of \bar{u} are chosen randomly in the plane perpendicular to the molecular axis.

The vibrational energy levels of a CO₂ molecule which is modelled as a combination of four independent harmonic oscillators are determined by

$$E_{vib} = \sum_{j=1}^4 \left(n_j + \frac{1}{2} \right) E_{vj}, \quad (15)$$

where n_j is the vibrational energy level of the j th vibrational mode. A similar Metropolis MC method as described above can be employed to initialize vibrational energy of each molecule at the given temperature. Since the vibrational quantum effects cannot be neglected, it is not appropriate to initialize the vibrational velocities of the molecules. In practice, the vibrational energies do not change during the simulation once they are initialized.

4.2. Equilibration

In the equilibration process, the volume and total energy of the system should be relaxed to values that

correspond to the desired temperature and pressure. Once these two values are found, they are used as preset values in the constant NVE ensemble. Therefore, the equilibration procedure is needed before starting the calculations of thermophysical properties.

To equilibrate the system to the desired temperature and pressure, the system is coupled to a constant temperature and pressure bath using the approach proposed by Berendsen *et al.* [28]. At each time step, the translational velocities are scaled by a factor

$$\lambda = \left[1 + \frac{\Delta t}{\tau_T} \left(\frac{T_0}{T} - 1 \right) \right]^{\frac{1}{2}}, \quad (16)$$

where T_0 is the desired temperature, T is the current translational temperature, Δt is the time step and τ_T is a preset time constant. The scale factor can force both the translational and rotational kinetic temperatures to the desired temperature since the energy exchanges between the translational and rotational motions are fast. Meanwhile, the molecular centre-of-mass coordinates are scaled by a factor of μ , and the volume of the simulation box is scaled by a factor of μ^3 , where

$$\mu = \left[1 + \frac{\Delta t}{\tau_p} \left(\frac{P}{P_0} - 1 \right) \right]^{\frac{1}{3}}, \quad (17)$$

where P_0 is the desired pressure, P is the instantaneous pressure, and τ_p is a time constant. The long range correction to the pressure [22] is calculated by orientational averaging of the virial beyond the cut-off radius. It is found in the simulation that $\tau_T \approx 25$ ps and $\tau_p \approx 10$ ps are appropriate for CO₂ gas studied in this work. Thanks to all these methods we used in the initialization and equilibration, the system can be well equilibrated within 500 ps. An example of the equilibration process of CO₂ gas at 300 K and 30 atm is shown in Figure 2(a) and 2(b). From Figure 2 we can see after the temperature and pressure are relaxed to the desired values, the total internal energy E and the volume V of the system both fluctuate around a constant value. After the system reaches the equilibrium, the equilibration process runs for 2 ns more to determine the desired energy and volume from the average of those fluctuating values. The desired V can be used to calculate the density of the gas at the corresponding temperature and pressure.

The calculated densities together with experimental data and the gas densities predicted by using the second virial coefficient of CO₂ are shown in Figure 3. The deviations of the calculated densities from experimental values are negligibly small except at the highest pressure of our calculation. The maximum deviation,

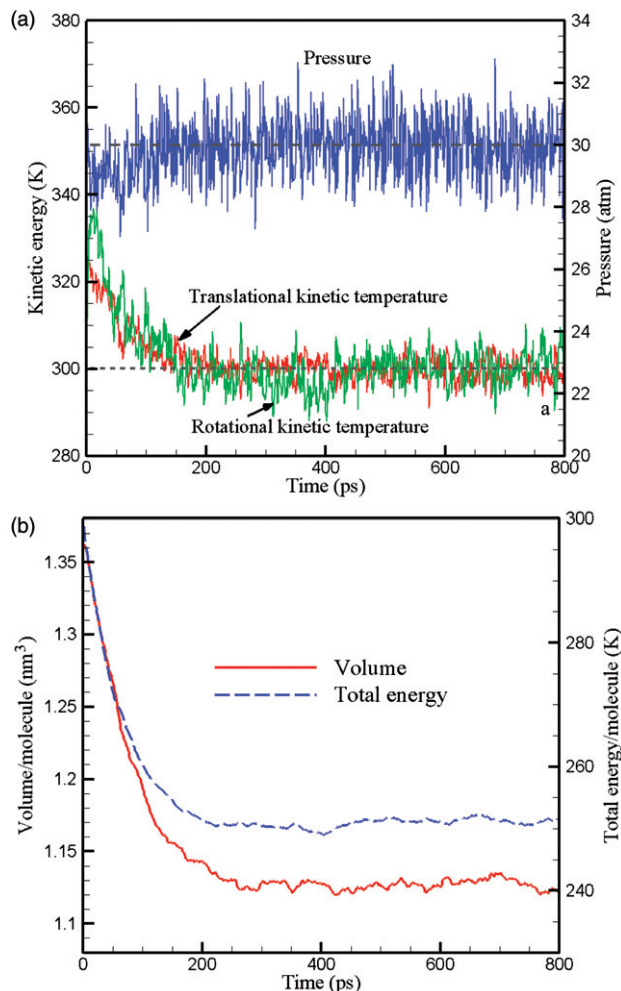


Figure 2. Equilibration process of CO₂ gas at 300 K and 30 atm: (a) temperature and pressure vs time; and (b) volume and total energy vs time.

4.4%, is found at 300 K, 50 atm and density of about 135 kg/m³ (3 mol/L). From Figure 3 we can see the second virial coefficient becomes inadequate to accurately predict gas density when the CO₂ density is higher than 70 kg/m³. In the moderate high density region, the third virial coefficient contribution becomes non-negligible. The pair-additive potential employed in this work can partially account for the third virial coefficient because the third virial coefficient depends on both the pair interactions and non-additive three-body interactions. Therefore, our MD simulation based on the BUK potential predicts much better results than those predicted by using the second virial coefficient, but the deviation still exists due to the neglect of the three-body contributions to the intermolecular potential. At higher densities, the deviations are supposed to be even greater and the results will

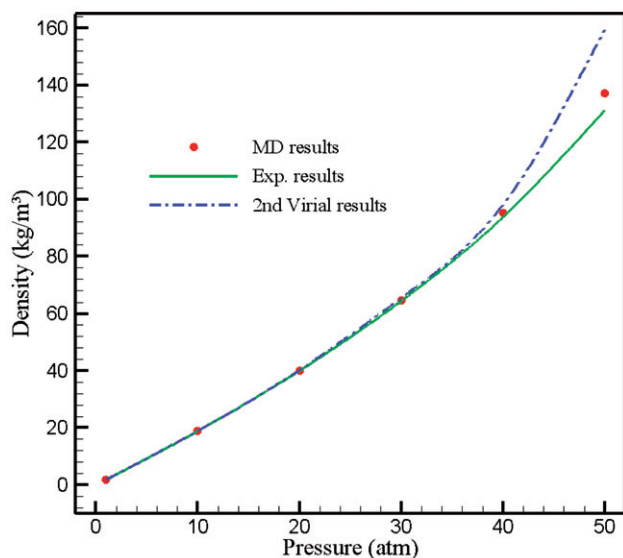


Figure 3. CO₂ gas density vs pressure at 300 K. The BUK potential predicts the second virial coefficient to be $-121.3 \text{ cm}^3/\text{mol}$ at 300 K. The value is used to calculate the density from the second virial correction.

be unacceptable. This is a systematic error of applying the BUK potential to high density CO₂ fluids and hence cannot be improved by simulation techniques. Therefore, 135 kg/m^3 or 3 mol/L is about the upper limit of the CO₂ density above which the thermo-physical properties cannot be reliably predicted from the potential for the CO₂ dimer.

5. Simulation details and the results

The shear viscosity, thermal conductivity, and heat capacity of CO₂ gas at different pressures are all produced from the equilibrium MD simulations. The equations of molecular translational motions are integrated by the Verlet leap-frog algorithm. For linear molecules like CO₂, the Singer leap-frog algorithm [29] can be applied to integrate the equations of molecular rotational motions. Compared to the standard implicit quaternion algorithm [22], the Singer algorithm preserves the linear rigid molecular structure and improves the energy conservation so that a considerably large step size can be employed in the simulations to save total computational cost.

Since the molecular vibrational energies are frozen in each MD simulation, the variations of molecular vibrational energies are considered separately. Using the MC method described in the last section, 2000 distributions of vibrational energies are used to initialize the vibrational energies of the molecules in the system. Hence, each MD simulation actually

started with 2000 different initial vibrational energy distributions but with the same initial configuration and initial translational and rotational velocities. In the calculation of thermal conductivities, the corresponding time autocorrelation functions of the energy current calculated from different initial states are averaged to determine the final time autocorrelation function at the given temperature and pressure. The time step size used in the simulation are chosen so that the total energy of the system is always kept constant within 1 part in 10^4 . Thanks to the modified BUK intermolecular potential and the Singer leap-frog algorithm which improve the numerical stability, a step size up to 12.5 fs can be used for the CO₂ gas at 1 atm and 300 K. The step sizes for higher pressures in this work are all set as 8.5 fs to ensure the energy conservation.

The shear viscosity and thermal conductivity are both transport properties which have long correlation times in the gas phase. Accurate determinations of the ensemble averages in Equations (4) and (6) require extremely long simulations whose length would be more than 10^4 times of the correlation time [30]. The calculated time correlation functions of the off-diagonal elements of the pressure tensor and energy current are shown in Figure 4(a) and 4(b) for pressures at 10 atm, 20 atm and 50 atm. It is seen from these figures that the correlation time of the energy current are a little larger than that of the pressure tensors and both correlation times decrease with pressure. Hence, the total simulation lengths required for the calculations of shear viscosity and thermal conductivity decrease with pressure from $7 \mu\text{s}$ at 1 atm to 200 ns at 50 atm. The computational cost for such long simulation lengths is very high because of the complex expression of the BUK potential used in this model. Hence, at each pressure, the long simulations are divided into 100 shorter parallel runs which are independently initialized and equilibrated at the given temperature and pressure. The final results are obtained by averaging the results calculated from shorter parallel runs. The statistical errors are obtained from the mean-square deviation of the correlation functions. The time integrals of the calculated autocorrelation functions are the shear viscosities and thermal conductivities at the corresponding temperature and pressures. Compared to the above two transport properties, the heat capacity is a static property and hence easier to be calculated. The heat capacities at different pressures are obtained directly from the fluctuations of potential energies as shown in Equation (10). The calculated isochoric heat capacities, shear viscosities, and thermal conductivities,

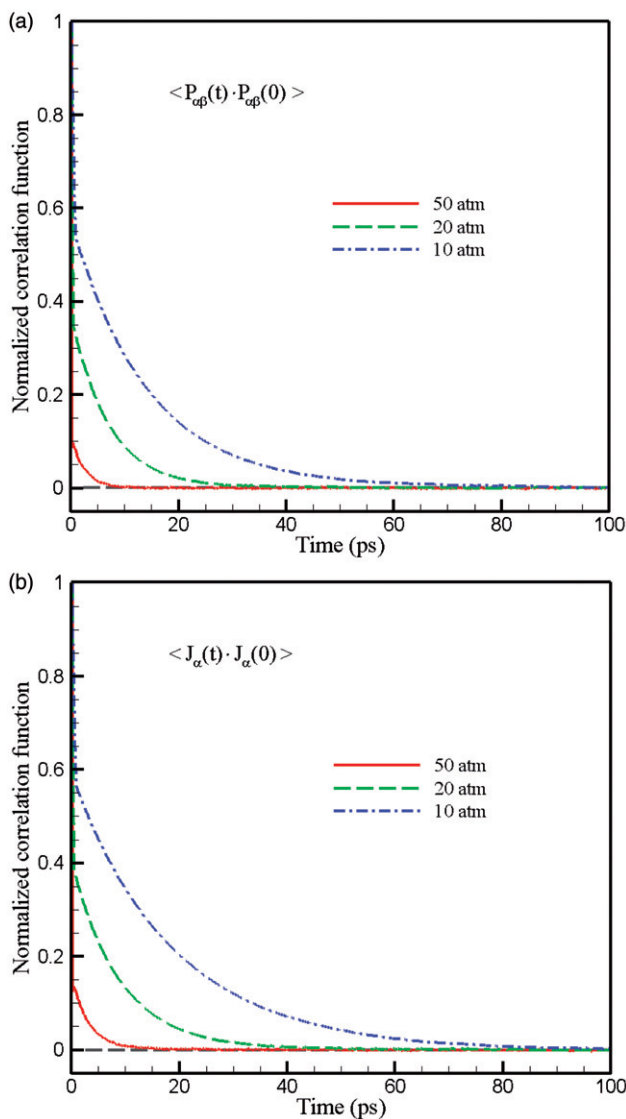


Figure 4. Normalized autocorrelation functions of (a) off-diagonal elements of pressure tensors and (b) energy current at 10 atm, 20 atm and 50 atm and 300 K.

together with the experimental data [31,32] are shown in Figures 5 to 7.

Similar to the calculated densities, the deviations between the calculated heat capacity and experimental data are negligible (within 1%) except at the highest pressure as shown in Figure 5(a). The largest deviation of about 4.7% is found at 50 atm. Since the BUK potential does not take into account the three-body contribution, the deviation will be even larger at higher pressures if we still employ the same potential in the calculation. In order to improve the accuracy of the calculated heat capacities at higher densities, the parameters in the original *ab initio* potential need to be

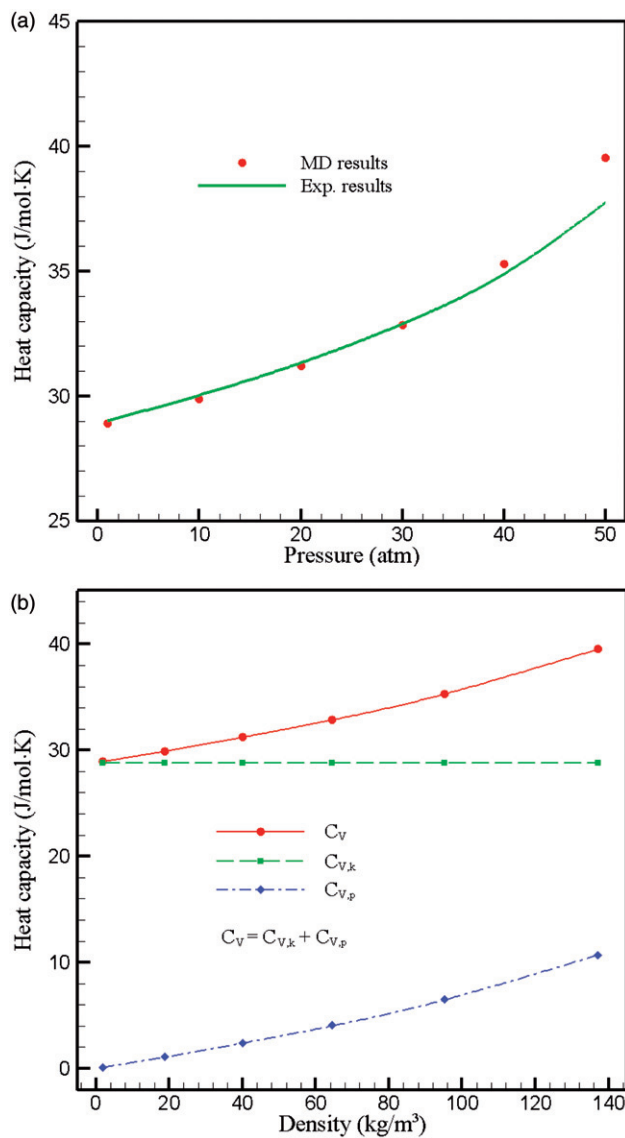


Figure 5. (a) Isochoric heat capacity vs pressure at 300 K. (b) Kinetic and potential contributions to the heat capacity as a function of density.

adjusted to include the average three-body effects. So far, a very accurate *ab initio* calculation of an intermolecular potential which includes the three-body effects is unavailable. Hence, the potential model must be optimized to the available experimental data to get better calculation results of thermophysical properties of dense fluids. From Figure 5(b) we can see the increase of the heat capacity at constant temperature is purely attributed to the increase of the potential contribution to the heat capacity. Although the highest density in our calculation is still far less than the critical density of the CO_2 , the weight of the potential

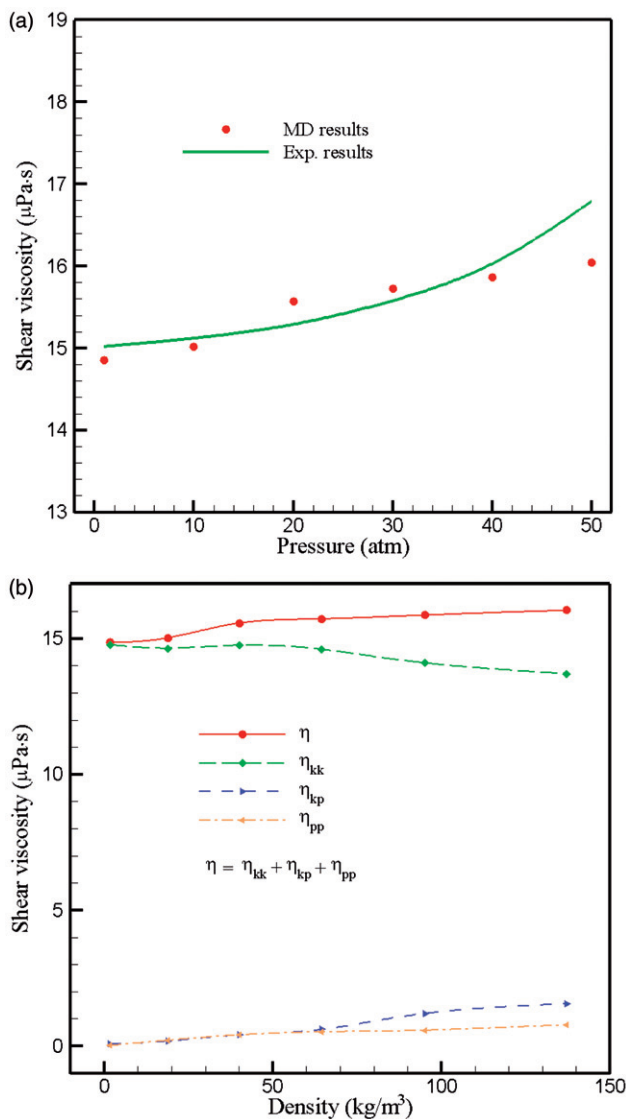


Figure 6. (a) Shear viscosity vs pressure at 300 K. (b) Viscosity contributions η_{kk} , η_{kp} and η_{pp} as a function of the gas density. The statistical error is within 1.6%. The uncertainty of the experimental data is 0.9%.

contribution $C_{V,p}$ in the heat capacity has reached 25% which shows a significant contribution.

The dependence of the calculated shear viscosity on the pressure shown in Figure 6(a) seems a little irregular. This is because the statistical uncertainty of the calculated viscosity is about 1.6%, whereas the maximal increment of the calculated viscosity between any two adjacent pressures in the calculation is only 3.7%. Hence, we can only see the viscosity generally increases with pressure, but the clear dependence is blurred by the statistical uncertainty. Nevertheless, the calculated viscosities have generally a very good agreement with the experimental data. The deviations

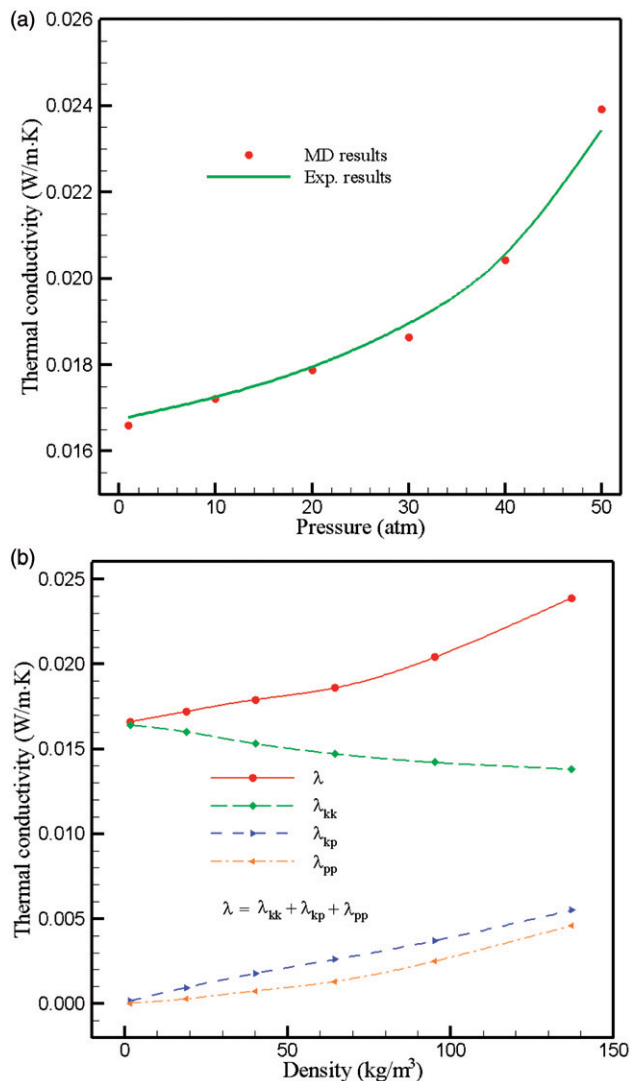


Figure 7. (a) Thermal conductivity vs pressure at 300 K. (b) Thermal conductivity contributions $\lambda_{T,kk}$, $\lambda_{T,kp}$ and $\lambda_{T,pp}$ as a function of the gas density. The statistical error is within 1.2%. The uncertainty of the experimental data is 2%.

are within 1.8% except at 50 atm. At the highest pressure, the deviation is about 4.5% which is mainly caused by the neglect of three-body contribution to the potential. Compare to heat capacity, the shear viscosity as well as thermal conductivity cannot be divided into pure kinetic and potential contributions. There also exist kinetic-potential cross contributions to these two properties as discussed in Section 3. Figure 6(b) depicts the density dependence of the three viscosity contributions. In the density range of our calculation, the kinetic-kinetic contribution η_{kk} decreases with density, while the kinetic-potential contribution η_{kp} and potential-potential contribution η_{pp} both increase with density. The kinetic-potential contribution is

generally a little larger than the potential–potential contribution. The above observation agrees with the density dependence of the viscosity contributions of a LJ model fluid at the subcritical gaseous states calculated by Meier *et al.* [23]. The viscosity calculated in this work is dominated by the kinetic–kinetic viscosity contribution. The kinetic–potential contribution and the potential–potential contribution only account for, respectively, 10% and 5% at the highest density of the calculation.

As shown by Figure 7(a), the calculated thermal conductivity agrees very well with the experimental data. Similar to the other three thermophysical properties, the maximal deviation of 2% is found at the highest pressure. The density dependence of the three thermal conductivity contributions depicted in Figure 7(b) is similar to that of the three viscosity contributions. The difference is the kinetic–potential $\lambda_{T,kp}$ and the potential–potential $\lambda_{T,pp}$ contributions to the thermal conductivity are more significant. At the highest density, $\lambda_{T,kp}$ and $\lambda_{T,pp}$ account for, respectively, 23% and 19% of the thermal conductivity. The statistical uncertainty of the calculated thermal conductivity is estimated to be within 1.2%. The contribution of the vibrational energy term to the total thermal conductivity can be easily examined by calculating the difference between the thermal conductivity which includes the vibrational energy term and the one which sets the vibrational energy to zero. The weights of the vibrational energy contribution in the total thermal conductivity at 1 atm, 10 atm, 20 atm, 30 atm, 40 atm and 50 atm were calculated, and they are, respectively, 22.6%, 21.6%, 20.6%, 19.5%, 17.8% and 15.0%. Hence, there is a significant contribution from the vibrational energy term to the thermal conductivity for dense CO₂ gas even around room temperature.

6. Conclusions

In this work, the density, isochoric heat capacity, shear viscosity, and thermal conductivity of CO₂ gas in the pressure range of 1–50 atm and 300 K are calculated directly from computer simulations without using any experimental data. The potential contributions to the thermophysical properties are studied at every simulated state point, and their characteristic dependence on density is described. The MC method is employed in the model to include the quantum effects of the vibrational motions. For the intramolecular dynamics of CO₂ molecules, the assumptions of rigid-rotor for rotational motion and of quantum harmonic oscillator for vibrational motion are both validated by good agreements between the calculated thermophysical properties and experimental data. For the

intermolecular interactions, accurate thermophysical properties can be predicted by a pair-additive potential which is obtained from an *ab initio* calculation of the intermolecular potential of a CO₂ dimer if the CO₂ density is less than 135 kg/m³ or 3 mol/L. For the calculations of thermophysical properties at higher densities, the *ab initio* intermolecular potential of a CO₂ dimer becomes inaccurate and the three-body contribution to the intermolecular potential must be taken into account. So far, the three-body contribution cannot be accurately obtained without experimental data. Therefore, 135 kg/m³ is the upper limit of the CO₂ density in which the thermophysical properties can be accurately calculated from molecular simulation without using any experimental data.

CO₂ is a small molecule. The frozen vibrational energy assumption for CO₂ molecule is valid at temperatures up to 1000 K [16] since all the vibrational modes of CO₂ have a high energy gap between two neighbouring vibrational energy levels. For larger molecules, however, there might exist torsional motions which are typically at lower frequencies than bond vibrations. In this case, it might be necessary to treat some vibrational modes in a classical way and the rest of them by a quantum mechanical way as described in this work. In all cases, a quantum mechanical treatment of some vibrational modes must be performed; otherwise a significant underestimate of the thermal conductivity of a polyatomic fluid would be found in the calculation. As the vibrational energy for a given molecule is independent of time during the simulation when a quantum treatment of vibrational energy is carried out, its contribution to the thermal conductivity might be reducible to a simpler, perhaps analytic form.

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