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Feasible Molecular Dynamics Simulation and Consistency of Critical Carbon Dioxide Thermophysical Properties

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ABSTRACT: A method of approaching goal values is proposed for the simulation parameter determination. An economic-scale particle system is built for critical carbon dioxide (CO_2) system simulations. The approaching method is applied to a critical CO_2 system by trial simulation. With the simulation converging to experimental values, the obtained parameter settings help simulation to make practical sense. The measured values of thermal conductivity and viscosity are taken as approaching goal values. A molecular dynamics simulation of these two thermophysical properties is performed. The parameter settings are obtained after approaching the simulation for thermal conductivity and viscosity. As a verification, diffusion of critical CO_2 is simulated by the obtained settings. Parameters obtained from the approaching method give rise to diffusion simulation results with experimental agreement. The achieved parameters can directly be used to simulate thermophysical properties of the critical CO_2 system, providing reference settings for the simulation of the critical CO_2 system. The superiority of critical CO_2 in thermal and physical aspects is theoretically confirmed.
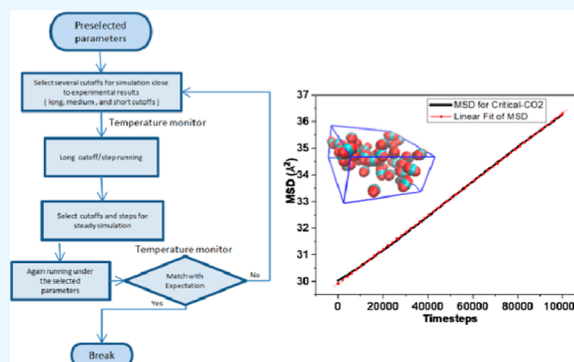
1. INTRODUCTION

Supercritical fluid is fluid in a special state with phase characteristics of liquid and gas. Molecular dynamics simulation is an optimal option to describe such a special system. Generally, supercritical states are under relatively high temperature and pressure conditions, compared with normal states. High temperature and pressure are normally dangerous. A high-temperature and -pressure probe or test is an advanced technology with sophisticated requirements, especially for the microsystem. Molecular dynamics simulation is able to give the theoretical evaluation of the microsystems under serious or special situations.[1−3] As for simulation running parameters, there are generally two situations faced in the process of molecular dynamics simulation. According to different research methods and performance sequences, these two considered situations are illustrated as follows.[4] The first situation is pure theoretical simulation before experimental results are known or regardless of experimental results. In this situation, the selection of parameters is open for the simulation results with some degree of openness. Simulation results are usually not unique in this situation. Often combined with theoretical analysis methods and specific physical scenarios, it can give the optimal or most likely possible results. The second situation is that related experimental work was carried out. Some experimental data have been obtained. Even some conclusive data have been determined after being processed. In this situation, the simulation calculation has a clear direction. Hence, the selection of setting parameters is available only within further restrictive

requirements. Selection in this situation is often the so-called semiexperience method. In this situation, unifying the results of theoretical simulation and experiment is a challenge in simulation. How to obtain effective simulation parameters, making the simulation results consistent with experimental results as much as possible, is related to the simulation reasonability. The investigation in this work belongs to the second situation in which the result has been experimentally determined. The effective parameters for simulation calculations are determined through the consistency requirements between theoretical calculation and experimental results.

Normally, the experimental result is obtained by the statistical result of multiple measurements. The result of the experimental measurement is a value with uncertainty, which is recorded by a mean value with error. In general theoretical simulations, the selection of parameters usually has a permitted range, in addition to satisfying some theoretical requirements. As for the molecular dynamics simulation, parameter selection for theoretical simulation is one of the practical problems faced in the simulation process. Moreover, researchers always try to make
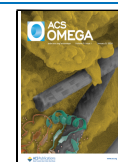
the simulation results close to the ideal real value. Meanwhile, the economics of computer calculation are necessarily considered in simulations to save computing resources. Furthermore, the stability of the results must be considered from the aspect of the simulation itself. The stability of results is related to the problem of computational convergence factually.[5,6] With the development of simulation to the present, although there is literature on the realization of long-time simulation in the order of milliseconds,[7] the saving and rational use of computing resources is still important in the simulation process. From a theoretical aspect, if the design model is reasonable enough, the results of molecular dynamics simulation will converge to the real value in infinite time. However, considering the actual situation, it is not that the longer the time takes for the simulation calculation, the better the result is for simulations. From the consideration of appropriateness, effectiveness, stability, and economy, molecular dynamics simulation should be set appropriately. Nevertheless, there is no unified method for the setting of a simulation system, especially on different aspects of simulation. In practical manipulation, the parameters should be set according to the actual simulation situation, experiences, or references of similar simulation systems with close scale, size, scenario, etc.

In order to overcome various practical problems in simulation, many methods for simulation settings are used in the literature, such as the variable cutoff radius algorithm in molecular dynamics simulation,[8] the method of improving step length,[5,6] and the extension of simulation time.[7] For the simulation of the carbon dioxide (CO_2) system, completely consistent parameters have not been used in the literature. There is also no uniform method to obtain simulation operating parameters. The often-used method is multiple trial simulation. In this work, an economic scale particle system is built for reliable equilibrium molecular dynamics simulations of transport properties of fluids. A general program procedure approaching a goal value to determine simulation running parameters is provided. This procedure provides directional guidance for setting simulation parameters.

Medium thermal and mass transfer properties are important factors affecting the reaction in media.[9,10] Therefore, there is a lot of discussion on the property of thermal and mass transfer for reaction media in engineering fields.[11,12] In the case of CO_2 or critical CO_2 simulation, there are simulations of thermal conductivity, viscosity, and diffusion properties of CO_2.[4,13,14] In the simulation process, molecular model parameters are usually evaluated by comparing the simulation of thermodynamic properties with experimental values.[15] However, in specific simulation processes of other physical properties, some running parameters that need to be set during the simulation, including cutoff, step size, step number, etc. are also involved. Only when these settings are properly matched, the simulation calculation achieves optimal computer operation and satisfactory simulation results.

As is well-known, reasonable and complete settings make simulation results get to an ideal value. Even the simulated result is more accurate and reliable than the experimental measurement due to the measurement errors. Regardless of errors, the experimental value is directly taken as the approaching goal value. The approach procedure for determining consistent simulation parameters is performed. In terms of the approaching method, continuous adjustments of the set parameters, for the CO_2 system in the *NVT* ensemble, make trial simulation approach experimental results during the trial simulation course.

Meanwhile, the approaching process realizes the calibration function of the simulation calculation. The whole adjustment process answers how to set the cutoff, step length, the number of running steps, etc. for the corresponding scale system. The molecular system size matches the scale of the microsystem and the related research scale.[11,16] This approaching course achieves the most economical simulation parameters for consistent results of the actual system due to the timely termination of the open degree of parameters in the approaching course. In this work, the proposed approach method is applied to the critical CO_2 system as concrete simulation running cases for the investigation of thermophysical properties of critical CO_2.

2. SIMULATION MODEL AND CALCULATION DETAILS

2.1. CO_2 Molecular System. The Lennard-Jones force field used in the simulation ref [17] gives the CO_2 EPM2 model parameters. Comparing the density−temperature curve predicted by the parameters of this model with the experimentally measured curve near the critical point, we determined the model described by these parameters, which can accurately determine the critical point and fits well. The literature discusses two cases. The first case is the complete processing of the molecule into a rigid body. The second case considers the contribution of the bond angle potential energy, with the molecular bond length fixed but the bond angle dimension opened. For the second case of opening bond angle, the simulation results show good agreement between experiment and theory. Among different force fields, EPM2 is fast to get steady and suitable to the pure CO_2 system.[12] Most of the EPM2 parameters are used in this work. Thermal conductivity and viscosity of critical CO_2 were obtained through simulation calculation and then compared with the experimental measurement results. Simulation operating parameters are adjusted according to the coincidence of the theoretical calculation value. In order to expand the search scope of parameters and further open the dimensions of the CO_2 molecular bond, the equilibrium length $l_{c−o}$ of the bond is selected as the fixed length 1.149 Å of EPM2 in the literature. The bond energy is selected as the widely accepted value of 799 kJ·mol^{-1}.[18] The potential energy constant k_l takes the quadratic average of the bond energy over the equilibrium length, which is about 144.675 kcal·mol^{-1}·Å^{-2}. Charge q_c of the carbon atom is still +0.6512e. Charge q_o of the oxygen atoms is equalization of the charge number for the carbon atom, with a value of −0.3256e. So the molecule is electrically neutral. Parameters $\varepsilon_{c−o}$, $\varepsilon_{o−o}$, and $\varepsilon_{c−c}$ take values of 28.129, 80.507, and 47.588 K, respectively. The values of $\sigma_{c−c}$, $\sigma_{o−o}$, and $\sigma_{c−o}$, are, respectively, 2.757, 3.033, and 2.892 Å. The equilibrium angle θ_0 is 180°. k_θ is set to 1236 kJ·mol^{-1}·rad^{-2}.[17]

Molecular system simulation is carried out in the *NVT* ensemble. The temperature of the CO_2 system is set at 304.107 K. Simulation system density is 0.468 g·cm^{-3}. The simulation region is at a critical state, as adopted in numerous pieces of literature.[17] In this way, the parameter usage is inherited. To match the set conditions, the number of molecules in the simulation system includes 45 CO_2 molecules. The initial configuration is obtained by generating molecules in a random position. The size of the simulation box is taken as 24 × 24 × 12 Å. The simulation calculation is performed with the help of a large-scale atomic/molecular parallel computing simulator.[19]

2.2. Approach Procedure for Simulation Parameters. In order to make the simulation result and experiment value reference match well as much as possible, the simulation process is performed within the range of possible parameters. During the

trial simulation for matching results, running simulation parameters of the molecular system will be selected. The trial sequence is an arbitrary permutation of the adjusted parameters, cutoff, step length, and step number. The performed results obey the approach principle. This work adopts the method of trial cutoff first, and then the number of steps and step length are determined. In order to save computing resources, a shorter equilibrium step number is used to meet the equilibrium requirements in the trial running process. In the final simulation process, the step number can be increased appropriately to improve the stability of the simulation calculation results. It depends on the concrete situation of the simulation. In the trial running seeking process, a specific procedure is divided into the following substeps.

Step 1: Initial trial simulation. Select a series of cutoff and step length values. Perform the initial running for equilibrium with a few steps. Then, the physical property curve of the simulation is obtained. Select the parameter interval from trial simulations, for which the theoretical simulation results and experiment values are consistent as much as possible. The deviation degree of the simulation numerical result deviated from the experimental measurement is roughly judged in terms of the following definition

$$\text{deviation} = \frac{\Delta}{\exp . \text{ Value}} = \frac{|V_{cal} - V_{exp}|}{V_{exp}} \quad (1)$$

Approaching evaluation is in terms of deviation Δ between theoretical simulation and experiment. Parameters corresponding to small deviations are picked out as the preselected parameters. If the primary searching scope does not cover the full range but all the deviations are relatively large, the selection range will be further extended until the deviation reaches an acceptable level. In this step, several cutoffs are often picked out, of which the results are close to the experimental results. The corresponding parameters are taken as temporary candidate parameters. The simulation details of preliminary running under preset values are supplied in part 1 of the Supporting Information.

Step 2: Stability monitor for preset value running. Adjust the number of running steps from small to large step number for the trial run. During trial running, we learn about the convergence of the calculation results under prolonged steps. Meanwhile, the stability of results should be monitored. The calculated result needs to converge to the experimental result under the stable running step number. If the result is not stable, then the preset parameters need to be adjusted further. In this trial, the step size is adjusted. However, a stable running step number was obtained in this step. Then, the step number meeting the requirements is preliminarily determined for trial simulation. Generally, under the selected number of running steps and other preset parameters, the calculated results tend to be stable. The stability information is provided in part 2 of the Supporting Information.

Step 3: Adjustment of the preselected parameters. In order to make the simulation converge to experimental results, the step size was adjusted to run the trial simulation. Adjust the step to obtain the matched result as much as possible. Generally, the step size is smaller, and the result is closer to the real situation of the simulation system. Meanwhile, it is necessary to meet the requirements of the simulation system for step length. To confirm the possible step length, several step length values are selected in a certain step length interval for trial running. According to the results of the trial simulation, some appropriate

adjustment is carried out. Experimental results will fall in a certain interval or close to a certain side. This matching characteristic between simulation and experiment provides a direction for the adjustment of the step length. The step length is finely tuned in the interval where the experimental result falls. Then, the increment of step length is reduced again for the trial approach. The step length, giving rise to close simulation results of the experiment, is selected as the new candidate parameter. Parts 3 and 4 of the Supporting Information present details on the adjustment and refinements.

Step 4: Stability estimation. Due to the adjustment of preset values, the stability of the simulation system running needs to be evaluated again. Simulation calculation runs under different steps and the predetermined parameters in previous steps to observe the stability of the calculated results. The stability of the resulting solution often is significantly improved compared to the initial settings. If there is an increased requirement on step number for stable running, it means that convergence moves in the direction of multiple steps. A suitable step number must be reselected from larger step numbers. A large step number gives rise to better stability. Nevertheless, considering economic principles, the step number should not be too large. Therefore, the number of running steps should not only stabilize the simulation results but also be moderate to reduce the consumption of computing resources. Part 5 of the Supporting Information describes the stability information after adjustments.

Step 5: Repeat or break. Repeat previous steps under the newly selected number of stable running steps until the deviation and stability of parameters meet the requirements. However, if the consistency between simulation and experiment is satisfied well, under steady convergence running, the procedure will break. In practical course, some cases may not be convergent to experimental reference values, but the molecular system is already convergent to steady values. Namely, there is a large difference between theoretical simulation and practical situations. Then a rescale, relative value, or direct result is taken as the discussion reference. In this case, the procedure will also break. The last trial running parameters are optimal for the consistency of this simulation system. A general performing procedure is presented in the program block diagram of Figure 1. During this course, the system temperature should be monitored from time to time. At least, for the initial simulation and the final simulation, the system temperature monitor needs to be applied to ensure that the simulation system runs under the set temperature conditions. The temperature monitor for this work is shown in Figures S2 and S8 of the Supporting Information. The simulation system temperature is around the set value.

For the economic CO_2 system, one-round trial running already gives rise to the desired deviation and stability. So from step 4 to step 5, the procedure will break. The execution process of the CO_2 system dynamic simulation for seeking parameters is provided in the Supporting Information. Running parameters for approaching the adjustment course are listed in Table S1. Dynamic adjustment of running settings can be known from the change in different steps.

3. RESULTS AND DISCUSSION

Simulation results demonstrate the consistency of molecular dynamics simulation. After the last trial simulation, the simulation result under the desired approaching effect is listed in Table 1. Meanwhile, the experimental data and the calculated

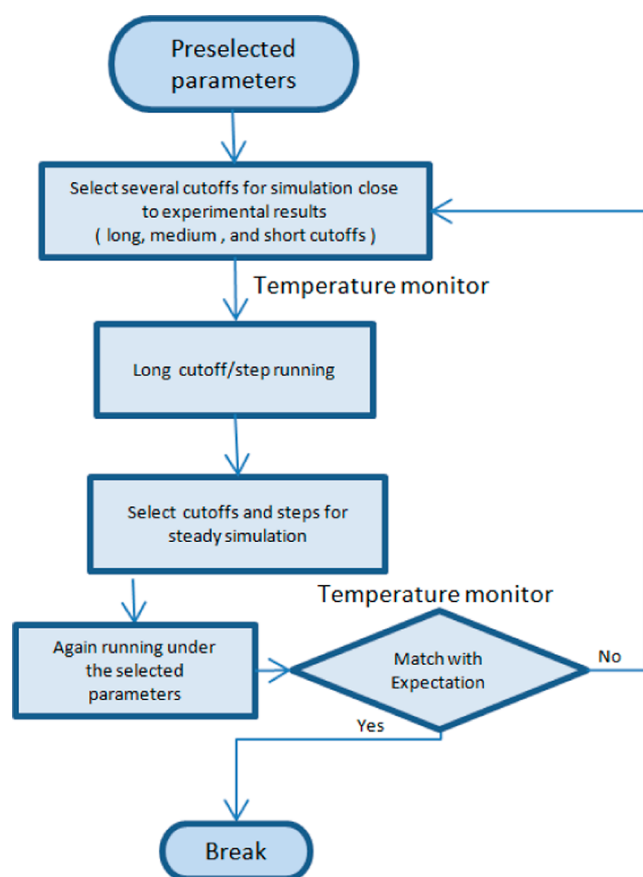**Figure 1.** Basic program idea of the approaching progress.

Table 1. Experimental Thermal Conductivity and Viscosity and Calculated Values

	thermal conductivity (mW m^{-1} K^{-1})	viscosity (μPa s)
exp	~81.67[20]	~46.91[20]/35.54[22]
cal	83.28~82.33	38.06~40.56

values for thermal conductivity and viscosity are listed in Table 1 together as a comparison. The calculated results in Table 1 indicate that the simulation approaches the thermal physical parameters, thermal conductivity and viscosity, obtained by experiments.[20] The measurements of viscosity were performed with an oscillating-disk viscometer with a proven record of accuracy. Transient hot-wire measurements are used to obtain the zero-density thermal conductivity of CO_2.[20−22] Then viscosity and thermal conductivity are obtained by the representative equations.[20] Simulation calculations show agreement with experimental data with a difference that can be accepted.

In order to verify the actual effectiveness of simulation parameters obtained by approach trial simulation, the obtained parameters are used to perform a simulation of another important property of the CO_2 system: the diffusion coefficient. In this case, the simulation result is compared with the simulation and experimental measurement results in the literature. Diffusion simulation mainly uses the Einstein relationship. The calculation result of the diffusivity can be calculated based on the mean square displacement of the molecular system. The specific relationship is as follows

$$D = \lim_{t \to \infty} \frac{1}{2dNt} \left\langle \sum_{j=1}^{N} [\mathbf{r}_j(t) - \mathbf{r}_j(0)]^2 \right\rangle \tag{2}$$

The diffusion coefficient also can be given according to the Green−Kubo relationship. The Einstein relationship is used more often in the literature. The literature generally considers that these two relations are equivalent. Some discussions on the equivalence and results of these two relationships are given in the literature.[23] In these relations, r_j is the position vector of atom j, d is the dimension, and v_j is the velocity vector of the j-th atom. However, due to simplicity and ease of operation, Einstein's relation is usually used more often. The calculation relationship of the diffusion coefficient can be simplified as

$$D = \lim_{t \to \infty} \frac{1}{2dt} \mathrm{MSD}(t) \tag{3}$$

where MSD is the mean square displacement, defined as $\mathrm{MSD}(t) = \frac{1}{N} \left\langle \sum_{j=1}^{N} [\mathbf{r}_j(t) - \mathbf{r}_j(0)]^2 \right\rangle$.

The calculated results show that the diffusion coefficient for the critical CO_2 system is well-matched with the experimental value by using the simulation parameters from the approach method in the previous section. Figure 2 presents the curve of
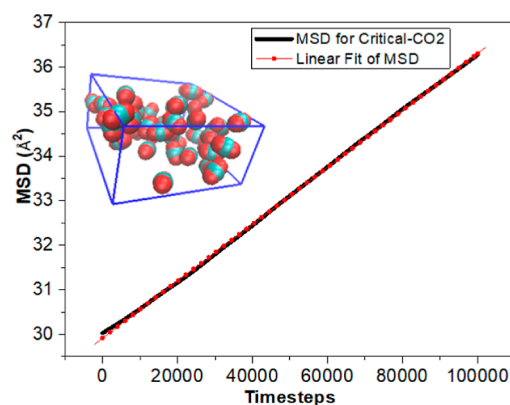

Figure 2. Mean square displacement of the critical CO_2.

the MSD time of the CO_2 molecule. The diffusion coefficient from the slope of MSD for pure CO_2 is about 3.55×10^{-8} m^2 s^{-1}. This result is close to the results of experimental test regions and consistent with previous similar simulations in magnitude order.[24−26] Therefore, the parameters are effective for the critical CO_2 simulation. Apart from the diffusion, other physical properties of the model are also applicable, and the diffusion is taken as a typical case. Density is discussed in some other related research in the form of number density.[27]

Till now, a series of simulation parameters not only meeting the requirements of simulation calculations but also utilizing few computing resources have been gradually presented in the process of approach adjustment. Large-scale molecular systems will consume large computation resources, not only computation hours but also RAM, for reading and processing the information of molecules. An economic molecular system takes up fewer computation resources. In the trial running course, some computation hours will be consumed, but the calculation of cases will not be so large based on the determination achieved from trial running. The time step 0.003 fs is shorter than 2.0 fs or the typical 1.0 fs,[1,16] as well as 0.25, 0.1, and 0.01 fs in numerous pieces of literature.[2,3,28] The simulation of one case uses 3 ps

under the determined settings, less than the typical 10 ps during the trial running for one case or 4 ns, 2.5 ns, and 500 ps in refs 2, 3, and 16. Moreover, using these parameters the results of simulation calculation and experimental measurement reach a good consistency. These obtained simulation parameter settings are used for the CO_2 system and play a role in calibration. The physical sense given by the simulation result can be compared with the actual measured value. Parameters determined by the approach help the simulation results make practical sense.

4. CONCLUSIONS

This article proposes the approach method for thermophysical property parameters by trial simulation. An economic scale of a 45-particle system is built for CO_2 molecular dynamics simulations. In terms of the idea for approaching the experimental reference value of thermal conductivity and viscosity, trial simulation parameters were scanned in a wide range. Estimating the convergence and stability of simulation calculation, economic and simplicity principle is obeyed in the trial simulation course. Molecular dynamics simulation parameters of the critical CO_2 system are obtained by continuously adjusting the preset parameters in trial simulation.

Theoretical simulation thermal conductivity and viscosity are $83.28 \sim 82.33$ mW m^{-1} K^{-1} and $38.06 \sim 40.56$ μPa s, respectively, which are close to experimental reference values. The obtained simulation parameters are used to calculate the diffusion coefficient of critical CO_2. Simulation diffusion coefficient is 3.55×10^{-8} m^2 s^{-1}. The calculation result demonstrates that the simulation parameters obtained by the approach method make the diffusion coefficient simulation match well with experiment. In the parameter determination course, the parameters of the EPM2 model are used for the molecular model. During the system running course, cutoff, step length, and step number adopt 12 Å, 0.003 fs, and 1,000,000, respectively. The system temperature is maintained near the center of the preset critical temperature 304.107 K. Based on these running parameter settings, it performs a relatively stable molecular dynamics simulation. The simulation results are in good agreement with the experimental reference values. Therefore, the simulation parameters from the approaching procedure provide a reference for the molecular dynamics simulation of the CO_2 system. The approach procedure is an effective method for the determination of simulation settings. This procedure is not limited to the CO_2 system and is also not limited to the critical system, which is generally applicable to molecular dynamics simulation. The experiment value consistency approach helps the simulation discussion make practical sense. The high thermophysical property performance of critical CO_2 in application is confirmed by theoretical simulation.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c06752.

> Execution process of simulation for seeking parameters, including preliminary running under preset values, stability of the simulation system, molecular simulation under short steps, refinement of step settings, and simulation system stability under refined parameters, for demonstrating the approaching course, temperature monitoring, and variance, and determination of running parameter settings (PDF)

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Notes

The author declares no competing financial interest.

■ ACKNOWLEDGMENTS

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