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Molecular Dynamic Simulation Study of the Diffusion of Gases in Water

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Using molecular dynamics simulation, the diffusion of 9 kinds of gases were simulated in the canonical number of atoms, volume and temperature (NVT) ensemble. The mean square displacement data were analyzed by the differentiation-interval variation method. The calculated values were compared with the experimentally obtained values found in the literature. The error between calculated diffusion coefficients and experimental values is between 14 and 37 %, which is less than 50 %. Moreover, analysis of the diffusion coefficient shows that the diffusion coefficients of the same system differ a lot when they were calculated with different samples. The diffusion coefficient of molecules in system containing maximum samples is more close to the experimental value than others. Sample has the same effect on diffusion coefficients at different temperature.

Key Words: Molecular simulation, Molecular dynamics, Gas, Diffusion coefficient.

INTRODUCTION

The diffusion coefficients of gases in water play an important role in the description of chemical processes. Methane is the simplest nonpolar molecular and has hydrophobe property[1]. The study of dynamic behaviour of methane in water is of great benefit for deep research of collapse of big molecular such as protein. In addition, the study of this system can also provide mechanism explain for hydrate phenomenon appeared during transportation of natural gas. Ammonia and carbon dioxide are common gases in carbamide hydrolase process. Their diffusion coefficients are important parameters in sorption and desorption process. Oxygen is important in super critical water oxidation (SCWO)[2], which is a new environmental friend technic for dealing with organic residue. Among this research region, the diffusion coefficient of oxygen in water is of prime important. Much works have been done to get the diffusion coefficient of various gases in water. Wise and Houghton[3] has measured neon, krypton,xenon, carbon monoxide and nitric oxide in water at 10-60 ºC by microscopicaly following the collapse of small stationary bubbles against a horizontal wall. Verhallen[4] has measured the diffusion coefficients of helium, hydrogen, oxygen and nitrogen in water at temperatures between 10 and 60 ºC by taking the permeability of a stagnant liquid layer in the quasi-steady state method.

However, those methods above are time consuming and expensive and we are still lack of experimental values. If computer simulations could present ideal structure of system and reasonable motion parameter of molecule, this can avoid expensive experiments, especially for systems at critical situation which experiment can't implement. Now, this field is mature enough to provide reliable predictions in many instances and it shows an unprecedented ability to extrapolate prediction from small to complex molecules, from low to high pressures and from low temperatures to high temperatures. As such, molecular simulation is now considered in the chemical industry as capable of filling the gap between experimental data and engineering models in various circumstances such as unknown chemicals, extreme conditions of temperature or pressure, toxic compounds, *etc.*[5].

Many researches have been directed toward studying small molecule system in the literature. An infinite dilute aqueous solution of formaldehyde has been carried out by molecular dynamics calculation[6,7]. Mean square displacement is calculated with different potentials and diffusion coefficient is evaluated from the slope of the mean square displacement according to Einstein's relationship. A diffusion of 0.6 M aqueous solution of potassium nitrate has been calculated by molecular dynamics and Monte Carlo calculation[8]. Molecular dynamics is used to calculate the pure diffusivities and Monte Carlo calculation is used to calculate the effective diffusivities. The diffusion coefficients also follow from the Einstein's relationship.

In this paper, gas's diffusion in water was determined by molecular dynamics simulations in atomistic scale. These computer simulations provide insights into the molecular mechanisms of transport which can not be obtained by conventional experiment.

SIMULATION METHODS

All simulations are carried out by DISCOVER[9] module which based on molecular mechanics (MM) method. The DISCOVER module is embedded in the Material Studio software package. All calculations are based on COMPASS[10] force field. COMPASS force field is the first force field getting from *ab initio* calculation. Non-bond interacting function and force constant among this force field are optimized by molecular dynamics simulation of crystal and liquid. Non-bonded interaction includes van der Wall interaction and electrostatic interaction. van der Wall interaction is described by Lennard-Jones-9-6 function:

$$\mathrm{EvdW} = \sum_{i,j} \varepsilon_{ij}\left[2\left(\frac{r_{ij}^{0}}{r_{ij}}\right)^{9} - 3\left(\frac{r_{ij}^{0}}{r_{ij}}\right)^{6}\right]$$

Electrostatic interaction describes the contribution of coulomb interaction among electrostatic of every atom. It is described by the following function:

$$E_{elec} = \sum_{i>j} \frac{q_i q_j}{r_{ij}}$$

Calculation of non-bonded parameter may consume much CPU time during simulation process. Usually, atom-based method is set for van der Wall interaction and Ewald method is set for electrostatic interaction. Considering that our system is mainly composed of small inorganic molecules (water and gases), group-based method are set for both van der Wall and static interaction. Results proved that taking this method can save much CPU time without affecting the precision of simulation result.

Molecular dynamics simulations are performed in the canonical number of atoms, volume and temperature (NVT) ensemble and a constant temperature of 298.15 K. Simulation systems are thermostatted by Andersen method. Initial configuration is composed of an orthorhombic cell with periodic-boundary in three directions. Initial direction of water is random. The number of configurations is set 10. Initial position of gas is taken random. Initial velocity of each molecule is taken by Maxwell distributing method and then reconfirm the velocity to ensure total quantum of system to be zero. Considering that the system is mainly composed of small molecules, Time step is taken 0.5 fs to avoid high speed circle and ensure the stability of function. Cut-off radii is set 9.5 A. Total simulation time is 40 ps and frame output every 250 steps.

CALCULATION OF DIFFUSION COEFFICIENT

Usually, the mean square displacement (MSD) curves are obtained by analyzing the particle positions recorded in molecular dynamics simulation. There are two methods for analyzing the MSD curves *i.e.*, the conventional method and the differentiation-interval variation method[11].

In the conventional method, the Einstein model is used to calculate the diffusion coefficient:

$$D_\alpha = \frac{1}{6N_\alpha} \lim \frac{d}{dt} \sum_{i=1}^{N\alpha} < [r_i(t) - r_i(0)]^2 >$$

Data averaging is performed over a large time scale. However, for MSD curves, there are always irrational molecule movements as shown in Fig. 1. The Einstein model treats these data as normal data, thus they are involved in the calculation of the final results, leading inevitably to errors in diffusion coefficient values.

In the differentiation-interval variation analysis method, a MSD curve is first divided into n segments. The diffusion coefficient of the jth segment is as follows:

$$D_j = \frac{1}{2}[\frac{y_{j+1} - y_j}{x_{j+1} - x_j} + \frac{y_j - y_{j-1}}{x_j - x_{j-1}}] \tag{1}$$

The diffusion coefficient of the entire system is the average of the above diffusion coefficients.

$$\overline{D} \equiv \frac{1}{n} \sum_{j=1}^{n} D_j \tag{2}$$

$$\sigma^2 \equiv \frac{1}{n-1}\sum_{j=1}^{n}(D_j - \overline{D})^2 \tag{3}$$

Define function Z as

$$Z \equiv \frac{\sigma^2 t_{max}^2}{b(b-a)} \tag{4}$$

The restrictive conditions are assumed to be as follows: the values of b–a/t_{max} and b/t_{max} be maximum and that of Z be minimum. Then the value of diffusion coefficient $\overline{D}$ can be achieved by changing the values of a and b, which are certain time points on the simulation line, they also represent the reasonable initial and end times on the MSD curve.

In this study, differentiation-interval variation analysis method is taken for the calculation of diffusion coefficient. Differentiation-Interval variation analysis method deal with MSD curve to get the average diffusion coefficient $\overline{D}$. This method is programmed into software by C++ language.

Calculation and analysis of the diffusion coefficient of nine gases: Nine gas-water systems are simulated by molecular dynamics method and then analyzed by differentiation-interval variation analysis method[12]. Taking oxygen-water system for example, there are 3 oxygen molecules and 765 water molecules in system. Other parameters are as same as described above. Mean square displacement curve of oxygen is as Fig. 1.

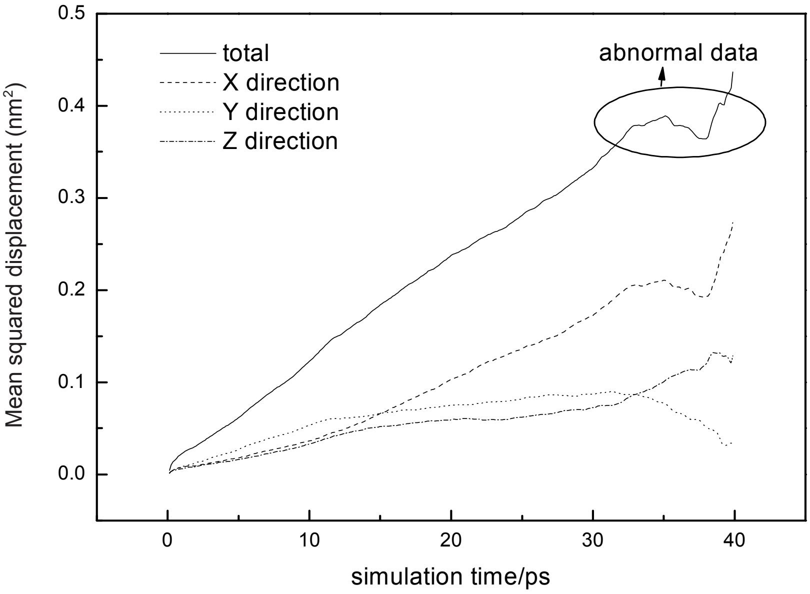

Fig. 1. Mean square displacement (MSD) curves of aqueous oxygen solution

Data in MSD curve are analyzed by differentiation-interval variation analysis method in order to get precise value of diffusion coefficient. As are described above, a and b need to be set by numerous comparison of calculations. However, when there is a good linearity in MSD curve 'a' can be set before analysis by analyzing energy_ temperature curve during simulation. For this system, it shows that energy and temperature come to stable at 0.375 ps. So the first value of 'a' is set 0.375 ps. The other values of 'a' are all above this value. One set are shown in Fig. 2. There are no obvious difference among Z when 'a' is taken different values (Fig. 2). Considering that $(b–a)/t_{max}$ are to be maximum, 'a' are taken 0.375 ps. The value of Z is min and $(b–a)/t_{max}$ is maximum. When a and b are taken 0.375 ps and 29.625 ps, respectively. is 40 ps. The value of $\overline{D}$ has been finally obtained. Other gas-water systems can be obtained using the same method. Simulation values and experimental values of several gases are shown in Table-1.

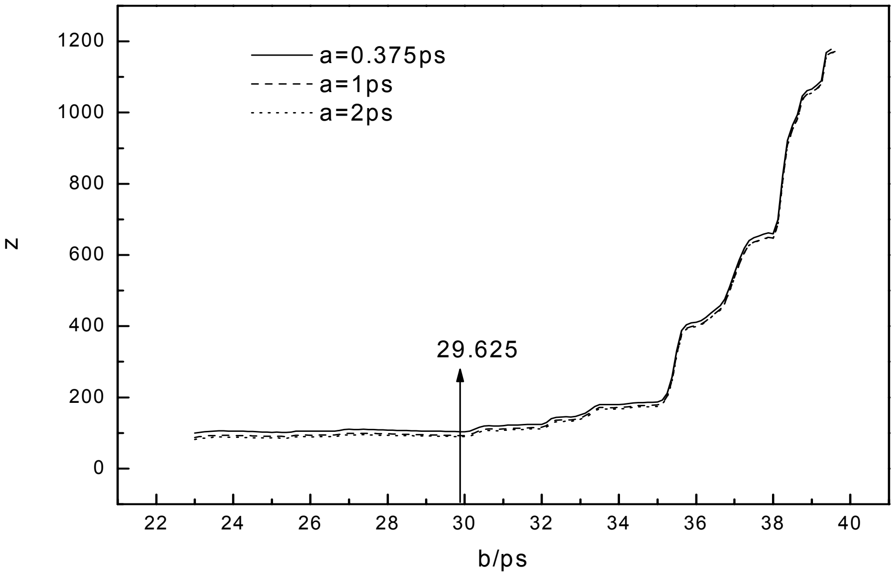

Fig. 2. Differentiation-interval variation analysis curves of aqueous oxygen solution

There are 9 simulation values of gases in Table-1, 4 of them are (oxygen, carbon dioxide, methane and ammonia) have experimental values which are comparable. Oxygen-water system is simulated at 4 kinds of temperatures. Simulation values increase along with the temperature. This trend is in accord with theoretical value. However, not all the correspondingly experimental values accord this trend. There is an exception when temperatures are 293 and 298.15 K, which arises from the difference of measurement applied. The first 7 simulation values are compared with experimental values. The error is between 14 and 37 %. This error is much less than other simulation values as reported in literatures[1].

TABLE-1
SIMULATION VALUE OF DIFFUSION COEFFICIENTS OF AQUEOUS GASES SOLUTION AND 6 GASES COMPARISON BETWEEN EXPERIMENTAL VALUE AND SIMULATION VALUE

Name	Temperature (K)	Experimental value (10^{-9} m^2 s^{-1})	Simulation value (10^{-9} m^2 s^{-1})
Oxygen	293.00	2.30 [Ref. 4]	1.72
	298.15	2.10 [Ref. 1]	1.80
	303.00	3.00 [Ref. 4]	2.01
	313.00	3.70 [Ref. 4]	2.30
Carbon dioxide	298.15	1.92 [Ref. 1]	1.36
Methane	298.15	1.49 [Ref. 1]	1.17
Ammonia	298.15	1.64 [Ref. 1]	1.37
Carbon monoxide	298.15	–	1.98
Sulfur dioxide	298.15	–	1.94
Carbon disulfide	298.15	–	1.01
Nitrogen oxide	298.15	–	2.43
Nitrogen dioxide	298.15	–	2.19

Diffusion coefficients of 5 other kinds of gases are calculated by the same simulating method. They are listed in Table-1. The simulation value of carbon monoxide is higher than that of carbon dioxide and the simulation value of carbon dioxide is higher than that of carbon disulfide. It is certain that the molecular weight of carbon disulfide is higher than that of carbon dioxide and the molecular weight of carbon monoxide is the lowest among them. The molecular volumes of them are as the same sequence. Their values are 52.8, 33.6 and 26.9 cm^3/mol, respectively. There is a relationship among diffusion coefficient, molecular volume and molecular weight. A equation can be calculated when enough data are available. In the past, it is already reported to empirical equation for getting diffusion coefficient when experiment was not convenience, such as Maxwell-Gilliland equation. However, those equations always have a limited region and a relative big error. Thus, the equation presented by simulation works will has a wide range.

Effect of molecular number on simulation result: Periodic-boundary condition is used in the building of gas-water system model. This hypothesis enables a simulation to be performed using a relatively small number of particles, in such a way that the particles experience forces as they were in bulk fluid. However, this hypothesis brings error to the final result. Number of molecule in cell has great effect on simulation result. Oxygen-water systems at two different temperatures (303 and 313 K) are taken for example. Different molecular number is taken for modeling, it is 1, 2 and 3, respectively. In order to ensure the constant of density of system, water molecule is added proportionably. Diffusion coefficients are analyzed by differentiation-interval variation analysis method. The relationship of diffusion coefficients and molecular number are shown in Fig. 3.

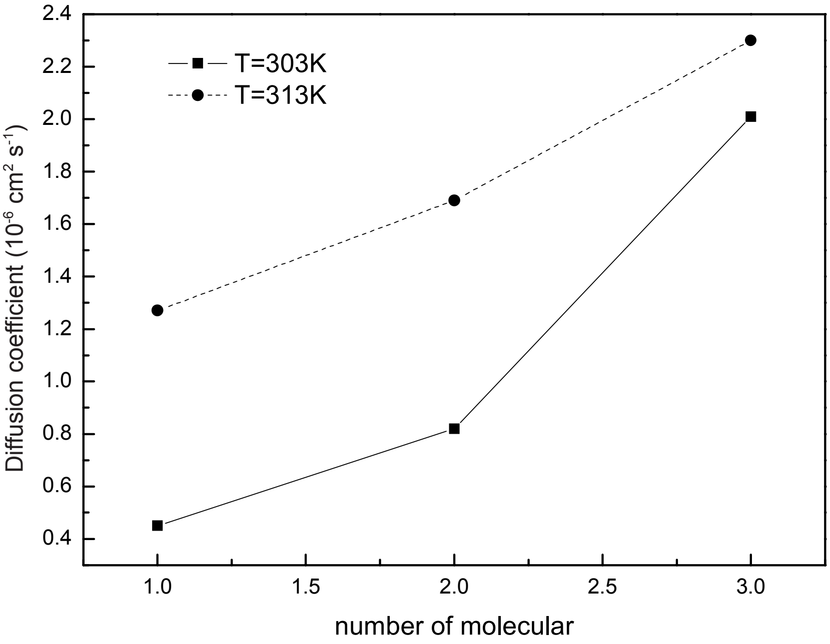

Fig. 3. Effect of molecule-number sample on diffusion coefficient

Fig. 3 shows that the diffusion coefficient rise obviously along with the molecular number and gradually come to the experimental value. The oxygen-water system (313 K) having three oxygen molecules is more logical than systems including one or two molecules. The diffusion coefficient is more close to experimental value than the other 2 systems, it is 2.30.

Based on above conclusion, molecular numbers are all taken the maximum number for any concentration of gas-water systems. The diffusion coefficient of low concentration gas-water systems are got by extending the diffusion coefficient of high concentration gas-water system.

Conclusion

Diffusion of nine gases were simulated in the canonical number of atoms, volume and temperature (NVT) ensemble by means of molecular dynamics simulation method. The diffusion coefficients were analyzed by differentiation-interval variation method. Results showed that the simulation method in this paper is reasonable for calculating diffusion coefficient. The error is between 14 and 37 %, which is less than results in other literatures. We found a relationship among diffusion coefficient, molecular weight and molecular volume. A model can be presented when enough data are available. Diffusion coefficients of the same solution differed a lot when they were calculated with different molecule-number and the one which had the maximum molecules was close to the experimental value.

Nomenclature

a, b = The certain time among simulating process, b > a as usual, ps; $\overline{D}$, D_α, D_j = Mean diffusion coefficient value of differentiation-interval variation analysis method., diffusion coefficient value of Einstein method, diffusion coefficient of the jth time space of differentiation-Interval variation analysis method, Å^2 ps^{-1}; E_{elec} E_{vdW} = Static interaction energy, vdW interaction energy, kcal mol^{-1}; ε_{ij} = Dielectric constant; n = The number of segment divided in differentiation-interval variation analysis method; N_α = Atom number in system; α^2 = The square difference of D_j and $\overline{D}$, m^{-2}; q_i, q_j = Interactive charge; $r_{i(t)}$, $r_{i(0)}$, r_{ij} = The displacement at t time, the initial displacement,the effective radii of vdW interaction, Å; t_{max} = simulating time, ps; x_{j-1}, x_j, x_{j+1} = Value of different time on mean square displacement curve, ps; y_{i-1}, x_i, x_{i-1} = Corresponding value of mean square displacement with different time, Å^2; Z = User-defined function.

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