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DETERMINING DIFFUSION COEFFICIENTS OF OXYGEN IN SUPERCRITICAL WATER WITH MOLECULAR DYNAMICS

by

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The supercritical water oxidation is a significant way for the waste disposal. The diffusion of the oxygen in the water at the infinite dilution is simulated at 300 K and 1 atm, and 650 K, 673 K, 773 K, 873 K, 973 K, and 250 atm with the molecular dynamics software. The mean squared displacement method is used to calculate the diffusion coefficient. At 300 K, 1 atm, our calculation gives $0.20 \cdot 10^{-8}$ m²/s, which is very near to three empirical equations. When the condition is beyond the critical point, these empirical equations lost their accuracy, and only Kawasaki-Oppenheim equation can be compared to our calculation results. At supercritical conditions, we illustrate the diffusion coefficients with the Arrhenius equation and the activation energy is 22.54 kJ/mol.

Key words: *diffusion, oxygen, molecular dynamics, supercritical water oxidation, Arrhenius equation*

Introduction

Supercritical water (SCW) is defined as the water beyond the critical point which is 374 °C and 22.1 MPa. Under such condition, the physical and chemical properties of the SCW are very different from ambient, such as the low viscosity, high diffusivity and low dielectric constant [1]. The SCW becomes a non-polar fluid completely miscible with organics so that it can be used to advantage in the destruction of wastes [2, 3]. Thus, SCW oxidation (SCWO) is a green technology capable of treating a wide variety of hazardous and non-hazardous wastes. The homogeneous reaction takes place between the oxidizable material and oxygen. In a short residence time, organic wastes are quickly oxidized to water, CO_2 and other small molecules. Since oxygen plays an important role in SCWO, its transport property such as diffusion in SCW need to be carefully investigated because it is essential for optimizing reactors. Reasonable diffusion can avoid local overheating and incomplete reaction. Thus, diffusion coefficient of oxygen in SCW has to be precisely acquired.

Among the thermodynamic properties, the diffusion coefficient is of great value to serve as the basis for mass transfer phenomena. There have been many researches focusing

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on oxygen diffusion in water. Han and Bartels [4] determined the diffusion of O_2 in H_2O and D_2O as a function of temperature from –0.5-95 °C. Over such temperature range, significant deviation from both Arrhenius and Stokes-Einstein behavior is found. Marupatch *et al*. [5] measured oxygen diffusion coefficients in various synthetic liquid phases containing salt, glucose or surfactant. When compared to clean water, noticeable reductions of diffusion coefficient were observed. The variation with the compound concentratio was modelled and found dependent on the nature of the compound added. Nowadays, molecular dynamics (MD) has become a popular way to calculate properties with high-performance computers. Zhou *et al*. [6] calculated diffusion coefficient of oxygen in water at 703.15 K and 30 MPa. Thap and Adhikari [7] conducted MD simulations and found that diffusion coefficient of oxygen in water at 288 K, 293 K, 298 K, 302 K, and 306 K followed Arrhenius equation a very good extent. However, for oxygen diffusion in SCW, there are few reports due to experiment limit. Ge *et al*. [8] suggested that the Darken equation may not be valid for oxygen diffusion in SCW. Especially for common operatio temperature for SCWO, oxygen diffusion in SCW still needs further discussion.

In this study, we computed the diffusion coefficient with MD. Mean squared displacement (MSD) method was used to calculate the diffusion coefficient at 300 K, 650 K, 673 K, 773 K, 873 K, and 973 K. At 300 K, the pressure was 1 atm. While for other temperatures, the pressure was 250 atm. The slope of MSD *vs*. time is proportional to diffusion coefficient of the certain atoms.

Simulation details

These simulations employed the large-scale atomic/molecular massively parallel simulator (LAMMPS) [9]. Being a classical MD software, it has remained in active development and addition features and improvements are constantly being contributed by researchers and developers. In this paper, TIP4P/2005 model was used for water because of its accuracy and computationally efficiency. The model of oxygen was taken as diatomic formed by two identical sites. The periodic boundary was set for three axes. Considering there is no chemical bond breaking, the time step was 0.5 fs [10]. The intermolecular potential was approximated by harmonic potential:

$$U_{bond} = \frac{1}{2} K_{bond} (r - r_0)^2 \quad U_{angle} = \frac{1}{2} K_{angle} (r - r_0)^2 \tag{1}$$

Lenard-Jones (LJ) potential was used to describe the intermolecular potential and the long-range part of the Coulombic interactions was computed using the particle-particle particle-mesh method [11]:

$$U_{lj} = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad U_{coul} = \frac{q_i q_j}{4\pi\varepsilon_0 r} \tag{2}$$

where r is the intermolecular distance, U – the potential energy, ε – the depth of the LJ potential well, σ – the LJ separatio distance at zero energy, and q – the charge on the atom. The cut-off for Lennard-Jones potential is 12 Å and the coulombic cut-off is 10 Å. The pair coefficients setting in LAMMPS is controlled by Lorentz-Berthelot [12] mixing rules:

$$\sigma_{12} = \frac{\sigma_1 + \sigma_2}{2} \quad \varepsilon_{12} = \sqrt{\varepsilon_1 \varepsilon_2} \tag{3}$$

All parameters used are shown in tabs. 1-3.

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Table 1. Parameters in H₂O and O₂ model

	ε [eV]	σ [Å]	Charge [e]
H₂O			
O-O	$8.0417 \cdot 10^{-3}$	3.1589	-1.1128
O-H	0	0	
H-H	0	0	0.5564
O₂			
O-O	$5.2098 \cdot 10^{-3}$	3.029	0

Table 2. Parameters in bond and angel potential for H₂O and O₂

		Bond potential
	K_{bond} [eVÅ⁻²]	r^0 [Å]
O-H (H₂O)	0	0.9572
O-O(O₂)	0	1.208
		Angle potential
	K_{angle} [eVrad⁻²]	θ_0 [Å]
H-O-H (H₂O)	0	104.52

Table 3. Average temperature for each simulation system

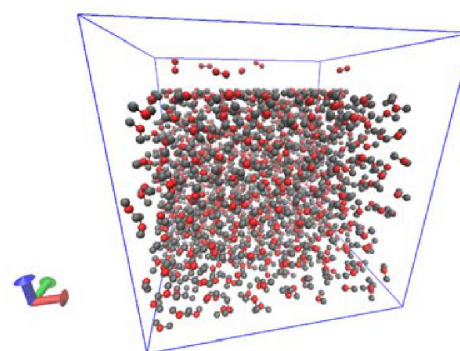| *T, P*	Temperature [K]
300 K, 1 atm	299.94 ± 1.76
650 K, 250 atm	650.06 ± 2.99
673 K, 250 atm	672.87 ± 2.85
773 K, 250 atm	773.29 ± 2.07
873 K, 250 atm	873.12 ± 2.69
973 K, 250 atm	973.04 ± 2.05

Figure 1. Snapshot of the initial structure of oxygen diffusion in water

Since shake algorithm [13] was used to fix the bond and angle during the simulation, the *K*-value is set to 0.

To satisfy the infinite dilution for oxygen in water, there are 890 water molecules and 6 oxygen molecules. The initial structure is shown in fig. 1. The upper are oxygen molecules and the lower are water molecules.

A 1 ns equilibratio run was performed first in NVE ensemble with Berendsen thermostat, the simulation then underwent 1 ns in NVT ensemble to control temperature and then was performed in NVE ensemble for 1 ns to generate MSD data for calculating diffusion coefficient.

Results and discussion

To validate our simulation system, the system energy profile at 300 K, 1 atm is presented in fig. 2. The total energy is the sum of kinetic energy and potential energy at certain condition. At the very beginning, the system is not steady. After around 10 ps, each kind of energy starts to remain steady.

Figure 3 shows the system temperature during the first equilibratio run at 300 K, 1 atm. From this figure, it verifies that our equilibratio run worked well after we created velocity for each atom at the beginning when the temperature is 449.58 K. As the simulation
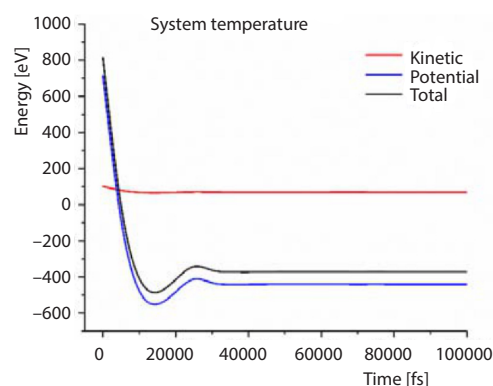

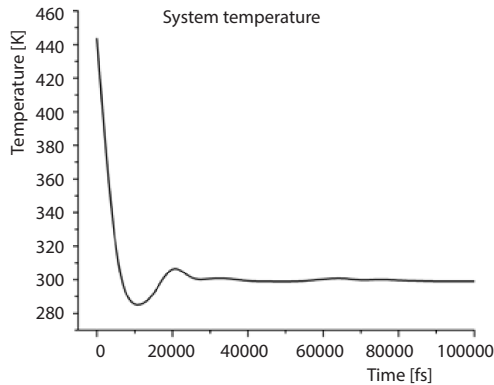**Figure 2. System energy for the first equilibratio run at 300 K, 1 atm**

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Figure 3. System temperature for the first equilibratio run at 300 K, 1 atm

moves on, the system temperature reaches our setting and vibrates near 300 K due to thermal physics. Because other conditions share the same trend in figs. 2 and 3, we do not present them here again.

The system temperature at equilibrium at all conditions is shown in tab. 3. All averages are quite near to the setting and the deviation is small which means that the simulation systems are all scientifically credible and capable for calculation of oxygen diffusion in water at infinite dilution.

In order to compare our simulation results, here we used three classical empirical equations. They are Wilke and Chang [14] equation, Lusis and Ratcliff [15] equation, and Haduk and Laudie [16] equation in the following:

$$D_{AB}^{\infty} = 7.4 \cdot 10^{-8} \frac{T(xM_B)^{0.5}}{\mu_B V_A^{0.5}} \tag{4}$$

$$D_{AB}^{\infty} = 8.52 \cdot 10^{-8} \frac{T}{\mu_B V_B^{1/3}} \left[1.40 \left(\frac{V_B}{V_A} \right)^{1/3} + \frac{V_B}{V_A} \right] \tag{5}$$

$$D_{AB}^{\infty} = \frac{13.26 \cdot 10^{-5}}{\mu_B^{1.4} V_A^{0.589}} \tag{6}$$

where D [cm²s⁻¹] is the diffusion coefficient, T [K] – the temperature, x – the association parameter of solution B, M_B [g·mol⁻¹] – the molar mass of solution B, μ_B [mPa·s⁻¹] – the viscosity of solution B, and V_A and V_B [cm³g·mol⁻¹] are the molecular volume of solute A and solution B at normal boiling point. In this work, for both three equations, O_2 refers to A and H_2O refers to B.

Besides Kawasaki and Oppenheim (KO) [17] equation was added for supercritical conditions and Kallikragas *et al.* [18] have fitted their data to an exponential equation of temperature. This equation is:

$$D\rho = aT + \rho(b_1 T^{-2} + b_2 T^{-1} + b_3 + b_4 T) +$$
$$+ \rho^2 \ln \rho (c_1 T^{-2} + c_2 T^{-1} + c_3 + c_4 T) + \rho^2 (d_1 T^{-2} + d_2 T^{-1} + d_3 + d_4 T) \tag{7}$$

where α, a, b, c, and d are the fitting parameters, T [K] – the temperature, and ρ [gcm⁻³] – the water density. The diffusion coefficient is in 10^{-9} m²/s. The fitting parameters are shown in tab. 4. It should be noted that these parameters are especially modified based on their simulation results.

Table 4. Fitting parameters of eq. (10)

a	α	b_1	b_2	b_3	b_4	c_1
1.82779	0.422868	1.0	-102443	334.021	−0.11924	1.0
c_2	c_3	c_4	d_1	d_2	d_3	d_4
−102959	334.195	−0.11752	1.0	100433	−347.059	0.12556

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The diffusion coefficient of oxygen in water is defined based on the linear part of the MSD of the specific molecules. According to Einstein equation, the diffusion coefficient is calculated by:

$$D = \lim_{t \to \infty} \frac{<|r_i(t) - r_i(0)|^2>}{6} \tag{8}$$

where $r_i(t)$ is the position vector of each molecule at time t. The brackets indicate time and particle average of specific group of molecules.

Figure 4. shows the MSD *vs.* simulation time at equilibrium. Due to the random thermal motion, these lines may not seem like a straight line, but it behaves a linear trend on the whole. To calculate is as accurate as possible, we draw a plot of ln(MSD)-ln(t) in addition. If MSD is linear with time, then the slope of ln(MSD) to ln(t) must eq. (1). So only the intervals whose slope drops in 0.995-1.005 are chosen to calculate the diffusion efficient.

Table 5. shows our calculation results of diffusion coefficient at all conditions. At 300 K, 1 atm, our result is $0.20 \cdot 10^{-8}$ m^2/s which is very consistent with others work. Also, it is very near to result from the first three empirical equations. At 650 K, 250 atm, there still remains small difference between our result and the first three empirical equations. That means that our simulation system and calculation method worked well. When it comes to other supercritical conditions whose temperature are from 673-973 K, it is obvious from fig. 5 that the first three empirical equations all give bad results. This is because they are all based on ideal Einstein equation. But supercritical water is highly non-ideal. And the temperature range is far away from the ambient, which is the application range of the first three empirical equations.

From fig. 5, we can see only results from eq. (10) can be compared with our calculation results. The small difference between our results and eq. (10) my come from different choice of water model, oxygen LJ parameters and MD settings. There are few reports about equations of diffusion in SCW. But since our simulation system and calculation method are trustful, we may be confident that our calculation results provide a good attempt and reference here.
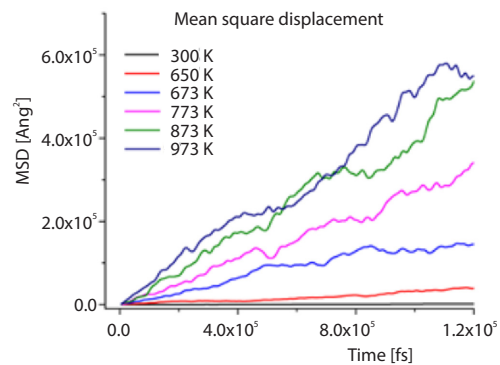

Figure 4. Mean squared displacement of different temperatures

Table 5. Calculation results of diffusion coefficient

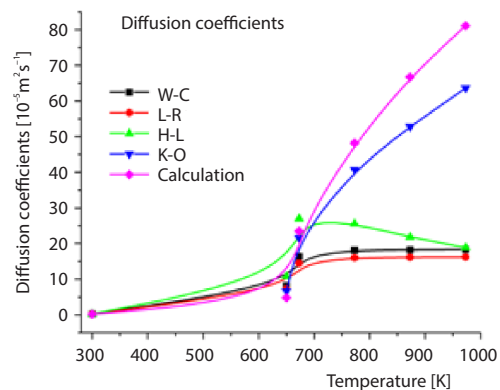| Temperature and pressure	Diffusion coefficient 10^{-8}m^2/s
300 K, 1 atm	0.20 ±0.01
650 K, 250 atm	4.81 ±0.50
673 K, 250 atm	23.45 ±4.97
773 K, 250 atm	48.18 ±5.69
873 K, 250 atm	66.69 ±7.42
973 K, 250 atm	81.12 ±5.15

Figure 5. Diffusion coefficients *vs.* temperature; W-C refers to eq. (7), L-R refers to eq. (8), H-L refers to eq. (9), and K-O refers to eq. (10)

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Temperature usually plays a vital role in diffusion. The Arrhenius equation has been used multiple times [19] to explain this relation as shown in eq. (13), where D_0 denotes the pre-exponential factor, E_a – the activation energy for diffusion, N_A – the Avogadro's constant, k_B – the Boltzmann constant, and T [K] – the temperature.

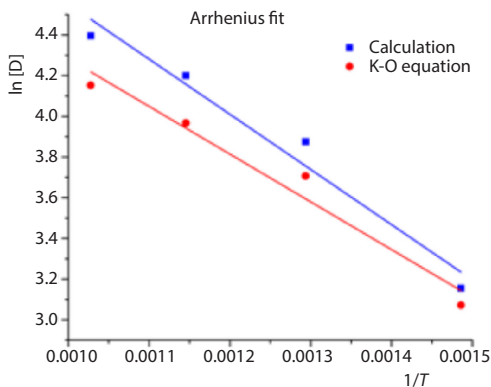$$D = D_0 \exp\left(\frac{-E_a}{N_A k_B T}\right) \tag{9}$$

Figure 6. Arrhenius plot of diffusion coefficient

Figure 6 shows logarithmic plot with reciprocal of temperature. Note that because 650 K, 250 atm is very near to the critical point, its density, 495.41 kg/m³ is far bigger than the density in 673-973 K which is 173.91-60.96 kg/m³. Thus, we only plot within this temperature range. In general, this linear fit is very reliable with both our result and result from Kawasaki-Oppenheim equation. The activation energy from our result is 22.54 kJ/mol while it is 19.50 kJ/mol from Kawasaki-Oppenheim equation. Our activation energy is close to 23.77 kJ/mol [4]. These numbers are the typical activation energy of gas diffusion in liquid.

Conclusion

A simulation system for calculation of diffusion coefficient of oxygen in SCW has been built with MD. Three empirical equations and Kawasaki-Oppenheim equation were compared to our calculation results. It can be seen that the difference between the first three equations is small since they are all based on Einstein equation and modified for aqueous solution at ambient temperature. At 300 K, 1 atm, our result is accurate when compared to the first three equations. However, when it is far from the critical point, the first three empirical equations are not authentic and only Kawasaki-Oppenheim equation fit our calculation results. At 673 K, 250 atm, our calculation result gives $23.45 \cdot 10^{-8}$ m²/sand Kawasaki-Oppenheim gives $21.58 \cdot 10^{-8}$ m²/s. From 673 K to 973 K which is far away from the critical point, the Arrhenius equation describes the relation between diffusion coefficients and temperature accurately. And the activation energy is 22.54 kJ/mol. Inthe nutshell, our simulation can provide a well attempt to calculate the diffusion coefficient with MD. It can bring up some suggestions about SCWO process.

Acknowledgment

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