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Solubility of CO₂ in Cryogenic Methane: Molecular Dynamics Study

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It is necessary to estimate the solubility of solids in liquid solvents during cryogenic processes. In this paper, a new approach is presented to calculate CO₂ solubility in cryogenic methane by molecular dynamics simulation. The isothermal-isobaric ensemble is employed to simulate the solution system while different CO₂ potential models interplay with the LJ sphere of CH₄. The classical nucleation theory is referenced to statistic number of solid phase CO₂. Ultimately, the solubility of CO₂ is the sum of total CO₂ to deduct the numbers of CO₂ in the solid phase. The results show that LJ and rigid CO₂ models are less appropriate for the new method. The flexible models are partly accordance with experimental data.

Key Words: Carbon dioxide, Methane, Solubility, Molecular dynamics simulation.

INTRODUCTION

The staggering advancement of modern society is attended by Energy Crisis and Greenhouse Effect. Natural gas of clean and efficient energy resource, which consists mainly of methane has drawn more attention[1]. There is abundant natural gas form in marine sediments[2]. The best plan for transporting the tapped gas to land is liquefied natural gas (LNG). When natural gas is cooled to 110 K under atmospheric pressure it will be liquid state and shrink its volume more than 600 times[3]. Carbon dioxide is one of the common impurities in natural gas which may precipitate and plague with equipments during the cryogenic process. Technically, solid deposits may cause safety problems in natural gas industry. So it's necessary to investigate CO₂ solubility in liquefied natural gas[4].

Davis *et al.*[5] experimented solid-liquid-vapour phase behaviour of methane-carbon dioxide system in 1962. Generally, the classical thermodynamic methods are employed to study solubility. The solubility equation of solids solute in liquids is[6],

$$\ln \frac{f^L}{f^S} = \ln \frac{1}{x\gamma} = \frac{\Delta h^f}{RT_t}\left(\frac{T_t}{T}-1\right) - \frac{\Delta c_p}{R}\left(\frac{T_t}{T}-1\right) + \frac{\Delta c_p}{R}\ln\frac{T_t}{T} \quad (1)$$

Unfortunately, the classical thermodynamics tell us a little about activity coefficient.

Alternatively, experimentalists provide auxiliary correlations of activity coefficient, for instance, Scatchard-Hildebrand equation, Wohl equation, Flory-Huggins equation, Wilson equation and NRTL equation which are based on the theoretical foundation of Gibbs-Duhem equation and excess Gibbs energy[4,6-12]. Stefani *et al.*[13] measured solubility of carbon dioxide in liquid oxygen at temperature between 90 and 110 K by using a static-analytic method and calculated activity with the help of NRTL equation. Shen and Lin[14] studied CO₂ solubility in saturated liquid methane with Scatchard-Hildebrand equation. However, there isn't a common method that could accurately calculate solubility of CO₂ in liquid methane.

Molecular simulations, as a new method of thermodynamics with the development of computer technology, have been used to study the solubility problems. Kuznetsova and Kvamme[15] reported the thermodynamic properties of carbon dioxide from 200-300 K by molecular dynamics simulation. Memari *et al.*[16] studied solubility of gases in polyethylene with Monte Carlo simulations. More references[17-20] show that molecular simulation is a reliable technique to investigate the solubility issues. However, as far as we know, molecular dynamic simulation method has not been applied in the cryogenic process with solid phase. Consequently, we present a model to calculate the solubility of carbon dioxide in saturated liquid methane based on molecular dynamics simulation in the paper. This method can extend to other similar solubility in cryogenic solid phases.

EXPERIMENTAL

Model of simulation system: Since there is no chemical reaction in this cryogenic proceeding, it is convenient to simu-

late the physical interactions between different particles by molecular dynamics simulation. Furthermore, the slight soluble cryogenic solid prevent the conventional molecular dynamics simulation of solubility. Hence, we propose the model of solution as Fig. 1. The particles of CO_2 and CH_4 are arranged in the cubic box. The isothermal-isobaric (NPT) ensemble is employed to simulate solution system while most molecules of CO_2 gather to be solid cluster. After solution system become equilibrium state, the solubility of CO_2 in cryogenic methane is determined by deducting the amount of the solid phase CO_2.
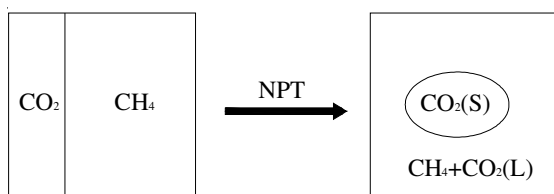

Fig. 1. Model of simulation system

Potential models: In the molecular dynamics simulation system motion of particles is described by Newton's second law[21]. Therefore, accurate intermolecular potential plays an important role in computing process. For CH_4, the classical 12-6 Lennard-Jones (LJ) potential is adequate to determine properties of liquid phase[22]. In this model molecular of CH_4 is regarded as a sphere.

$$U_{LJ} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right] \quad (2)$$

where U_{LJ} is the potential energy, r_{ij} is the distance between two interacting particles i and j, σ and ε are the adjustable parameters for the LJ potential. Whereas, one apparent difficulty arises due to the present CO_2 models are different to describe the solid phase. As a result, all CO_2 models (LJ model, rigid model and fully flexible model) will be tested in this paper. Even though the elementary physical model (EPM2) widely used in rigid model[23], potential from Zhang and Duan[24] is chosen in this work to optimize for CO_2.

$$U_{ij} = U_{short} + U_{Coulombic} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6\right]$$
$$+ \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad (3)$$

The potential is a summation of short-range interaction between three atoms and coulombic interaction between charges where short-range interactions are calculated with LJ function, eqn. 2. q is the partial charge designated on the center of each atom. The angle of O=C=O in rigid model fixed as 180°.

The total potential energy of fully flexible model[25], which is updated from the rigid models, is calculated by

$$U_{total} = U_{Intramolecular} + U_{Intermolecular} \quad (4)$$

The non-bond interactions, $U_{Intermolecular}$, are described by rigid potential, eqn. 5. The intramolecular part, $U_{Intramolecular}$, consists of harmonic bond stretching and bond angle vibration terms is

$$U_{Intramolecular} = \frac{1}{2}k_r\left(r - r_0\right)^2 + \frac{1}{2}k_\theta(\theta - \theta_0)^2 \quad (5)$$

where r, r_0, θ and θ_0 are the measured bending length, the equilibrium bending length, the measured bending angle and the equilibrium bending angle, respectively. k_r and k_θ are the force constants. Unlike the rigid model, parameters of different fully flexible models are greatly discrepant. Thus, two fully flexible models are implemented.

The LJ interactions between different particles are determined by Lorentz-Berthelot combing rules[26],

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (6)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \quad (7)$$

All the parameters for CH_4 and CO_2 in this study are listed in Table-1.

Simulation details: 6000 particles of CH_4 and 2000 particles of CO_2 are computed in the LJ model system by using our program named SCP (Simulator for Cryogenic Process). Initially, these particles are uniformly arranged in a cube box as the left part of Fig. 1. The density of saturated liquid methane is 310 kg/m³ at 170 K. The parallelepiped periodic boundary condition is applied in X, Y, Z coordinates. Berendsen *et al.*[27] method is employed to keep the system as NPT ensemble. The Velocity-Verlet[28] algorithm is used to resolve the equations of motion of particles. The time step is 4 fs. Process steps are 50000 with 5000 equilibration steps. In order to save CPU time, a cut off distance of $4\sigma_{CH_4}$ is adopted.

In the complicated rigid model and fully flexible model, DL_POLY[29] is used to calculate mixture system by 512 particles of CO_2 and particles of 3584 CH_4. The initial arrangement is

TABLE-1			
PARAMETERS FOR METHANE AND CARBON DIOXIDE IN THIS STUDY			
LJ [Ref. 22]	Rigid [Ref. 24]	Fully Flexible A [Ref. 25]	Fully Flexible B [Ref. 33]
$\sigma_{CH4} = 0.37327$ nm	$\sigma_C = 0.27918$ nm	$\sigma_C = 0.2757$ nm	$\sigma_C = 0.28$ nm
$\varepsilon_{CH4} = 1246.5$ J/mol	$\varepsilon_C = 239.7$ J/mol	$\varepsilon_C = 233.8$ J/mol	$\varepsilon_C = 233.9$ J/mol
$\sigma_{CO2} = 0.3627$ nm	$\sigma_O = 0.3$ nm	$\sigma_O = 0.3033$ nm	$\sigma_O = 0.3028$ nm
$\varepsilon_{CO2} = 1919$ J/mol	$\varepsilon_O = 687$ J/mol	$\varepsilon_O = 669.1$ J/mol	$\varepsilon_O = 668$ J/mol
–	$r_{C=O}{}^a = 0.1163$ nm	$r_{C=O} = 0.1163$ nm	$r_{C=O} = 0.1162$ nm
–	$q_C = 0.5888$ e	$q_C = 0.6512$ e	$q_C = 0.6516$ e
–	$q_O = -0.2944$ e	$q_O = -0.3256$ e	$q_O = -0.3258$ e
–	–	$\theta_{O=C=O} = 180°$, $k_r = 1.07\times10^9$ J/(mol nm²), $k_\theta = 1.236 \times 10^6$ J/(mol rad²)	$\theta_{O=C=O} = 180°$, $k_r = 6 \times 10^3$ J/(mol nm²), $k_\theta = 1.1 \times 10^5$ J/(mol rad²)

$^a r_{C=O}$ is the carbon-oxygen bond length.

similar to LJ model. Parallelepiped periodic boundary condition and Berendsen *et al.*[27] method are still applied. The particle motion equation is solved by using Leapfrog Verlet algorithms[30]. The most popular technique, Coulombic interactions are handled by the Ewald sum[31]. While timestep is 5 fs and total steps are 50000 with equilibration steps of 5000 for rigid model and fully flexible model B. On the other hand 2.5 fs and total steps are 100000 with 10000 equilibration steps for fully flexible model A. The cut off distance is 1 nm.

The temperature of solution system is maintained at cryogenic liquid methane to study the solubility from 112-170 K. It should be mentioned that it is difficult to obtain strict saturated liquid by molecular dynamics simulation. Instead, subcooled liquid, which deviates little from saturated state, is acquired.

RESULTS AND DISCUSSION

Before discussing the solubility, liquid density of LJ model is tested and compared with experimental data of National Institute of Standards and Technology, US[32]. The average absolute deviation between simulated results and experimental data is less than 5 %. This proves that our SCP program is valid.

Carbon dioxide distribution of equilibration: The positions of carbon atom in CO₂ molecular for four models are shown as Fig. 2 while the temperature of the system keeps 129.65 K. The carbon dioxide in LJ model and rigid model diffuse in the cubic box but molecules of carbon dioxide in flexible models really concentrate like solid state. Fig. 3 shows that radial distribution function (RDF) of the carbon prove flexible models to be more suitable for describing solid carbon dioxide. Technically, the positions of the first peak and minima of the radial distribution function curve in flexible models are slightly less than the result of supercritical CO₂[33].

(a) LJ   (b) Rigid

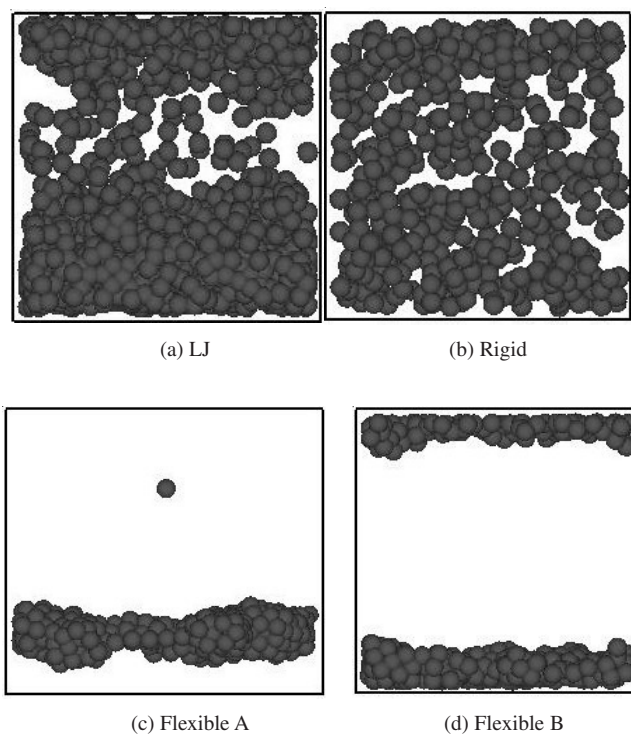(c) Flexible A   (d) Flexible B
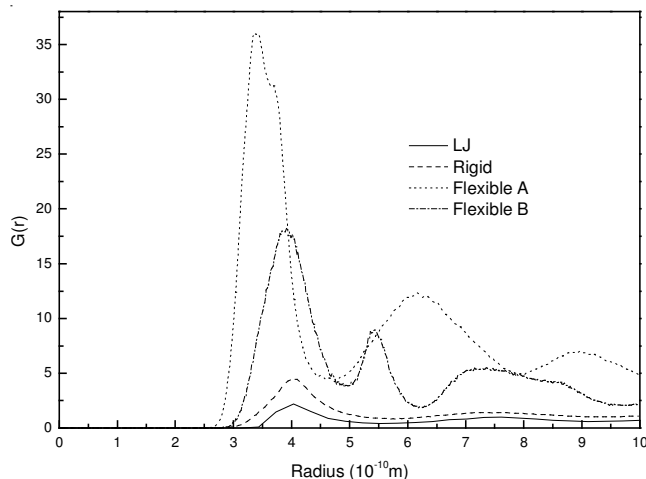
Fig. 2. Snapshot of carbon distribution

Fig. 3. Radial distribution function of C-C

Solubility: The slight solubility of CO₂ in cryogenic methane is difficult to statistic by using the conventional method[17]. A new method which counts the cluster number of solid particles togather is presented to determine solubility of CO₂ in cryogenic methane. Classical nucleation theory (CNT)[34] is used to solve this problem and each cluster must has at least five neighboring atoms within the distance of 1.5 times the LJ length parameter[35]. Hence, this cluster is considered as state of solid. In this paper LJ model uses the distance of 1.5 times the LJ length parameter to determine slight solubility of CO₂ in cryogenic methane but the rigid model and fully flexible model will adopt new distance of cluster. This is because models of CO₂ in LJ, rigid and fully flexible potential functions are different. During simulation processes CO₂ particles are directly counted in LJ model while carbon atoms, which represent position of CO₂ molecules, are counted in other models.

Because most particles are within position of first minima in radial distribution function curves shown in Fig. 3, the radius of the first minima location is used to statistics solid cluster in rigid and flexible models according to results of radial distribution function. The experimental data provided by Davis is used to correct this statistical distance. So the statistical distance of the cluster in LJ model is $1.5\sigma_{CO_2}$ (being equal to 0.544 nm). For rigid, flexible A and flexible B models, the statistical distance of the cluster is chosen as 1.1, 0.39 and 0.5 nm, respectively.

The statistical results of solubility of carbon dioxide in methane are shown in Fig. 4. It is found that the trend of the relation between the solubility of carbon dioxide in methane and temperature agrees with experimental results. The results of LJ and rigid models are deviated far from the experimental result as expected. The result of flexible A matches with experimental result between 145-150 K and the result of flexible B coincides at lower temperature, less than 145 K. The large deviation of LJ and rigid model reveal these models being not well suitable in cryogenic. The atom interactions, bond interplays and angle changes should not be neglected under the condition of cryogenic CO₂ configuration.

For flexible models, the precise distances are shown in Table-2 under the condition of different temperatures. It should be noticed that these precisely distances are in a range within
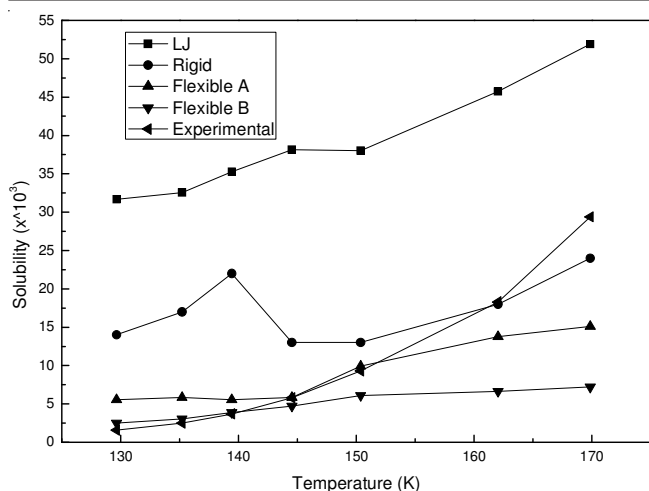
Fig. 4. Solubility of carbon dioxide in methane. (Solubility is in mole fraction. Experimental data is from Davis *et al.*[5])

TABLE-2
PRECISE DISTANCE OF EACH TEMPERATURE
FOR FLEXIBLE MODELS

Temperature (K)	PDA[a] (10^{-10} m)	PDB (10^{-10} m)
129.65	3.75	4.32
135.21	3.85	4.48
139.43	3.92	4.70
144.54	3.92	4.90
150.37	4.00	5.05
162.04	4.80	5.10
169.87	4.80	5.20

PDA[a] is precise distance (PD) of fully flexible A model.

1×10^{-10} m. The C=O bond length and O=C=O angle in flexible models are estimated. However, there exists large divergence while the O=C=O angle of flexible A model and C=O bond length of flexible B model are compared with standard state of CO_2 configuration. As a result, the flexible model is more suitable than other models and but not perfect for calculating CO_2 solubility in cryogenic methane. An improved flexible model of CO_2 is required in cryogenic in order to obtain high precision solubility of CO_2 solubility in cryogenic methane.

Conclusion

A new approach is presented to calculate CO_2 solubility in cryogenic methane by molecular dynamic simulation. The NPT ensemble is employed to simulate the solution system. This is the first time of applying molecular dynamic simulation to calculate solid solubility in cryogenic liquid. This method can be extended to other similar cryogenic process.

The results show that LJ and rigid models are deviate far from the experimental result because of neglecting reality atom interactions, bond interplays and angle changes in cryogenic CO_2 configuration. The flexible models are partly accordance with experimental data. This means that molecular dynamic simulation can be used to simulate the cryogenic process if the potential function is appropriate.

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