Notes

Monte Carlo Simulation of Pure CO_2, *n*-Butane and *n*-Decane in Supercritical CO_2

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Received December 21, 1998

Molecular dynamics and Monte Carlo simulations are useful for understanding chemical and physical systems. There has been much progress in the development of Monte Carlo simulations. Frenkel[1] *et al.* have developed the configurational bias Monte Carlo (CBMC) method for the simulation of chain molecules in dense systems. In this simulation, the entire molecule does not move at random, but a chain molecule is cut at a randomly selected segment, and then the molecule is grown segment by segment. CBMC simulation was used to investigate the adsorption of *n*-alkanes in zeolites,[2] vapor-liquid phase equilibria of *n*-alkanes,[3] vapor-liquid coexistence in Langmuir monolayer of pentadecanoic acid.[4] Pablo[5] *et al.* proposed the continuum configurational bias (CCB) Monte Carlo method, which is similar to the CBMC method, and have used it to study the chemical potentials of chain molecules[6] and polyethylene[7] at equilibrium. These methods have improved the efficiency of simulations compared with conventional Monte Carlo simulations.

Supercritical fluid extraction has received much interest in the food, pharmaceutical, petroleum and other industries. Carbon dioxide is a preferred supercritical solvent, since it[8] is nontoxic, nonflammable, and relatively inexpensive. Its low critical temperature is especially suitable for thermally labile materials.

In this work, NPT ensemble Monte Carlo simulations were performed to calculate static properties of pure carbon dioxide and its mixtures with *n*-alkanes above the critical point of carbon dioxide. Also the CBMC method and reptation moves were used in the simulation of *n*-alkanes. The calculated properties were compared with the experimental values.

Model and Simulation Methods

For the CO_2 molecule, the two-center Lennard-Jones (2CLJ) model proposed by Murthy and Singer[9] was used, in which the CO_2 molecule is assumed to be composed of two sites connected by a rigid length of 0.237 nm. The CH_3 and CH_2 groups in *n*-alkane molecules[7] were considered as single interaction sites, connected by rigid bonds of length 0.153 nm, with the bond angle ∠CCC fixed at 112°. The potential between sites in different molecules or the potential between sites separated by more than three bonds were calculated by Lennard-Jones (LJ) potential.

$$u_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{1}$$

where u_{ij} is the pairwise potential and r_{ij} is the distance between sites i and j. The size parameter[3] σ of the CH_3 and CH_2 groups was assumed to be 0.394 nm. The energy parameter[3] ε/k was 90.5 K for CH_3 and 49.3 K for CH_2 , where k is Boltzmann constant.

For each site of CO_2, the value $\sigma = 0.2989$ nm was taken from the 2CLJ model.[9] But a slightly smaller value of ε was used in this work. The value of ε/k for CO_2, determined to fit the density and internal energy[10] of pure CO_2, was assumed to be 150.512 K. The potential between CO_2 molecules calculated with these values of ε and σ includes the contribution of potential arising from the quadrupole-quadrupole interaction between CO_2 molecules.

For the unlike interactions, the modified Lorentz-Berthelot rules in which the cross energy parameter ε_{ij} is represented by the inter-site interaction parameter between unlike pair molecules δ_{ij} were used as follows :

$$\sigma_{ij} = 0.5\,(\sigma_{ii} + \sigma_{jj}) \tag{2}$$

$$\varepsilon_{ij} = (1 - \delta_{ij})\,(\varepsilon_{ii}\,\varepsilon_{jj})^{0.5} \tag{3}$$

where σ_{ij} is the cross size parameter.

In addition to LJ interaction, the torsional energy was taken into account as in the following equation.[11]

$$u_t(\phi) = 0.5\,V_1\,(1 + \cos\phi) + 0.5\,V_2\,(1 - \cos 2\phi) + 0.5\,V_3\,(1 + \cos 3\phi) \tag{4}$$

In Eq. (4) ϕ is the dihedral angle and $u_t(\phi)$ is the torsional energy for CH_n-CH_n-CH_n-CH_n, where CH_n denotes CH_3 or CH_2 group. $V_1 = 5.906$ kJ/mol; $V_2 = -1.134$ kJ/mol; and $V_3 = 13.159$ kJ/mol.

The NPT ensemble Monte Carlo simulation[12] was applied to 256 molecules in a central cell with periodic boundary conditions. For simulation of *n*-alkane molecules the CBMC method and reptation moves were employed. In reptation moves,[12] one end of a chain molecule moves to a new position, all the other segments move one site along the chain and the tail position becomes vacant. All the interactions were truncated if the inter-site distance is larger than cutoff distance, which was half the length of the periodic box. The corrections to the potential arising from truncations of inter-site interactions were taken into account using the method given by Jorgensen.[11] The types of Monte Carlo moves were (1) translating a CO_2 molecule in randomly chosen cartesian direction; (2) rotating a CO_2 molecule; (3) the regrowing of parts of a alkane molecule using the CBMC method; (4) reptation move of a alkane molecule; and (5) volume change. Each configuration in simulation was generated by a randomly selected Monte Carlo move. The relative probabilities that the moves are attempted in simulation of a mixture were taken as 35%, 35%, 10%, 10%, and 10% for move (1), (2), (3), (4), and (5), respectively. Those in simulation of pure CO_2 were taken as 45%, 45%, and 10% for move (1), (2), and (5), respectively. The molecule for the trial move was selected at random.

In move (2), the center of the rotation was at the center of the CO_2 molecule, and the molecule was rotated about an axis parallel to a randomly chosen cartesian axis. In move (3), regrowing began at a randomly selected segment, and whether to regrow toward the head or the tail was chosen randomly. The number of trial orientations was fixed at 6. The CBMC method followed closely the procedure described by Frenkel.[13] In move (4), it was chosen randomly whether to move randomly the head or the tail. For move (1), (2), and (5), the maximum move was adjusted to give a average acceptance ratio of 40% every 10000 configurations.

The initial configurations were taken as face-centered cubic lattices. The number of configurations generated in equilibration run was 4×10^5 for pure CO_2 and 6×10^5 to 1.2×10^6 for mixture, and for equilibrium run, 2×10^5 for pure CO_2 and 2×10^5 to 6×10^5 for mixture. The simulation run was divided into many blocks, each of which consists of 10000 configurations. The properties of the system were calculated by accumulating and averaging the properties every 20 configurations over the equilibrium period, and the estimated errors[14] for properties were obtained by calculating the standard deviation of the block average properties.

Results and Discussion

Table 1 shows the simulation results for pure CO_2 along with the experimental results.[10] The simulation results of internal energy and density agree considerably well with the experimental values over a wide range of temperatures and pressures.

Table 1. Internal energy (U) and fluid density (ρ) of pure CO_2

Temp. (K)	Pressure (MPa)	U (kJ/mol)		ρ (g/cm^3)	
		expl.*	simulation	expl.*	simulation
230	10.0	-13.49	-11.90±0.26	1.152	1.070±0.019
250	10.0	-12.40	-11.00±0.25	1.077	0.994±0.020
270	10.0	-11.18	-10.40±0.30	0.989	0.951±0.023
300	10.0	-8.92	-8.67±0.28	0.802	0.811±0.026
344.3	12.74		-4.40±0.26	0.380**	0.400±0.025
350	5.0	-1.19	-1.10±0.06	0.090	0.090±0.003
350	10.0	-2.85	-2.82±0.16	0.229	0.239±0.013
350	20.0	-6.62	-6.56±0.42	0.615	0.629±0.039
350	50.0	-9.22	-8.86±0.23	0.885	0.851±0.018
377.6	16.38		-4.01±0.30	0.358**	0.380±0.032
400	20.0	-4.09	-3.71±0.19	0.381	0.361±0.013
400	100.0	-9.32	-9.14±0.26	0.933	0.899±0.019
500	20.0	-2.33	-2.32±0.15	0.235	0.236±0.012
500	50.0	-5.04	-5.03±0.16	0.535	0.522±0.016
600	20.0	-1.62	-1.66±0.08	0.180	0.180±0.005
600	50.0	-3.62	-3.83±0.18	0.415	0.411±0.013
700	20.0	-1.23	-1.34±0.06	0.149	0.150±0.004
700	50.0	-2.79	-3.07±0.12	0.343	0.344±0.010

*from ref. 10, **calculated by Bender's equation of state[10]

Estimating the value of δ_{ij} is difficult because thermodynamic properties are significantly sensitive to the interaction potentials. For interactions between CO_2 and *n*-butane or *n*-decane, the values of δ_{ij} were determined from fitting to the vapor-liquid equilibrium data[15~16] for binary mixtures in this work. The values of δ_{ij} were set at 0.14 for CO_2/*n*-butane and 0.20 for CO_2/*n*-decane. The values of ε_{ij} are much smaller

Table 2. Simulation results for mixture (n_s; the number of *n*-alkane molecules in simulation box, x_s; mole fraction of *n*-alkane, U; internal energy of mixture, E_{tor}; torsional energy of *n*-alkane)

Temp. (K)	Pressure (MPa)	n_s	x_s	U (kJ/mol)	E_{tor} (kJ/mol)	ρ (g/cm^3)	$< r^2 >$ (nm^2)
				Mixture CO_2/*n*-butane			
344.3	8.05	62	0.2422	-3.64±0.59	2.99±0.15	0.289±0.045(0.314)*	0.1295
	7.67	56	0.2188	-3.11±0.42	3.03±0.15	0.249±0.031(0.255)	0.1300
	7.67	1	0.0004	-1.94±0.18	3.07±0.14	0.162±0.012	0.1298
377.6	7.425	114	0.4453	-3.45±0.46	3.29±0.14	0.253±0.027(0.26)	0.1268
	6.758	109	0.4258	-2.10±0.28	3.27±0.15	0.179±0.015(0.202)	0.1269
				Mixture CO_2/*n*-decane			
344.3	12.70	12	0.0469	-5.82±0.38	19.10±1.10	0.536±0.033(0.535)	0.8901
	12.70	1	0.0004	-4.58±0.29	19.10±0.85	0.405±0.027	0.8825
	12.55	9	0.0352	-5.28±0.27	18.90±0.93	0.483±0.025(0.490)	0.8938
	10.73	3	0.0117	-3.62±0.21	19.20±0.68	0.326±0.021(0.301)	0.8817
377.6	16.48	27	0.1055	-5.82±0.35	21.00±0.90	0.544±0.023(0.554)	0.8675
	16.38	18	0.0703	-4.68±0.36	20.80±0.80	0.458±0.029(0.500)	0.8760
	16.38	1	0.0004	-4.08±0.34	20.90±0.75	0.387±0.033	0.8747
	15.85	12	0.0469	-4.33±0.44	20.80±0.83	0.426±0.039(0.435)	0.8786
	12.54	5	0.0195	-2.97±0.21	21.00±0.81	0.290±0.021(0.273)	0.8713

*The numbers in parentheses indicate experimental densities[15] of mixtures CO_2/*n*-butane and those[16] of mixtures CO_2/*n*-decane.

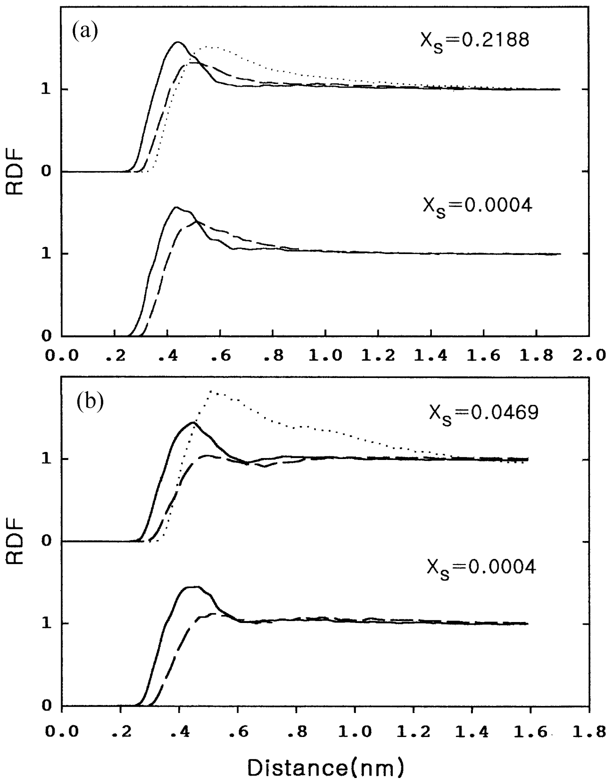

Figure 1. (a) Radial Distribution Function (RDF) in mixture CO_2/*n*-butane at 7.67 MPa and 344.3 K, and (b) that in mixture CO_2/*n*-decane at 12.70 MPa and 344.3 K; ——: CO_2-CO_2, - - - : CH_n-CO_2, ······: CH_n-CH_n.

than predicted by the normal mixing rules. This may be mainly due to the fact that the interaction of the quadrupole-quadrupole does not exist between CO_2 and *n*-butane or *n*-decane. The experimental densities of the mixture at vapor-liquid equilibrium and the calculated densities are shown in Table 2. The calculated densities agree qualitatively with the corresponding experimental values. The mean-square end-to-end separation was calculated by the following equation.[17]

$$< r^2 > = <(\mathbf{r}_1-\mathbf{r}_t)^2> \qquad (5)$$

where $\mathbf{r}_1$ and $\mathbf{r}_t$ are the position vectors of the first site and the last site in *n*-alkane molecule, respectively. In Eq. (5), the symbol $< r^2 >$ denotes the ensemble average of r^2. As shown in Table 2, $< r^2 >$ and the torsional energy of the *n*-alkane molecule are almost independent of pressure, concentration, and density for both mixtures CO_2/*n*-butane and CO_2/*n*-decane. However $< r^2 >$ and the torsional energy of the *n*-decane molecule at 344.3 K are somewhat different from their values at 377.6 K. This may mean that *n*-decane in supercritical CO_2 is more stable at 344.3 K than at 377.6 K. Figure 1(a) and 1(b) show the radial distribution function (RDF) of CO_2-CO_2, CH_n-CO_2, and CH_n-CH_n in two mixtures with different concentrations of *n*-butane and *n*-decane. Figure 1(a) and 1(b) show that the RDF's of CO_2-CO_2 and CH_n-CO_2 in both mixtures are nearly independent of the concentraction of *n*-alkanes. The peak of CH_n-CO_2 in mixture CO_2/*n*-butane is higher than the peak in mixture CO_2/*n*-decane. The difference between peak heights results mainly from two factors. First, the interaction between CO_2 and a site of *n*-butane is stronger compared with the interaction between CO_2 and a site of *n*-decane. Second, CO_2 molecules are screened by the other sites in the same *n*-decane molecule. Because of the weak interaction between CO_2 and *n*-decane as shown in Figure 1(b), *n*-decane strongly tends to form a cluster with *n*-decane. Figure 2 illustrates clustering between *n*-decane molecules.

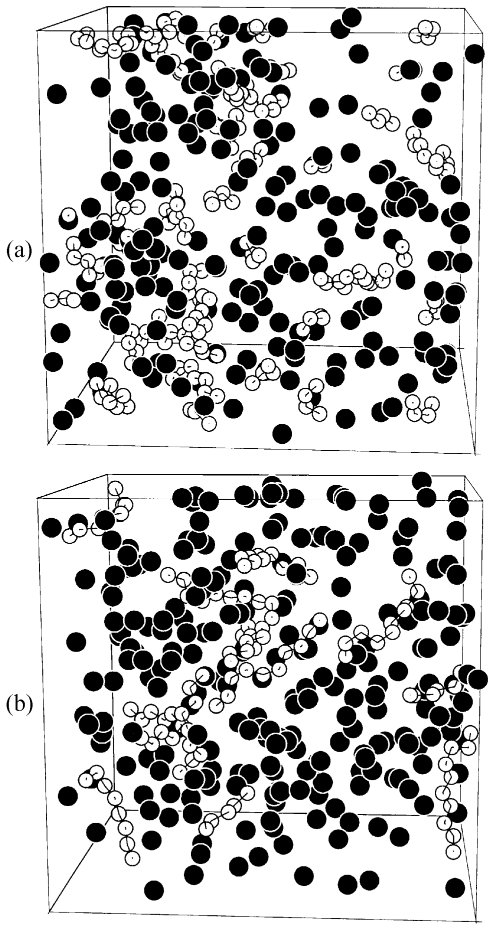

Figure 2. (a) Snap shot for the configuration of mixture CO_2/*n*-butane with x_s = 0.2188 at 7.67 MPa and 344.3 K, and (b) that of mixture CO_2/*n*-decane with x_s = 0.0469 at 12.70 MPa and 344.3 K; ● : CO_2 molecule, ○ : CH_n group.

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