Supporting information

Molecular Dynamics Simulation of Transport and Structural Properties of CO_2 Using Different Molecular Models

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Part 1. Density

Table S1. Thermodynamic data on saturation curve for carbon dioxide in liquid phase at temperatures of 223 and 243 K[a]

T/K	T_r/K	p_s[a]/MPa	ρ_s[a]/g·cm^{-3}	V_s[a]/mL·g^{-1}	ω_{SKR}	Phase
243.00	0.7988	1.4206	1.0764	0.92905	0.2373	liquid
223.00	0.7331	0.67819	1.1551	0.86571	0.2373	liquid

[a]The experimental p_s, ρ_s, V_s from NIST[26]. The critical point of carbon dioxide is T_c = 304.13 K, p_c = 7.3773 MPa, ρ_c = 0.4676 g·cm^{-3}.

1.1 NAM equation[27]

$$\frac{v-v_s}{v_\infty-v_s}=C\frac{J+L(p_r-p_{r,s})+M(p_r-p_{r,s})^3}{F+G(p_r-p_{r,s})+I(p_r-p_{r,s})^3}$$
$$J=j_0+j_1(1-T_r)^{1/3}+j_2(1-T_r)^{1/3}$$
$$F=f_0(1-T_r)$$
$$C=c_0+c_1\omega_{SRK} \quad (1)$$
$$v_\infty=\Omega\frac{RT_c}{P_c}$$
$$\Omega=\Omega_0+\Omega_1\omega_{SRK}$$

Table S2. Global parameters for NAM equation

j_0	1.3168×10^{-3}	M	8.6761×10^{-6}	c_0	5.5526
j_1	3.4448×10^{-2}	f_0	48.8756	c_1	–2.7659
j_2	5.4131×10^{-2}	G	0.7185	Ω_0	7.9019×10^{-2}
L	9.6840×10^{-2}	I	3.4031×10^{-5}	Ω_1	-2.8431×10^{-2}

1.2 EA equation[28]

$$V=V_s\left[1-D\ln\left(\frac{B+p}{B+p_s}\right)\right]$$
$$\frac{B}{P_c}=b_0+b_1\left(\frac{\rho_s}{\rho_c}\right)^{0.75}+b_2\left(\frac{\rho_s}{\rho_c}\right)^{1.5} \quad (2)$$
$$D=d_0+d_1\left(\frac{\rho_s}{\rho_c}\right)^{0.75}+d_2\left(\frac{\rho_s}{\rho_c}\right)^{1.5}$$

Table S3. Global parameters for the EA equation

b_0	10.56325	b_1	–18.8394	b_2	7.73738
d_0	–0.11219	d_1	0.263867	d_2	–0.08802

1.3 Modified Chang and Zhao (MCZ) equation[29,30]

$$\frac{V}{V_s} = \frac{A + C^{(D-T_r)^B}(p_r - p_{r,s})^E}{A + C(p_r - p_{r,s})^E}$$
$$A = a_0 + a_1 T_r + a_2 T_r^3 + a_3 T_r^6 + a_4 / T_r \quad (3)$$
$$B = b_0 + \frac{b_1}{b_2 + \omega_{SRK}}$$
$$C = c_1 (1 - T_r)^{c_2} + \left[1 - (1 - T_r)^{c_2}\right] \exp\left[c_3 + c_4 (p_r - p_{s,r})\right]$$

Table S4. Global parameters for the MCZ equation

a_0	482.85416	b_0	0.0264002	c_1	9.2892236
a_1	–1154.2977	b_1	0.42711522	c_2	2.5103968
a_2	790.09727	b_2	0.5	c_3	0.59397220
a_3	–212.14413	D	1.00001	c_4	0.0010895002
a_4	93.4904	E	0.80329503	–	–

1.4 TBH equation[31]

$$V = V_s (1 - c \ln \frac{\beta + p}{\beta + p_s})$$
$$\beta = P_c \left[-1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + d(1 - T_r) + e(1 - T_r)^{4/3}\right] \quad (4)$$
$$e = \exp(f + g\omega_{SRK} + h\omega_{SRK}^2)$$
$$c = j + k\omega_{SRK}$$

Table S5. Global parameters for the TBH equation

a	–9.070217	f	4.79594	j	0.0861488
b	62.45326	g	0.250047	k	0.0344483
d	–135.1102	h	1.14188	–	–

Nomenclature of above equation of density calculation:

p pressure (MPa)

T Temperature (K)

v volume ($m^3 \cdot kmol^{-1}$)

v_∞ molar volume at infinite pressure ($m^3 \cdot kmol^{-1}$)

V molar volume ($mol \cdot L^{-1}$)

Greek letters

ω_{SRK} acentric factor based on Soave–Redlich–Kwong equation of state

ρ molar density ($mol \cdot m^{-3}$)

Subscript

c critical

r reduced

s saturated

Table S6. The relative deviation between calculated density and experimental values by using different empirical equations[a]

p/MPa	243 K								
	Expt	NAM	Error /%	EA	Error /%	MCZ	Error /%	TBH	Error /%
10	1.1036	1.1070	0.31	1.1062	0.24	1.1067	0.28	1.1014	–0.20
20	1.1294	1.1296	0.02	1.1296	0.02	1.1333	0.34	1.1255	–0.34
30	1.151	1.1495	–0.13	1.1489	–0.18	1.1544	0.29	1.1461	–0.43
50	1.1864	1.1830	–0.28	1.1809	–0.47	1.1872	0.07	1.1801	–0.53
75	1.2216	1.2163	–0.43	1.2131	–0.69	1.2184	–0.27	1.2142	–0.60
88	1.2374	1.2309	–0.53	1.2276	–0.79	1.2318	–0.45	1.2295	–0.64
100	1.2507	1.2430	–0.61	1.2400	–0.86	1.2431	–0.61	1.2424	–0.66
125	1.2756	1.2653	–0.81	1.2632	–0.98	1.2638	–0.93	1.2667	–0.70
150	–	1.2844	–	1.2836	–	1.2817	–	1.2880	–
200	–	1.3163	–	1.3185	–	1.3117	–	1.3247	–
p/MPa	223 K								
10	1.1754	1.1795	0.35	1.1770	0.14	1.1765	0.09	1.1745	–0.08
20	1.1943	1.1963	0.17	1.1934	–0.08	1.1963	0.17	1.1927	–0.14
30	1.2109	1.2115	0.05	1.2073	–0.29	1.2127	0.15	1.2088	–0.17
50	–	1.2378	–	1.2313	–	1.2391	–	1.2367	–
75	–	1.2651	–	1.2564	–	1.2646	–	1.2657	–
88	–	1.2774	–	1.2681	–	1.2758	–	1.2790	–
100	–	1.2878	–	1.2782	–	1.2852	–	1.2903	–
125	–	1.3073	–	1.2975	–	1.3026	–	1.3119	–
150	–	1.3244	–	1.3150	–	1.3176	–	1.3311	–
200	–	1.3536	–	1.3457	–	1.3430	–	1.3645	–

[a]The experimental data from NIST[26].

Table S7. The density of pure carbon dioxide used in this simulation to calculate the simulation box[a] (g·cm^{-3})

T/K	10 /MPa	20 /MPa	30 /MPa	50 /MPa	75 /MPa	88 /MPa	100 /MPa	125 /MPa	150 /MPa	200 /MPa
450	0.1316	0.2851	0.4303	0.6262	0.7616	0.8099	0.8470	0.9092	0.9582	1.0337
424	0.1451	0.3255	0.4898	0.6849	0.8111	0.8559	0.8904	0.9485	0.9946	1.0659
373	0.1888	0.4813	0.6625	0.8192	0.9183	0.9546	0.9831	1.0319	1.0714	1.1337
333	0.2908	0.7246	0.8303	0.9339	1.0092	1.0383	1.0617	1.1027	1.1366	1.1912
298	0.8189	0.9149	0.9671	1.0346	1.0913	1.1146	1.1481	1.1679	1.1969	1.2447
273	0.9748	1.0211	1.0548	1.1048	1.1505	1.1700	1.1863	1.2161	1.2418	1.2849
243	1.1036	1.1294	1.1510	1.1864	1.2216	1.2374	1.2507	1.2756	1.2880[b]	1.3247[b]
223	1.1754	1.1943	1.2109	1.2378[c]	1.2651[c]	1.2774[c]	1.2878[c]	1.3073[c]	1.3244[c]	1.3536[c]

[a]The density without special illustration is experimental value from NIST[26].

[b]Calculated by TBH equation.

[c]Calculated by NAM equation.

Part 2. Self-diffusion coefficient

2.1 LJ-2 equation[34]

$$D_{\mathrm{LJ}2} = \frac{21.16}{\rho\sigma_{\mathrm{eff}}^2}\sqrt{\frac{1000RT}{M}} \times \exp\left\{-\frac{0.75\rho^*}{1.2588-\rho^*} - \frac{0.27862}{T^*}\right\},$$
$$\sigma_{\mathrm{eff}} = 2^{1/6}\sigma_{LJ}\left[1+\left(\frac{T^*}{T_0^*}\right)^{1/2}\right]^{-1/6}. \quad (5)$$

2.2 LJ-4 equation[35]

$$D_{\mathrm{LJ}4} = 21.16\frac{A_{\mathrm{D}}}{\rho\sigma_{\mathrm{eff}}^2}\sqrt{\frac{1000RT}{M}} \times \exp\left\{-\frac{0.75\rho^*}{1.2588-\rho^*} - \frac{E_{\mathrm{D}}}{RT}\right\}$$
$$\sigma_{\mathrm{eff}} = 2^{1/6}\sigma\left[1+\left(\frac{T}{T_{\mathrm{D}}}\right)^{1/2}\right]^{-1/6}. \quad (6)$$

2.3 EWJ equation[36,37]

$$D_{\mathrm{HS}} = D_0\left(1-\rho^*/1.09\right)\left[1+\rho^{*2}\left(0.4-0.83\rho^{*2}\right)\right]$$
$$D_0 = \frac{3}{8}\frac{1}{\rho\sigma^2}\left(\frac{kT}{\pi m}\right)^{1/2} \quad (7)$$

Nomenclature of above equation of self-diffusion coefficient calculation

A_{D} roughness or shape factor
E_{D} energy parameter
LJ Lennard-Jones fluid model
M molecular weight (g·mol^{-1})
R ideal gas constant (= 8.3144 J·mol^{-1}·K^{-1})
T temperature (K)
T_{D} temperature parameter
T^* $kT/\varepsilon_{\mathrm{LJ}}$= reduced temperature (K)
T_0^* parameter
HS hard-sphere fluid
k Boltzmann constant (= 1.38048×10^{-23} J·K^{-1})
m mass of the molecule (kg)

Greek letters

ε energy parameter (J·mol^{-1})
ρ number density (cm^{-3})
ρ^* reduced number density (= $\rho\sigma^3$, where $\sigma = \sigma_{\mathrm{LJ}}$ or σ_{eff}) (cm^{-3})
σ molecular diameter (cm)
σ_{eff} effective diameter (cm)

Table S8. Comparison of calculated self-diffusion coefficient by using different empirical equations with experimental values[a] (10^{-9} $m^2 \cdot s^{-1}$)

p/MPa	450 K				424 K			
	Expt	LJ-2	EWJ	LJ-4	Expt	LJ-2	EWJ	LJ-4
10	–	231	243	248	–	199	212	210
20	–	81.1	102	109	–	68.6	84.7	88.2
30	–	50.0	61.5	68.7	56.4	41.7	50.3	55.2
50	52.2	30.4	36.3	43.6	36.6	26.2	30.6	36.3
75	33.9	22.6	26.2	33.7	27.3	19.9	22.6	28.8
88	30.2	20.4	23.3	30.9	–	18.1	20.3	26.6
100	26.7	18.8	21.3	29.0	24.1	16.8	18.6	25.1
125	22.2	16.5	18.3	26.1	18.6	14.8	16.1	22.7
150	19.5	14.8	16.2	24.1	17.0	13.3	14.3	21.1
200	17.0	12.5	13.2	21.3	13.3	11.3	11.7	18.7
p/MPa	373 K				333 K			
10	–	135.9	149.1	137.6	–	76.9	85.9	75.3
20	–	41.0	48.3	48.5	26.9	23.2	24.6	24.9
30	33.7	26.3	30.3	32.5	20.8	18.3	19.1	20.5
50	24.3	18.6	20.8	24.2	16.0	14.5	14.8	17.0
75	18.9	15.0	16.3	20.3	–	12.2	12.2	14.9
88	–	13.8	14.9	19.1	–	11.3	11.2	14.2
100	15.4	12.9	13.8	18.2	11.1	10.7	10.5	13.6
125	–	11.5	12.1	16.8	–	9.64	9.33	12.7
150	12.4	10.5	10.8	15.7	8.98	8.81	8.40	11.9
200	10.3	8.96	8.98	14.1	7.71	7.56	7.02	10.8
p/MPa	298 K				273 K			
10	18.8	17.0	18.6	15.8	12.4	10.8	12.1	11.9
20	15.1	13.6	14.7	13.2	–	9.64	10.7	10.9
30	–	12.0	12.9	12.1	–	8.83	9.71	10.3
50	11.0	10.2	10.7	10.7	8.42	7.72	8.39	9.35
75	–	8.81	9.13	9.64	–	6.77	7.28	8.58
88	–	8.28	8.51	9.24	–	6.39	6.83	8.27
100	8.23	7.54	7.67	8.69	6.05	6.07	6.47	8.01
125	–	7.12	7.19	8.38	–	5.52	5.83	7.56
150	6.63	6.53	6.52	7.94	4.85	5.07	5.30	7.19
200	5.89	5.61	5.48	7.25	4.29	4.35	4.48	6.59
p/MPa	243 K				223 K			
10	7.34	6.78	7.95	7.74	4.86	4.90	6.06	5.76
20	–	6.29	7.34	7.36	–	4.60	5.69	5.54
30	–	5.89	6.86	7.06	–	4.34	5.37	5.35
50	5.19	5.27	6.10	6.57	3.48	3.94	4.87	5.05
75	–	4.68	5.39	6.12	–	3.55	4.38	4.75
88	–	4.43	5.09	5.92	–	3.38	4.17	4.62
100	3.85	4.22	4.84	5.76	2.92	3.24	4.00	4.51

Table S8 (continued)

p/MPa	243 K				223 K			
	Expt	LJ-2	EWJ	LJ-4	Expt	LJ-2	EWJ	LJ-4
125	–	3.84	4.39	5.46	–	2.98	3.68	4.32
150	3.18	3.66	4.17	5.31	2.52	2.76	3.41	4.15
200	2.83	3.14	3.56	4.90	2.12	2.41	2.98	3.87

[a]Experimental values from ref. 11.

Table S9. Comparison of simulated self-diffusion coefficients by using different models with experimental values[a] (10^{-9} $m^2 \cdot s^{-1}$)

T/K	10 MPa				20 MPa			
	Expt	MSM	EPM2	TraPPE	Expt	MSM	EPM2	TraPPE
450	–	–	280	–	–	–	109	–
424	–	–	221	–	–	–	89.5	–
373	–	–	154	–	–	–	51.4	–
333	–	–	86.6	–	26.9	26.3	26.4	24.7
298	18.8	19.1	18.8	18.1	15.1	15.3	15.4	15.0
273	12.4	12.3	11.6	10.4	–	–	10.3	–
243	7.34	7.60	7.30	6.95	–	–	–	6.02
223	4.86	5.57	5.43	4.83	–	–	–	4.34
T/K	30 MPa				50 MPa			
450	–	–	68.5	–	52.2	37.6	38.3	38.1
424	56.4	58.3	57.7	54.4	36.6	34.5	35.0	31.3
373	33.7	32.3	34.0	31.9	24.3	22.8	22.1	19.1
333	20.8	20.6	20.0	18.4	16.0	16.5	15.3	15.1
298	–	–	13.5	–	11.0	11.4	11.0	9.83
273	–	–	9.99	–	8.42	8.67	8.39	7.77
243	–	–	–	5.71	5.19	6.30	5.56	5.25
223	–	–	–	4.02	3.48	4.26	4.01	3.93
T/K	75 MPa				88 MPa			
450	33.9	30.2	28.6	27.2	30.2	25.8	25.6	25.6
424	27.3	24.1	25.9	24.9	–	–	21.4	-
373	18.9	18.5	17.6	15.2	–	–	16.0	–
333	–	–	12.4	–	–	–	11.9	–
298	–	–	9.06	–	–	–	8.97	–
273	–	–	7.20	–	–	–	6.50	–
243	–	–	–	4.61	–	–	–	4.20
223	–	–	–	3.59	–	–	–	3.30
T/K	100 MPa				125 MPa			
450	26.7	25.1	24.3	24.0	22.2	22.7	20.7	19.3
424	24.1	21.2	19.9	18.9	18.6	17.9	18.1	17.2
373	15.4	14.4	15.4	14.5	–	–	12.8	–
333	11.1	12.1	11.0	10.7	–	–	10.1	–

Table S9 (continued)

T/K	100 MPa				125 MPa			
	Expt	MSM	EPM2	TraPPE	Expt	MSM	EPM2	TraPPE
298	8.23	8.10	7.78	6.95	–	–	7.32	–
273	6.05	6.73	5.91	5.83	–	–	5.52	–
243	3.85	5.28	4.58	3.74	–	–	–	3.46
223	2.92	3.64	3.51	3.18	–	–	–	2.62
T/K	150 MPa				200 MPa			
450	19.5	18.0	17.9	17.7	17.0	15.3	16.8	13.1
424	17.0	16.1	16.7	14.9	13.3	12.2	12.8	12.6
373	12.4	12.0	12.8	10.8	10.3	9.32	9.62	9.42
333	8.98	9.05	8.58	8.12	7.71	7.66	7.72	6.37
298	6.63	6.93	6.41	6.02	5.89	5.63	5.74	4.59
273	4.85	5.70	4.84	4.62	4.29	4.35	4.35	3.98
243	3.18	4.19	3.84	3.21	2.83	3.61	3.19	2.80
223	2.52	3.21	2.72	2.42	2.12	2.64	2.54	2.27

[a]Experimental values from ref. 11.

Part 3. Viscosity

Table S10. Comparison of simulated viscosity by using different models with experimental values[a] (10^{-5} Pa·s)

p/MPa	450 K				424 K			
	Expt	EPM2	MSM	TraPPE	Expt	EPM2	MSM	TraPPE
10	2.368	2.338	2.147	2.330	2.287	2.172	2.194	2.170
30	–	–	–	–	4.015	3.818	4.083	3.804
50	5.341	5.194	5.441	5.522	5.880	5.875	5.930	5.758
75	6.990	7.114	6.575	7.076	7.661	7.650	7.695	8.194
100	8.400	8.455	8.487	8.837	9.188	9.592	9.592	9.424
125	9.709	10.01	9.672	9.986	10.62	11.10	10.79	11.12
150	10.98	11.23	11.20	12.22	12.01	12.22	12.34	12.78
200	13.50	13.84	13.38	14.09	14.77	15.20	15.15	16.22
p/MPa	373 K				333 K			
10	2.180	2.084	2.239	2.304	2.387	2.268	2.553	2.557
20	–	–	–	–	6.017	6.091	5.813	6.297
30	5.407	5.317	5.188	5.317	7.693	7.981	7.768	8.230
50	7.613	7.807	7.770	8.027	10.01	10.13	10.35	10.84
75	9.679	10.12	9.651	10.59	–	–	–	–
100	11.50	11.90	11.53	12.67	14.50	14.32	14.08	16.10
150	14.91	15.23	15.06	15.84	18.51	18.21	18.21	20.36
200	18.24	18.46	18.19	20.00	22.38	23.15	21.84	23.80
p/MPa	298 K				273 K			
10	7.411	7.412	7.412	7.982	11.42	11.33	10.91	12.07
20	9.522	9.835	9.649	9.870	-	-	-	-

Table S10 (continued)

p/MPa	298 K				273 K			
	Expt	EPM2	MSM	TraPPE	Expt	EPM2	MSM	TraPPE
50	13.49	13.79	13.16	14.61	17.29	17.08	16.16	17.98
100	18.63	19.46	19.45	21.15	23.00	22.13	22.36	24.95
150	23.27	22.91	21.80	25.39	28.19	27.39	26.73	30.84
200	27.74	27.66	27.10	30.00	33.18	31.94	30.55	36.67
p/MPa	243 K				223 K			
10	18.09	16.94	16.31	18.41	24.78	22.14	21.58	24.84
50	24.32	22.41	22.50	25.02	-	27.84	26.90	31.09
100	30.90	28.96	27.47	32.43	-	33.77	31.95	39.30
150	-	32.94	32.01	37.23	-	39.91	37.11	44.11
200	-	38.21	36.58	43.20	-	43.64	41.39	50.32

[a]Experimental data from NIST[26].