Supporting Information

Employing SAFT coarse grained force fields for the molecular simulation of thermophysical and transport properties of CO_2 – n-alkane mixtures

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Critical properties

The critical points of the model are calculated using the critical scaling rules (SI 1-3), where A, B, Φ and **Ψ** are fitting parameters. Start with Eq. (SI 1), the critical temperature (T_c) and Φ can be calculated by fitting the equation to a handful of temperature (T) and corresponding liquid and vapor densities (ρ_L and ρ_V). The resulting T_c is then used in Eq. (SI 2-3) to compute the critical density and pressure (ρ_c and P_c). The parameter values for different systems are displayed in Table S1.

$$\rho_L - \rho_V = \Phi(T_c - T)^{0.235} \quad \text{(SI 1)}$$

$$\frac{\rho_L - \rho_V}{2} = \Psi(T - T_c) + \rho_c \quad \text{(SI 2)}$$

$$\ln P = -A\frac{1}{T} + B \quad \text{(SI 3)}$$

Table S1 Experimental simulation critical properties for CO_2, n-decane and n-hexadecane computed using the scaling rules

Coefficients	Dimer CO_2	Mono CO_2	n-decane	n-hexadecane
A	1912.1	1857.4	5583.4	7168.0
B	8.2628	8.1932	10.398	10.951
Φ	268.06	368.97	115.21	108.74
Ψ	-1.3963	-1.1756	-0.4478	-0.9438

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Comparison of simulation results for pure CO_2 (density and vapor pressures)

A comparison is made between an unabridged selection of available simulation packages, including
- GROMACS[1], version (5.1.3) employing a single NVT cell to produce both the liquid and the vapor phases. Cutoff is set to 2 nm (roughly 7 σ) and no long range corrections are applied. 5000 molecules (10000 beads). Elongated boxes (in the *z* direction) are employed and the pressure is reported as the *zz* component of the pressure tensor.
- *DL_POLY* 4.09.02[2], employing the same methodology as above. The data included in this work are courtesy of Dr. Alin Marin Elena (Daresbury Laboratory).
- *ms2*[3] , employing the *NPT* ensemble with chemical potential calculated via Widom insertion method, together known as the NPT+μ method. Data included are courtesy of Prof. Jadran Vrabec (Technical University Berlin).
- MedeA®-GIBBS (9.6.2)[4] (employing Gibbs Ensemble Monte Carlo simulations) Cutoff used here was half the box size, roughly 3 nm. Runs were 100 M configurations, with the exception of the point at 280 K which was evaluated using 30 M configurations. Data included are courtesy of Dr. Marianna Yiannourakou (Materials Design).

For further comparisons, the model employed is a 2-bead Mie model of CO_2 (model b in table 1 : σ = 0.2850 nm ; ε/k_B = 190.14 K; λ_r = 13.77; λ_a = 6.0), beads linked at a distance of σ, with a rigid bond (or equivalently a stiff spring bond);

Table S2 MD simulated vapor pressures and saturated liquid densities for pure CO_2. Simulations carried out using the dimer CO_2 CG model in GROMACS (5.1.3), *DL_POLY* 4.09.02, *ms*2 and MedeA®-GIBBS (9.6.2)

	Theory	*DL_POLY* 4.09.02	GROMACS 5.1.3	*ms2*	MedeA®-GIBBS (9.6.2)
T /K	Vapor pressure /MPa				
220	0.606	0.496	0.652 ± 0.053	0.6363	0.629 ± 0.015
240	1.288	1.211	1.343 ± 0.126	1.264	1.284 ± 0.022
260	2.424	2.416	2.483 ± 0.254	2.412	2.422 ± 0.030
280	4.170	4.241	4.190 ± 0.444	4.07	4.083 ± 0.083
T /K	Saturated liquid density /kg.m^{-3}				
220	1156	1144	1149	1151	1153 ± 2
240	1082	1067	1075	1077	1077 ± 2
260	996	980	988	993	994 ± 2
280	886	868	875	889	888 ± 5

In Table S2, the first column corresponds to the prediction of the SAFT-VR-Mie theory. Within SAFT, the parameters of the theory are adjusted to obtain an optimal fit of the experimental VLE. In this comparison, these theory values are taken as surrogate reference values. In any case, the important comparison is *amongst* the simulation results, as they should all reproduce the same values, within the experimental uncertainty. For most cases, this is true, although the values provided by DL_POLY are seen to be outliers, particularly at low temperatures. This is not an exhaustive comparison, but is does show that care has to be taken in both the selection of the program employed to resolve the molecular simulations and in the subsequent interpretation of the results.

Simulation results pure CO_2 (viscosity)

Table S3 Shear viscosity values of CO_2 at 100 bar from 220K to 300K using EMD, and NEMD and %AAD computed against the smoothed experimental data[5]

T /K	Smoothed expt.	Two-bead CO_2				One-bead CO_2			
		EMD		NEMD		EMD		NEMD	
	η /cP	η /cP	*%AAD*	η /cP	*%AAD*	η /cP	*%AAD*	η /cP	*%AAD*
220	0.260	0.213	*18.30*	0.223	*14.21*	0.378	*45.30*	0.392	*50.51*
240	0.189	0.174	*8.04*	0.180	*5.23*	0.269	*42.21*	0.265	*39.87*
260	0.140	0.135	*3.08*	0.136	*2.80*	0.191	*36.70*	0.196	*40.37*
280	0.102	0.101	*1.63*	0.104	*2.08*	0.136	*32.82*	0.139	*36.41*
300	0.071	0.074	*4.74*	0.069	*3.11*	0.087	*22.20*	0.095	*33.27*

Dimensions of the simulation boxes for VLE

Table S4 Dimensions of box for pure components to achieve vapor-liquid phase separation at various saturation temperatures

T /K	Box dimension (x y z) /nm × nm × nm
	CO_2
220	5.908 × 5.908 × 17.723
240	6.011 × 6.011 × 18.032
260	6.120 × 6.120 × 18.359
280	6.235 × 6. 235 × 18.705
	n-decane
250	8.521 × 8.521 × 25.562
300	8.671 × 8.671 × 26.013
350	8.832 × 8.832 × 26.497
400	9.009 × 9.009 × 27.028
450	9.206 × 9.206 × 27.619
500	9.426 × 9.426 × 28.279
550	9.677 × 9.677 × 29.030
	n-hexadecane
450	9.183 × 9.183 × 27.548
500	9.350 × 9.350 × 28.049
550	9.594 × 9.594 × 28.781
600	9.724 × 9.724 × 29.173
650	9.937 × 9.937 × 29.812

Dimensions of the simulation boxes for viscosities

Table S5 Molar compositions and box dimensions for CO_2 + n-decane and CO_2 + n-hexadecane systems to achieve vapor-liquid phase separation at various pressures.

Target pressure /MPa	No. CO_2 molecules	No. hydrocarbon molecules	Box dimension (x y z)/nm × nm × nm
CO_2 + N-decane			
10	5388	612	5.80 × 5.80 × 29.0
9	5076	924	6.19 × 6.19 × 31.0
7	4590	1410	6.74 × 6.74 × 33.7
6	4356	1644	6.96 × 6.96 × 34.8
5	4000	2000	7.50 × 7.50 × 37.5
4	3500	1500	8.00 × 8.00 × 40.0
2	3000	3000	8.80 × 8.80 × 44.0
CO_2 + n-hexadecane			
T = 298.4 K k_{ij} = 0			
2	3000	1000	6.60 × 6.60 × 26.4
3	3200	800	6.45 × 6.45 × 25.8
4	3500	500	5.66 × 5.66 × 22.6
5	3800	200	5.20 × 5.20 × 20.8
T = 298.4 K k_{ij} = 0.1			
2	2000	2000	9.00 × 9.00 × 36.0
3	2500	1500	7.80 × 7.80 × 31.2
4	3000	1000	6.60 × 6.60 × 26.4
5	3400	600	6.00 × 6.00 × 24.0
T = 323.2 K k_{ij} = 0			
3	3000	1000	7.40 × 7.40 × 29.6
4	3000	1000	6.60 × 6.60 × 26.4
5	3200	800	6.45 × 6.45 × 25.8
6	3500	500	6.00 × 6.00 × 24.0
7	3700	300	5.66 × 5.66 × 22.6
T = 323.2 K k_{ij} = 0.1			
3	2500	1500	9.00 × 9.00 × 36.0
4	2500	1500	8.20 × 8.20 × 32.8
5	3000	1000	7.40 × 7.40 × 29.6
6	3000	1000	6.60 × 6.60 × 26.4
7	3200	800	5.60 × 5.60 × 22.4

CO_2-hexadecane without kij

These figures relate to Fig. 9 of the manuscript and show the quality of fit if no binary interaction parameter is used in the simulations.

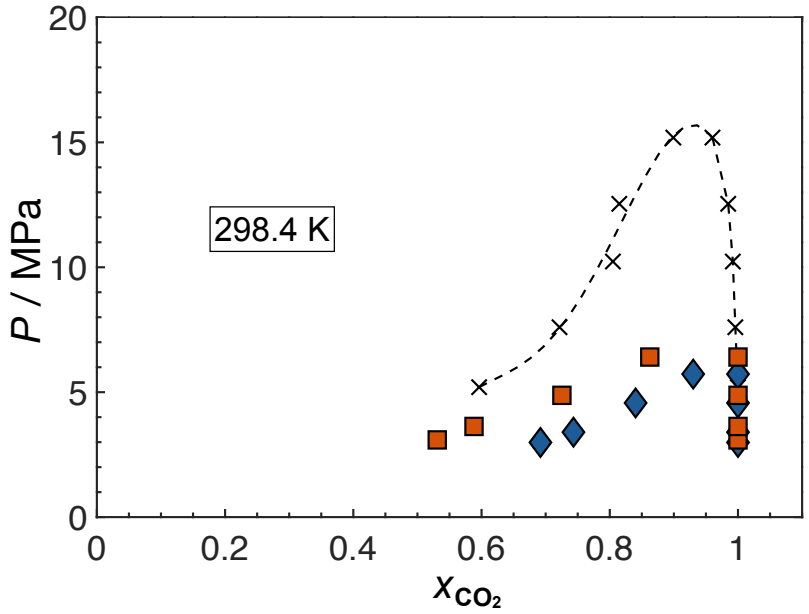


Figure S1 Pressure-composition diagram for the (CO_2 + n-hexadecane) mixture using either one-bead (mono) or two-bead (dimer) CO_2 models at 298.4 K without a cross binary interaction parameter, k_{ij}. Experimental measurements and simulation results are shown in crosses and diamonds/squares respectively.

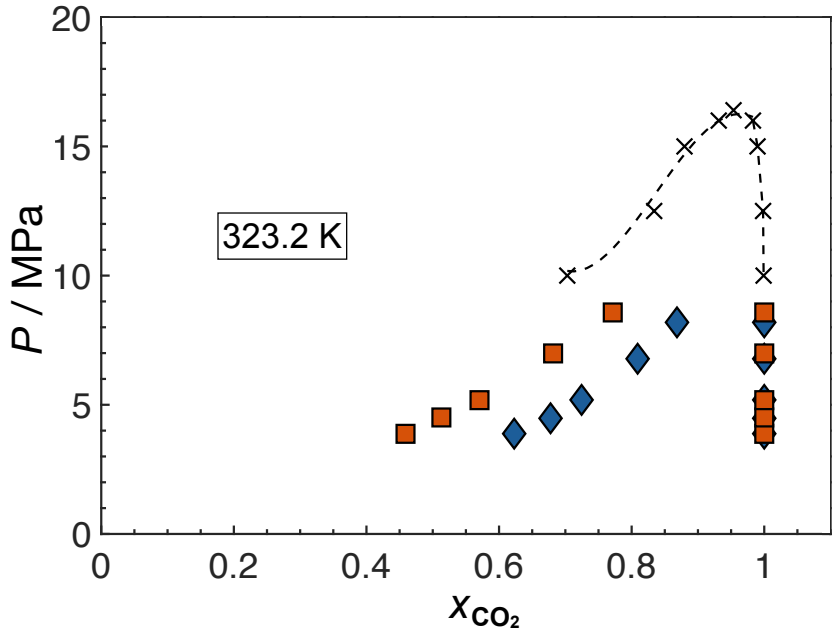


Figure S2 Pressure-composition diagram for the (CO_2 + n-hexadecane) mixture using either one-bead (mono) or two-bead (dimer) CO_2 models at 323.2K without a cross binary interaction parameter, k_{ij}. Experimental measurements and simulation results are shown in crosses and diamonds/squares respectively.

Simulation results (raw data)

Table S6 Viscosities of pure n-decane, n-hexadecane, binary mixture CO_2 + n-decane and CO_2 + n-hexadecane at various temperatures and pressures. 1 cP = 1 mPa.s

CO_2					
	Expt.	EMD		NEMD	
T /K	η /cP	η /cP	σ_η /cP	η /cP	σ_η /cP
Dimer CO_2					
220	0.260_2	0.212_6	0.019	0.223_2	0.0223
240	0.189_4	0.174_2	0.015	0.179_5	0.0252
260	0.139_5	0.135_2	0.008	0.135_6	0.0103
280	0.102_2	0.100_5	0.008	0.104_3	0.0025
300	0.071_0	0.074_4	0.007	0.068_8	0.0090
Mono CO_2					
220	0.260_2	0.378_1	0.030	0.391_7	0.0198
240	0.189_4	0.269_4	0.020	0.265_0	0.0043
260	0.139_5	0.190_7	0.020	0.195_8	0.0096
280	0.102_2	0.135_7	0.008	0.139_4	0.0073
300	0.071_0	0.086_8	0.004	0.094_7	0.0072

N-decane					
	Expt.	EMD		NEMD	
T /K	η /cP	η /cP	σ_η /cP	η /cP	σ_η /cP
100 bar					
319.35	0.724_1	0.875_1	0.204	0.784_5	0.140
348.45	0.533_5	0.542_7	0.119	0.538_2	0.107
369.85	0.435_8	0.426_2	0.059	0.425_7	0.093
418.75	0.297_0	0.308_1	0.040	0.318_7	0.037
470.05	0.203_3	0.202_0	0.023	0.210_6	0.031
600 bar					
319.05	1.155_4	1.380_3	0.235	1.234_7	0.248
348.25	0.847_5	0.983_8	0.225	0.973_8	0.132
370.15	0.689_3	0.790_7	0.170	0.810_7	0.138
419.15	0.479_1	0.511_3	0.110	0.491_3	0.122
470.15	0.348_3	0.363_2	0.083	0.377_4	0.057

N-hexadecane					
	Expt.	EMD		NEMD	
T /K	η /cP	η /cP	σ_η /cP	η /cP	σ_η /cP
69 bar					
333.15	1.705	1.473_5	0.211	1.559_3	0.112
348.15	1.329	1.397_1	0.198	1.419_6	0.169
363.15	1.145	1.152_6	0.119	1.153_9	0.103
388.15	0.831	0.816_7	0.108	0.814_2	0.035
413.15	0.621	0.669_2	0.020	0.652_3	0.116
620.5 bar					
333.15	2.990	2.759_0	0.417	2.890_4	0.558
348.15	2.364	2.558_5	0.459	2.532_5	0.348
363.15	1.929	1.952_0	0.208	2.134_7	0.305
388.15	1.396	1.520_1	0.177	1.562_1	0.357
413.15	1.014	1.233_6	0.194	1.220_6	0.284

CO_2 + n-decane					
	Expt.	EMD		NEMD	
T /K	η /cP	η /cP	σ_η /cP	η /cP	σ_η /cP
Low pressures (Dimer CO_2 + n-decane)					
311.21	0.360_1	0.350_7	0.075	0.370_9	0.038
343.18	0.289_3	0.267_3	0.027	0.299_7	0.037
373.36	0.212_9	0.222_1	0.030	0.215_5	0.028
403.30	0.169_2	0.166_4	0.022	0.176_6	0.024
Low pressures (Mono CO_2 + n-decane)					
311.21	0.360_1	0.476_2	0.095	0.483_9	0.076
343.18	0.289_3	0.344_0	0.045	0.357_7	0.037
373.36	0.212_9	0.262_5	0.035	0.268_1	0.040
403.30	0.169_2	0.206_8	0.027	0.219_0	0.032
High pressures (Dimer CO_2 + n-decane)					
311.21	0.464_0	0.472_4	0.067	0.489_6	0.069
343.18	0.333_6	0.353_0	0.058	0.350_5	0.057
373.36	0.266_1	0.277_8	0.035	0.300_5	0.037
403.30	0.215_3	0.207_3	0.035	0.209_5	0.033
High pressures (Mono CO_2 + n-decane)					
311.21	0.464_0	0.588_7	0.077	0.571_0	0.068
343.18	0.333_6	0.404_9	0.035	0.420_4	0.056
373.36	0.266_1	0.327_0	0.034	0.337_3	0.050
403.30	0.215_3	0.270_6	0.034	0.234_8	0.023

CO_2 + n-hexadecane					
	Expt.	EMD		NEMD	
T /K	η /cP	η /cP	σ_η /cP	η /cP	σ_η /cP
Low pressures (Dimer CO_2 + n-hexadecane)					
298.18	1.003	0.942_4	0.079	1.040_6	0.055
323.15	0.704	0.709_6	0.083	0.744_7	0.053
373.11	0.463	0.520_7	0.052	0.528_2	0.067
423.11	0.328	0.349_9	0.026	0.369_7	0.018
473.15	0.292	0.347_2	0.028	0.321_2	0.035
Low pressures (Mono CO_2 + n-hexadecane)					
298.18	1.003	1.167_1	0.130	1.188_9	0.125
323.15	0.704	0.957_5	0.112	0.933_0	0.109
373.11	0.463	0.638_5	0.033	0.624_8	0.040
423.11	0.328	0.435_8	0.027	0.432_5	0.029
473.15	0.292	0.384_5	0.022	0.380_1	0.028
High pressures (Dimer CO_2 + n-hexadecane)					
298.18	1.344	1.275_7	0.087	1.382_2	0.148
323.15	1.122	1.128_4	0.068	1.208_5	0.127
373.11	0.775	0.851_4	0.065	0.819_9	0.093
423.11	0.683	0.775_7	0.070	0.787_4	0.061
473.15	0.520	0.601_6	0.038	0.602_6	0.057
High pressures (Mono CO_2 + n-hexadecane)					
298.18	1.344	1.708_8	0.134	1.659_7	0.194
323.15	1.122	1.475_2	0.109	1.498_1	0.130
373.11	0.775	0.993_9	0.094	0.961_6	0.088
423.11	0.683	0.894_8	0.049	0.848_5	0.119
473.15	0.520	0.669_7	0.035	0.693_7	0.114

Graphs showing the percent deviations between the simulation results and experiments (pure fluids)

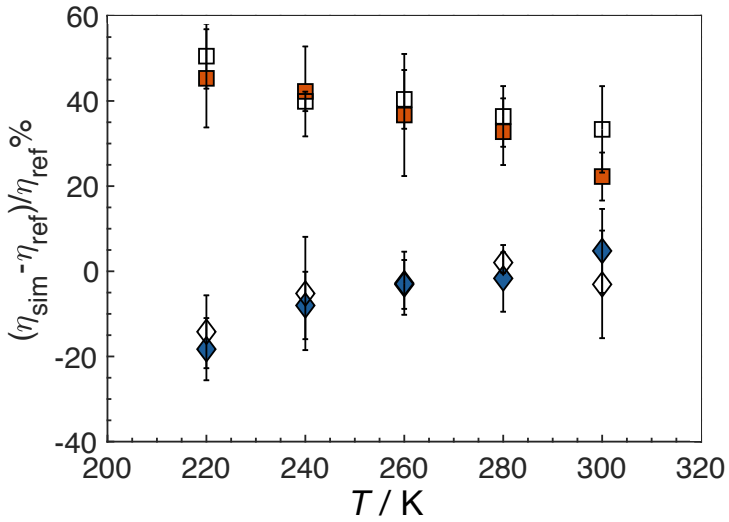


Figure S3 Percentage deviations between simulated CO_2 viscosity (η_{sim}) and reference (η_{ref}) values. Results for the one-bead CO_2 model (squares) are computed at 100 bar from 220K to 300K using EMD (filled symbols), and NEMD (empty symbols) algorithms as compared to the results generated using the two-bead model CO_2 (rhombi). Error bars are inherited from uncertainties of the simulated viscosities.

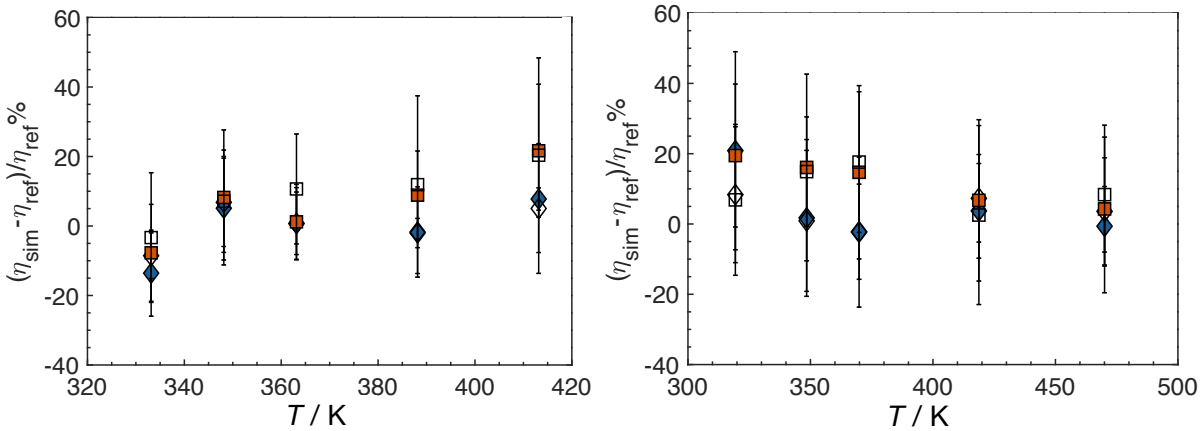


Figure S4 Percentage deviations between simulated n-hexane (left) and n-hexadecane (right) viscosity (η_{sim}) and reference (η_{ref}) values. Results are computed at 100 and 600 bar for n-hexane and 69 and 620.5 bar for n-hexadecane using EMD (filled symbols), and NEMD (empty symbols) algorithms. At higher temperatures the results are represented by squares and at low temperatures by rhombi. Error bars are inherited from uncertainties of the simulated viscosities.

Graphs showing the percent deviations between the simulation results and experiments (mixtures)

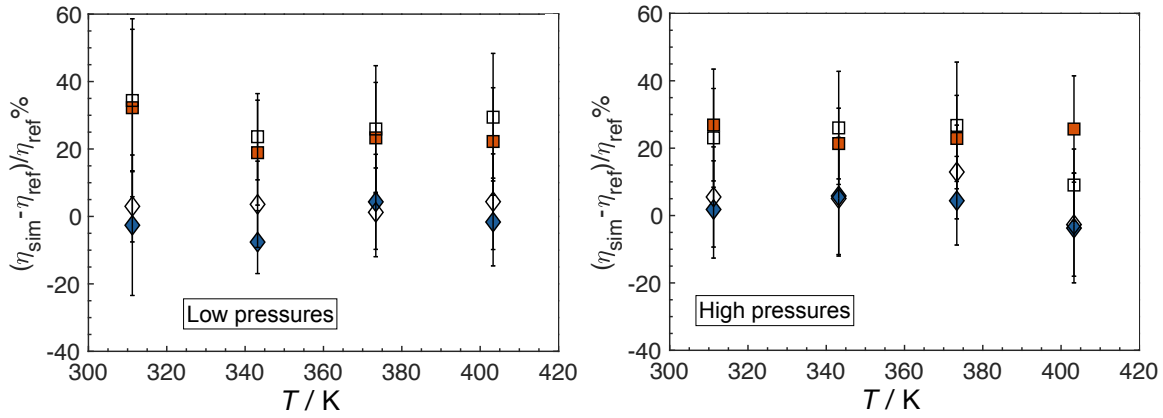


Figure S5 Percentage deviations between simulated CO_2 – n-decane binary mixture viscosity (η_{sim}) and reference (η_{ref}) values. Results generated using one-bead CO_2 model (squares) are computed using EMD (filled symbols), and NEMD (empty symbols) algorithms as compared to the results involving the two-bead model CO_2 (rhombi). Error bars are inherited from uncertainties of the simulated viscosities. The left figure corresponds to results at lower pressure conditions, while the right figure corresponds to higher pressure results.

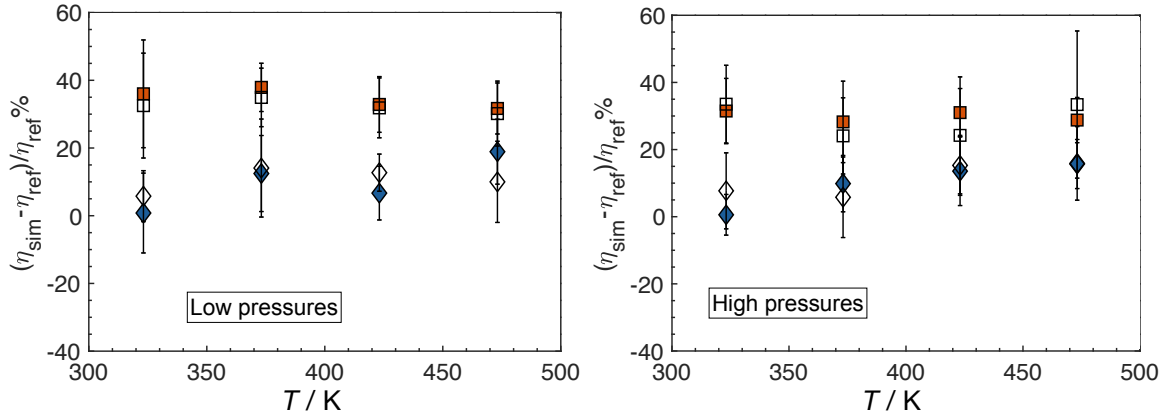


Figure S6 Percentage deviations between simulated CO_2 – n-hexadecane binary mixture viscosity (η_{sim}) and reference (η_{ref}) values. Results generated using one-bead CO_2 model (squares) are computed using EMD (filled symbols), and NEMD (empty symbols) algorithms as compared to the results involving the two-bead model CO_2 (rhombi). Error bars are inherited from uncertainties of the simulated viscosities. The left figure corresponds to results at lower pressure conditions, while the right figure corresponds to higher pressure results.

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