SUPPORTING INFORMATION

Monte Carlo Simulations of Fluid Phase Equilibria and Interfacial Properties for Water/Alkane Mixtures: An Assessment of Non-Polarizable Water Models and of Departures from the Lorentz-Berthelot Combining Rules

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DESCRIPTION

Tables listing all force field parameters, all simulation parameters, and numerical data.

Table S1. Lennard-Jones Parameters and Partial Charges for the Molecular Models

Model	Site	ε/k_B [K]	σ [Å]	q $\lvert e\rvert$	ξ_{ij} O–CH_x	O–CH_4	ζ_{ij} O–CH_3	O–CH_2
TraPPE–UA	CH_4	148	3.73	–				
	CH_3	98	3.75	–				
	CH_2	46	3.95	–				
TIP4P	O	78.0	3.154	–				
	H	–	–	+0.52				
	M	–	–	−1.04				
SPC/E	O	78.2	3.1655	−0.8476				
	H	–	–	+0.4238				
TIP4P/2005	O	93.2	3.1589	–				
	H	–	–	+0.5564				
	M	–	–	−1.1128				
TIP4P-1.1	O	78.0	3.154	–	1.1000	1.0000	1.0000	1.0000
	H	–	–	+0.52				
	M	–	–	−1.04				
TIP4P-1.2	O	78.0	3.154	–	1.2000	1.0000	1.0000	1.0000
	H	–	–	+0.52				
	M	–	–	−1.04				
SPC/E-1.7	O	78.2	3.1655	−0.8476	1.6773	0.9760	0.9767	0.9767
	H	–	–	+0.4238				
Helium	He	4.0	3.11	–				

Table S2. Bonded Parameters for the Molecular Models

Model	Bond Type	l_0 [Å]
TraPPE–UA	CH_x–CH_y	1.54
TIP4P	O–H	0.9572
	O–M	0.15
SPC/E	O–H	1.00
TIP4P/2005	O–H	0.9572
	O–M	0.1546

Model	Angle Type	k/k_B [K/rad^2]	θ_0 [°]
TraPPE–UA	CH_x–CH_2–CH_y	62500	114
TIP4P	H–O–H	Rigid	104.52
SPC/E	H–O–H	Rigid	109.47
TIP4P/2005	H–O–H	Rigid	104.52

Model	Dihedral Type	c_0/k_B [K]	c_1/k_B [K]	c_2/k_B [K]	c_3/k_B [K]
TraPPE–UA	CH_x–CH_2–CH_2–CH_y	0.00	355.03	−68.19	791.32

Table S3. Distribution of Monte Carlo Moves and DCCD-CBMC Details for Water/Methane System (2-Box NpT Gibbs Ensemble)

Move Type	Molecule or Box	Probability
Translations	Methane	0.132
	Water	0.396
Rotations	Methane	–
	Water	0.396
Regrowths	Methane	–
	Water	–
Particle transfers	Methane	0.010
	Water	0.062
Volume exchanges	Methane-rich	0.002
	Water-rich	0.002
CBMC Details		
CBMC inner cutoff		6.0 Å
First bead for water insertion		O
Number of trial sites for first bead insertion		32
Number of rigid-body rotations		16

Table S4. Distribution of Monte Carlo Moves and DCCD-CBMC Details for Water/Ethane System (2-Box NpT Gibbs Ensemble)

Move Type	Molecule or Box	Probability
Translations	Ethane	0.109
	Water	0.327
Rotations	Ethane	0.109
	Water	0.327
Regrowths	Ethane	–
	Water	–
Particle transfers	Ethane	0.042
	Water	0.082
Volume exchanges	Ethane-rich	0.002
	Water-rich	0.002
CBMC Details		
CBMC inner cutoff		6.0 Å
First bead for water insertion		O
First bead for ethane insertion		CH_3
Number of trial sites for first bead insertion		32
Number of rigid-body rotations		16

Table S5. Distribution of Monte Carlo Moves and DCCD-CBMC Details for Water/Propane System [3-Box NVT Gibbs Ensemble; Water-rich Liquid (WL), Propane-rich Liquid (PL), Propane-rich Vapor (PV)]

Move Type	Molecule or Box	Probability
Translations	Propane	0.120
	Water	0.080
Rotations	Propane	0.120
	Water	0.080
Regrowths	Propane	0.120
	Water	–
Particle transfers	Propane (WL/PV)	0.214
	Propane (PL/PV)	0.003
	Water (WL/PV)	0.256
	Water (PL/PV)	0.005
Volume exchanges	PL/PV	0.001
	WL/PV	0.001
CBMC Details		
CBMC inner cutoff		6.0 Å
First bead for water insertion		O
First bead for propane insertion		CH_3
Number of trial sites for first bead insertion		32
Number of rigid-body rotations		16

Table S6. Distribution of Monte Carlo Moves and DCCD-CBMC Details for Water/*n*-Alkane Systems Without Transfer of Alkanes [3-Box *NpT* Gibbs Ensemble; Water-rich Liquid (WL), Alkane-rich Liquid (AL), Vapor (V)]

Move Type	Mixture	Molecule or Box	Probability
Translations & Rotations	W/C5	Pentane	0.090
		Water	0.110
	W/C6	Hexane	0.082
		Water	0.118
	W/C7	Heptane	0.076
		Water	0.124
	W/C8	Octane	0.066
		Water	0.134
	W/C9	Nonane	0.062
		Water	0.138
Regrowths	All	Alkane	0.198
		Water	–
Particle transfers[a]	All	Alkane	–
		Water (WL/V)	0.368
		Water (AL/V)	0.032
Volume exchanges	All	Alkane	0.001
		Water	0.001
		Vapor	–

CBMC Details	
CBMC inner cutoff	6.0 Å
Description of first bead for water insertion	O
Number of trial sites for first bead insertion	32
Number of rigid-body rotations	16

[a]A total fraction of 40% for particle transfers of water yields about 0.5 accepted WL/V and AL/V transfer moves.

Table S7. Distribution of Monte Carlo Moves and DCCD-CBMC Details for Water/*n*-Alkane Systems with Transfer of Alkanes [3-Box *NpT* Gibbs Ensemble; Water-rich Liquid (WL), Alkane-rich Liquid (AL), Vapor (V)]

Move Type	Mixture	Molecule or Box	Probability
Translations & Rotations	W/C5	Pentane	0.090
		Water	0.110
	W/C6	Hexane	0.082
		Water	0.118
	W/C7	Heptane	0.076
		Water	0.124
	W/C8	Octane	0.066
		Water	0.134
	W/C9	Nonane	0.062
		Water	0.138
Regrowths	All	Alkane	0.198
		Water	–
Particle transfers	All	Alkane (AL/V)	0.01
		Water (WL/V)	0.098
		Water (AL/V)	0.002
		Impurities (WL/V)	0.09
Identity switch	All	WL/V	0.200
Volume exchanges	All	Alkane	0.001
		Water	0.001
		Vapor	–

CBMC Details	
CBMC inner cutoff	6.0 Å
Description of first bead for water insertion	O
First bead for alkane insertion	CH_3
Number of trial sites for first bead insertion	32
Number of rigid-body rotations	16

Table S8. Distribution of Monte Carlo Moves and DCCD-CBMC Details for Water/*n*-Alkane Systems [2-Box NpT Gibbs Ensemble; Water-rich Liquid (WL), Vapor (V)]

Move Type	Molecule or Box	Probability
Translations	Water	0.320
	Helium	0.044
	Alkanes	0.036
Rotations	Water	0.368
	Alkanes	0.032
Regrowths	Alkanes	0.030
Particle transfers	Water	0.137
	Alkanes	0.013
Identity switch	Alkanes	0.018
Volume exchanges	WL	0.001
	V	0.001
CBMC Details		
CBMC inner cutoff		6.0 Å
Description of first bead for water insertion		O
Number of trial sites for first bead insertion		32
Number of rigid-body rotations		16

Table S9. Distribution of Monte Carlo Moves and DCCD-CBMC Details for Water/*n*-Hexane Interfacial Tension System [1-Box Np_NAT Ensemble;]

Move Type	Molecule or Box	Probability
Translations	Water	0.302
	n-Hexane	0.048
Rotations	Water	0.302
	n-Hexane	0.048
Regrowths	Water	–
	n-Hexane	0.298
Volume moves		0.002
CBMC Details		
CBMC inner cutoff		6.0 Å

Table S10. Binary Water (1) + Methane (2) Mixture at $T = 366.5$ K

p/MPa	Model	$y_1/10^{-3}$	$u(y_1)/10^{-3}$	$x_2/10^{-3}$	$u(x_2)/10^{-3}$	S	$u(S)$
3.45	Expt.[1]	23.54					
	TIP4P	36.03	0.80	0.556	0.017	0.426	0.046
	SPC/E	9.90	0.31	0.465	0.016	0.866	0.051
	TIP4P/2005	8.42	0.21	0.383	0.019	1.028	0.047
	TIP4P-1.1	36.4	1.1	0.810	0.034	0.435	0.050
	TIP4P-1.2	36.69	0.63	1.227	0.050	0.444	0.043
	SPC/E-1.7	10.54	0.12	9.81	0.24	0.803	0.042
6.89	Expt.[1]	13.25					
	TIP4P	17.94	0.50	1.025	0.042	0.303	0.049
	SPC/E	4.90	0.16	0.870	0.033	0.995	0.052
	TIP4P/2005	4.16	0.11	0.723	0.037	1.158	0.047
	TIP4P-1.1	18.34	0.42	1.560	0.062	0.325	0.046
	TIP4P-1.2	18.67	0.51	2.330	0.045	0.343	0.048
	SPC/E-1.7	5.63	0.14	17.660	0.433	0.855	0.047
20.68	Expt.[1]	6.56					
	TIP4P	6.08	0.15	2.406	0.070	0.076	0.047
	SPC/E	1.647	0.048	1.10	0.10	1.382	0.049
	TIP4P/2005	1.456	0.024	1.657	0.055	1.505	0.043
	TIP4P-1.1	6.38	0.12	3.70	0.15	0.029	0.044
	TIP4P-1.2	6.57	0.12	5.71	0.23	0.003	0.044
	SPC/E-1.7	2.454	0.095	38.5	1.0	0.983	0.056
41.37	Expt.[1]	3.96					
	TIP4P	3.077	0.056	3.66	0.14	0.252	0.044
	SPC/E	0.869	0.059	3.11	0.19	1.516	0.078
	TIP4P/2005	0.778	0.038	2.64	0.14	1.627	0.063
	TIP4P-1.1	3.40	0.10	5.58	0.20	0.151	0.050
	TIP4P-1.2	3.87	0.11	8.56	0.24	0.023	0.050
	SPC/E-1.7	1.703	0.037	55.63	0.85	0.844	0.045
75.84	Expt.[1]	3.13					
	TIP4P	1.822	0.056	4.86	0.20	0.541	0.064
	SPC/E	0.479	0.018	4.30	0.32	1.877	0.055
	TIP4P/2005	0.471	0.033	3.49	0.21	1.894	0.081
	TIP4P-1.1	2.13	0.11	7.77	0.43	0.386	0.065
	TIP4P-1.2	2.399	0.094	11.54	0.69	0.266	0.056
	SPC/E-1.7	1.43	0.14	73.0	1.8	0.78	0.11

Mole fraction of water in methane-rich, vapor phase (y_1), mole fraction of methane in water-rich, liquid phase (x_2), score (S), and 95% confidence intervals (u).

Table S11. Binary Water (1) + Methane (2) Mixture at $T = 376.0$ K

p/MPa	Model	$y_1/10^{-3}$	$u(y_1)/10^{-3}$	$x_2/10^{-3}$	$u(x_2)/10^{-3}$	S	$u(S)$
10.90	Expt.[2]			1.40			
	TIP4P	16.06	0.33	1.64	0.032	0.156	0.045
	SPC/E	4.59	0.12	1.375	0.087	0.018	0.075
	TIP4P/2005	4.12	0.10	1.016	0.064	0.321	0.075
	TIP4P-1.1	16.79	0.54	2.359	0.085	0.522	0.054
	TIP4P-1.2	17.28	0.30	3.50	0.13	0.917	0.055
	SPC/E-1.7	5.68	0.13	23.31	0.60	2.812	0.048
20.60	Expt.[2]			2.30			
	TIP4P	8.45	0.20	2.60	0.11	0.123	0.058
	SPC/E	2.458	0.064	2.10	0.13	0.090	0.073
	TIP4P/2005	2.116	0.066	1.78	0.12	0.258	0.077
	TIP4P-1.1	8.98	0.25	3.80	0.19	0.503	0.065
	TIP4P-1.2	9.65	0.16	5.65	0.20	0.899	0.054
	SPC/E-1.7	3.519	0.066	37.01	0.71	2.778	0.044
30.20	Expt.[2]			3.00			
	TIP4P	5.82	0.27	3.29	0.12	0.092	0.054
	SPC/E	1.706	0.052	2.71	0.17	0.101	0.073
	TIP4P/2005	1.517	0.054	2.26	0.11	0.282	0.061
	TIP4P-1.1	6.40	0.19	5.05	0.20	0.521	0.057
	TIP4P-1.2	7.15	0.18	7.54	0.21	0.921	0.049
	SPC/E-1.7	2.825	0.070	45.89	0.78	2.728	0.043
40.20	Expt.[2]			3.50			
	TIP4P	4.53	0.14	3.92	0.13	0.114	0.051
	SPC/E	1.297	0.035	3.28	0.18	0.066	0.067
	TIP4P/2005	1.198	0.093	2.663	0.094	0.273	0.053
	TIP4P-1.1	4.78	0.12	5.78	0.29	0.501	0.064
	TIP4P-1.2	5.44	0.16	8.62	0.40	0.901	0.061
	SPC/E-1.7	2.59	0.17	53.4	1.3	2.725	0.047
49.90	Expt.[2]			4.10			
	TIP4P	3.72	0.17	4.182	0.080	0.020	0.044
	SPC/E	1.082	0.051	3.50	0.13	0.159	0.054
	TIP4P/2005	0.992	0.032	2.92	0.15	0.338	0.065
	TIP4P-1.1	4.23	0.14	6.41	0.13	0.446	0.045
	TIP4P-1.2	4.64	0.14	10.14	0.28	0.906	0.049
	SPC/E-1.7	2.36	0.15	59.5	1.1	2.674	0.044

Mole fraction of water in methane-rich, vapor phase (y_1), mole fraction of methane in water-rich, liquid phase (x_2), score (S), and 95% confidence intervals (u).

Table S12. Binary Water (1) + Methane (2) Mixture at $T = 477.5$ K

p/MPa	Model	$y_1/10^{-1}$	$u(y_1)/10^{-1}$	$x_2/10^{-1}$	$u(x_2)/10^{-1}$	S	$u(S)$
75.84	Expt.[1]	0.510					
	TIP4P	0.481	0.011	0.1622	0.0031	0.059	0.046
	SPC/E	0.1702	0.0033	0.1076	0.0021	1.097	0.044
	TIP4P/2005	0.1590	0.0028	0.0851	0.0020	1.166	0.044
	TIP4P-1.1	0.5423	0.0094	0.2187	0.0049	0.061	0.044
	TIP4P-1.2	0.641	0.020	0.2985	0.0077	0.228	0.051
	SPC/E-1.7	0.408	0.017	0.877	0.018	0.223	0.058
96.53	Expt.[1]	0.494					
	TIP4P	0.377	0.013	0.1765	0.0048	0.271	0.053
	SPC/E	0.1347	0.0026	0.1175	0.0031	1.299	0.044
	TIP4P/2005	0.1276	0.0041	0.0957	0.0018	1.354	0.051
	TIP4P-1.1	0.440	0.012	0.2388	0.0070	0.117	0.049
	TIP4P-1.2	0.508	0.016	0.3349	0.0093	0.028	0.050
	SPC/E-1.7	0.373	0.021	1.018	0.025	0.282	0.070
110.32	Expt.[1]	0.455					
	TIP4P	0.3259	0.0097	0.1815	0.0034	0.334	0.050
	SPC/E	0.1190	0.0030	0.1267	0.0026	1.341	0.047
	TIP4P/2005	0.1150	0.0049	0.0974	0.0025	1.375	0.059
	TIP4P-1.1	0.3849	0.0095	0.2496	0.0063	0.167	0.047
	TIP4P-1.2	0.453	0.017	0.3499	0.0096	0.0048	0.055
	SPC/E-1.7	0.342	0.013	1.089	0.011	0.284	0.056

Mole fraction of water in methane-rich, vapor phase (y_1), mole fraction of methane in water-rich, liquid phase (x_2), score (S), and 95% confidence intervals (u).

Table S13. Binary Water (1) + Ethane (2) Mixture at $T = 366.5$ K

p/MPa	Model	$y_1/10^{-3}$	$u(y_1)/10^{-3}$	$x_2/10^{-3}$	$u(x_2)/10^{-3}$	S	$u(S)$
3.45	Expt.[1]	22.46					
	TIP4P	32.96	0.48	0.441	0.035	0.384	0.043
	SPC/E	9.17	0.28	0.369	0.038	0.895	0.050
	TIP4P/2005	7.73	0.29	0.293	0.033	1.067	0.055
	TIP4P-1.1	33.78	0.93	0.894	0.055	0.408	0.048
	TIP4P-1.2	34.22	0.74	1.78	0.12	0.421	0.045
	SPC/E-1.7	9.99	0.22	29.5	1.1	0.810	0.045
6.89	Expt.[1]	12.38					
	TIP4P	14.58	0.31	0.796	0.083	0.164	0.045
	SPC/E	4.05	0.13	0.623	0.034	1.117	0.051
	TIP4P/2005	3.45	0.15	0.537	0.049	1.277	0.058
	TIP4P-1.1	15.01	0.28	1.57	0.10	0.192	0.044
	TIP4P-1.2	15.60	0.51	2.98	0.15	0.231	0.052
	SPC/E-1.7	5.115	0.094	41.65	0.97	0.884	0.044
20.68	Expt.[1]	6.43					
	TIP4P	3.32	0.11	1.219	0.066	0.661	0.052
	SPC/E	0.924	0.047	0.920	0.079	1.940	0.065
	TIP4P/2005	0.858	0.034	0.796	0.070	2.014	0.056
	TIP4P-1.1	3.82	0.18	2.36	0.24	0.522	0.061
	TIP4P-1.2	4.69	0.22	4.65	0.26	0.315	0.062
	SPC/E-1.7	2.51	0.13	57.6	1.6	0.940	0.065
41.37	Expt.[1]	4.06					
	TIP4P	2.034	0.066	1.38	0.18	0.691	0.052
	SPC/E	0.546	0.030	1.20	0.12	2.006	0.068
	TIP4P/2005	0.542	0.047	0.89	0.17	2.013	0.095
	TIP4P-1.1	2.39	0.12	2.82	0.22	0.529	0.064
	TIP4P-1.2	3.00	0.12	5.41	0.16	0.302	0.057
	SPC/E-1.7	2.07	0.15	67.2	2.4	0.672	0.083
75.84	Expt.[1]	3.02					
	TIP4P	1.346	0.031	1.602	0.086	0.808	0.046
	SPC/E	0.365	0.013	1.38	0.22	2.114	0.053
	TIP4P/2005	0.358	0.023	1.13	0.17	2.133	0.076
	TIP4P-1.1	1.606	0.065	3.05	0.26	0.632	0.057
	TIP4P-1.2	2.096	0.054	6.27	0.50	0.365	0.048
	SPC/E-1.7	1.61	0.18	73.7	2.2	0.63	0.12

Mole fraction of water in ethane-rich, vapor phase (y_1), mole fraction of ethane in water-rich, liquid phase (x_2), score (S), and 95% confidence intervals (u).

Table S14. Binary Water (1) + Ethane (2) Mixture at $T = 377.6$ K

p/MPa	Model	$y_1/10^{-3}$	$u(y_1)/10^{-3}$	$x_2/10^{-3}$	$u(x_2)/10^{-3}$/MPa	S	$u(S)$
3.78	Expt.[3]			0.391			
	TIP4P	46.64	0.78	0.495	0.041	0.235	0.091
	SPC/E	13.34	0.32	0.426	0.025	0.087	0.072
	TIP4P/2005	11.21	0.35	0.335	0.040	0.15	0.13
	TIP4P-1.1	47.02	0.73	0.990	0.046	0.929	0.061
	TIP4P-1.2	46.86	0.34	1.89	0.10	1.576	0.066
	SPC/E-1.7	14.60	0.35	27.60	0.66	4.257	0.047
7.72	Expt.[3]			0.661			
	TIP4P	19.76	0.51	0.871	0.081	0.28	0.10
	SPC/E	5.65	0.17	0.668	0.070	0.011	0.11
	TIP4P/2005	4.92	0.21	0.578	0.069	0.13	0.13
	TIP4P-1.1	20.34	0.33	1.679	0.063	0.932	0.055
	TIP4P-1.2	21.48	0.67	3.17	0.20	1.567	0.074
	SPC/E-1.7	7.12	0.19	41.4	1.3	4.137	0.051
23.82	Expt.[3]			1.132			
	TIP4P	4.82	0.11	1.360	0.088	0.184	0.076
	SPC/E	1.381	0.051	1.013	0.072	0.111	0.082
	TIP4P/2005	1.308	0.075	0.963	0.081	0.161	0.093
	TIP4P-1.1	5.44	0.12	2.55	0.16	0.810	0.074
	TIP4P-1.2	6.49	0.27	5.04	0.29	1.494	0.070
	SPC/E-1.7	3.65	0.12	57.6	1.2	3.930	0.045
48.33	Expt.[3]			1.329			
	TIP4P	2.748	0.090	1.544	0.078	0.150	0.065
	SPC/E	0.776	0.045	1.43	0.20	0.07	0.15
	TIP4P/2005	0.772	0.024	1.07	0.16	0.21	0.15
	TIP4P-1.1	3.42	0.28	3.02	0.17	0.821	0.068
	TIP4P-1.2	4.08	0.20	6.09	0.12	1.522	0.045
	SPC/E-1.7	3.34	0.45	67.5	2.2	3.928	0.051
68.50	Expt.[3]			1.514			
	TIP4P	2.127	0.035	1.78	0.18	0.16	0.11
	SPC/E	0.622	0.016	1.51	0.13	0.00034	0.093
	TIP4P/2005	0.637	0.039	1.25	0.12	0.20	0.10
	TIP4P-1.1	2.76	0.18	3.44	0.28	0.822	0.090
	TIP4P-1.2	3.23	0.11	6.40	0.39	1.441	0.073
	SPC/E-1.7	2.74	0.40	75.3	2.7	3.906	0.054

Mole fraction of water in ethane-rich, vapor phase (y_1), mole fraction of ethane in water-rich, liquid phase (x_2), score (S), and 95% confidence intervals (u).

Table S15. Binary Water (1) + Ethane (2) Mixture at $T = 466.5$ K

p/MPa	Model	$y_1/10^{-2}$	$u(y_1)/10^{-2}$	$x_2/10^{-2}$	$u(x_2)/10^{-2}$	S	$u(S)$
75.84	Expt.[1]	4.55					
	TIP4P	2.782	0.043	0.610	0.018	0.492	0.043
	SPC/E	0.994	0.025	0.386	0.016	1.522	0.047
	TIP4P/2005	0.993	0.025	0.318	0.013	1.522	0.047
	TIP4P-1.1	3.449	0.089	0.986	0.047	0.277	0.048
	TIP4P-1.2	4.16	0.13	1.707	0.047	0.091	0.050
	SPC/E-1.7	4.09	0.27	9.60	0.26	0.107	0.076
96.53	Expt.[1]	4.01					
	TIP4P	2.217	0.058	0.619	0.022	0.593	0.048
	SPC/E	0.807	0.019	0.416	0.0088	1.603	0.046
	TIP4P/2005	0.800	0.021	0.330	0.010	1.613	0.048
	TIP4P-1.1	2.729	0.086	1.054	0.034	0.385	0.051
	TIP4P-1.2	3.339	0.079	1.781	0.041	0.183	0.046
	SPC/E-1.7	4.00	0.35	10.40	0.22	0.0036	0.096
110.32	Expt.[1]	3.72					
	TIP4P	1.948	0.031	0.639	0.021	0.647	0.043
	SPC/E	0.708	0.015	0.426	0.021	1.659	0.046
	TIP4P/2005	0.720	0.019	0.331	0.015	1.642	0.048
	TIP4P-1.1	2.44	0.12	1.040	0.049	0.422	0.062
	TIP4P-1.2	3.11	0.11	1.697	0.051	0.180	0.052
	SPC/E-1.7	3.40	0.22	10.84	0.45	0.090	0.076

Mole fraction of water in ethane-rich, vapor phase (y_1), mole fraction of ethane in water-rich, liquid phase (x_2), score (S), and 95% confidence intervals (u).

Table S16. Binary Water (1) + Propane (2) Mixture at $T = 313.0$, 338.0, and 360.0 K

T / K	Model	y_1 $/10^{-3}$	$u(y_1)$ $/10^{-3}$	S	$u(S)$	x_1^{P} $/10^{-4}$	$u(x_1^{\mathrm{P}})$ $/10^{-4}$	S	$u(S)$
313.0	Expt.[a, 4]	4.95				6.71			
	TIP4P	5.36	0.20	0.078	0.055	2.81	0.10	0.871	0.055
	SPC/E	1.177	0.051	1.438	0.059	0.616	0.070	2.391	0.073
	TIP4P/2005	0.940	0.069	1.666	0.084	0.594	0.038	2.427	0.075
	TIP4P-1.1	5.65	0.11	0.132	0.045	3.607	0.090	0.621	0.047
	TIP4P-1.2	5.80	0.21	0.157	0.054	4.64	0.18	0.369	0.056
	SPC/E-1.7	1.249	0.051	1.378	0.057	2.79	0.10	0.878	0.054
338.0	Expt.[a, 4]	9.02				22.49			
	TIP4P	10.02	0.21	0.105	0.045	11.29	0.10	0.689	0.041
	SPC/E	2.406	0.049	1.322	0.045	2.75	0.10	2.104	0.054
	TIP4P/2005	2.103	0.085	1.457	0.057	2.74	0.13	2.106	0.061
	TIP4P-1.1	10.22	0.24	0.125	0.046	13.64	0.37	0.500	0.048
	TIP4P-1.2	10.58	0.16	0.160	0.043	16.94	0.37	0.284	0.046
	SPC/E-1.7	2.83	0.10	1.160	0.054	9.85	0.37	0.826	0.055
360.0	Expt.[a, 4]	12.78				54.2			
	TIP4P	12.79	0.65	0.043	0.065	36.5	1.0	0.397	0.049
	SPC/E	3.54	0.13	1.284	0.055	9.80	0.23	1.711	0.046
	TIP4P/2005	3.16	0.25	1.402	0.088	9.51	0.36	1.742	0.055
	TIP4P-1.1	14.18	0.41	0.103	0.049	43.31	0.82	0.224	0.044
	TIP4P-1.2	14.80	0.41	0.146	0.049	50.6	1.5	0.069	0.050
	SPC/E-1.7	4.75	0.38	0.994	0.089	25.7	1.0	0.748	0.056

[a]Data at these temperatures are from linear interpolation of two nearest temperatures. Mole fraction of water in propane-rich, vapor phase (y_1), mole fraction of water in propane-rich, liquid phase (x_1^{P}), score (S), and 95% confidence intervals (u).

Table S17. Binary Water (1) + Propane (2) Mixture at $T = 313.0$, 338.0 and 360.0 K

T / K	Model	x_2^{W} /10^{-4}	$u(x_2^{\mathrm{W}})$ /10^{-4}	S	$u(S)$	p_{vap} /MPa	$u(p_{\mathrm{vap}})$ /MPa
313.0	Expt.[a, 4]	2.005					
	TIP4P	1.79	0.16	0.128	0.099	1.676	0.011
	SPC/E	1.40	0.25	0.38	0.18	1.674	0.018
	TIP4P/2005	1.41	0.42	0.47	0.30	1.660	0.016
	TIP4P-1.1	4.60	0.41	0.83	0.10	1.670	0.017
	TIP4P-1.2	15.6	1.7	2.05	0.12	1.682	0.014
	SPC/E-1.7	492	18	5.502	0.054	1.653	0.024
338.0	Expt.[a, 4]	2.043					
	TIP4P	1.95	0.30	0.15	0.16	2.769	0.011
	SPC/E	1.68	0.16	0.20	0.10	2.724	0.051
	TIP4P/2005	1.31	0.18	0.46	0.14	2.775	0.056
	TIP4P-1.1	4.95	0.72	0.87	0.15	2.806	0.020
	TIP4P-1.2	13.8	1.9	1.90	0.14	2.808	0.018
	SPC/E-1.7	478	20	5.455	0.059	2.725	0.027
360.0	Expt.[a, 4]	2.495					
	TIP4P	2.62	0.21	0.079	0.090	4.196	0.046
	SPC/E	1.85	0.28	0.31	0.16	4.130	0.042
	TIP4P/2005	1.48	0.24	0.54	0.17	4.072	0.069
	TIP4P-1.1	6.53	0.32	0.960	0.063	4.143	0.013
	TIP4P-1.2	16.6	1.3	1.889	0.087	4.147	0.027
	SPC/E-1.7	436	12	5.163	0.048	4.077	0.067

[a]Data at these temperatures are from linear interpolation of two nearest temperatures.
Mole fraction of propane in water-rich liquid phase (x_2^{W}), saturated vapor pressur (p_{vap}), score (S), and 95% confidence intervals (u).

Table S18. Binary Water (1) + n-Alkane (2) Mixtures at $T = 298.15$ K and $p = 0.1013$ MPa

C_nH_{2n+2}	x_1^A /10^{-5}	x_1^A /10^{-5}	$u(x_1^A)$ /10^{-5}	S	$u(S)$	x_1^A /10^{-5}	$u(x_1^A)$ /10^{-5}	S	$u(S)$
	Expt.[5,6]		TIP4P				SPC/E		
5	40.4	9.02	0.17	1.500	0.044	1.775	0.064	3.126	0.054
6	43.0	8.81	0.22	1.586	0.047	1.76	0.11	3.198	0.075
7	45.6	8.89	0.34	1.636	0.055	1.718	0.031	3.279	0.044
8	50.0	8.88	0.26	1.728	0.049	1.679	0.089	3.396	0.067
9	54.0	8.86	0.23	1.808	0.048	1.711	0.052	3.452	0.050
			TIP4P/2005				TIP4P-1.1		
5		1.905	0.061	3.055	0.051	12.49	0.28	1.174	0.046
6		1.79	0.10	3.183	0.069	12.21	0.34	1.259	0.049
7		1.775	0.078	3.247	0.059	12.01	0.32	1.335	0.048
8		1.871	0.053	3.286	0.049	12.35	0.46	1.399	0.055
9		1.869	0.038	3.364	0.045	12.66	0.21	1.451	0.043
			TIP4P-1.2				SPC/E-1.7		
5		17.25	0.66	0.852	0.055	13.54	0.37	1.094	0.027
6		16.90	0.44	0.935	0.048	15.22	0.68	1.040	0.045
7		16.86	0.49	0.995	0.050	15.84	0.62	1.059	0.040
8		17.25	0.51	1.065	0.050	17.09	0.77	1.075	0.045
9		17.65	0.35	1.119	0.045	18.00	0.72	1.099	0.040

Mole fraction of water in n-alkane-rich liquid phase (x_1^A), score (S), and 95% confidence intervals (u).

Table S19. Binary Water (1) + n-Alkane (2) Mixtures at $T = 298.15$ K and $p = 0.1013$ MPa

C_nH_{2n+2}	x_2^W	x_2^W	$u(x_2^W)$	S	$u(S)$
	Expt.[5,7]		TIP4P		
5	9.87×10^{-6}	6.30×10^{-6}	0.76×10^{-6}	0.46	0.12
6	1.98×10^{-6}	1.33×10^{-6}	0.22×10^{-6}	0.42	0.18
7	4.03×10^{-7}	2.91×10^{-7}	0.66×10^{-7}	0.37	0.21
8	6.80×10^{-8}	6.4×10^{-8}	1.9×10^{-8}	0.31	0.16
9	1.71×10^{-8}	1.43×10^{-8}	0.52×10^{-8}	0.44	0.21
			SPC/E		
5		8.7×10^{-6}	2.6×10^{-6}	0.31	0.15
6		1.83×10^{-6}	0.53×10^{-6}	0.28	0.15
7		4.02×10^{-7}	0.88×10^{-7}	0.23	0.12
8		8.5×10^{-8}	1.6×10^{-8}	0.29	0.11
9		1.80×10^{-8}	0.46×10^{-8}	0.31	0.12
			TIP4P/2005		
5		6.3×10^{-6}	1.1×10^{-6}	0.48	0.18
6		1.33×10^{-6}	0.38×10^{-6}	0.47	0.30
7		2.54×10^{-7}	0.98×10^{-7}	0.62	0.27
8		4.5×10^{-8}	1.6×10^{-8}	0.55	0.36
9		6.7×10^{-9}	2.1×10^{-9}	1.01	0.30
			TIP4P-1.1		
5		3.72×10^{-5}	0.54×10^{-5}	1.31	0.16
6		1.00×10^{-5}	0.20×10^{-5}	1.59	0.20
7		2.76×10^{-6}	0.59×10^{-6}	1.89	0.22
8		7.3×10^{-7}	2.3×10^{-7}	2.31	0.32
9		2.11×10^{-7}	0.94×10^{-7}	2.37	0.45
			TIP4P-1.2		
5		2.25×10^{-4}	0.34×10^{-4}	3.11	0.15
6		8.1×10^{-5}	2.0×10^{-5}	3.67	0.26
7		3.29×10^{-5}	0.92×10^{-5}	4.33	0.33
8		1.36×10^{-5}	0.42×10^{-5}	5.22	0.34
9		5.0×10^{-6}	2.1×10^{-6}	5.55	0.42
			SPC/E-1.7		
5		4.61×10^{-2}	0.18×10^{-2}	8.449	0.039
6		4.13×10^{-2}	0.16×10^{-2}	9.945	0.037
7		3.43×10^{-2}	0.13×10^{-2}	11.350	0.038
8		3.10×10^{-2}	0.12×10^{-2}	13.029	0.039
9		2.556×10^{-2}	0.072×10^{-2}	14.214	0.028

Mole fraction of alkane in water-rich liquid phase (x_2^W), score (S), and 95% confidence intervals (u).

Table S20. Gibbs Free Energy of Transfer for Water/n-Alkane Mixtures at $T = 298.15$ K and $p = 0.1013$ MPa

C_nH_{2n+2}	$\Delta G^{W}_{wat\to vap}$ /kJ·mol^{-1}	$\Delta G^{W}_{wat\to vap}$ /kJ·mol^{-1}	$u(\Delta G^{W}_{wat\to vap})$ /kJ·mol^{-1}	$\Delta G^{W}_{wat\to vap}$ /kJ·mol^{-1}	$u(\Delta G^{W}_{wat\to vap})$ /kJ·mol^{-1}
	Expt.[8]	TIP4P		SPC/E	
5		25.426	0.037	29.479	0.091
6		25.416	0.057	29.510	0.074
7	26.4	25.372	0.093	29.451	0.036
8		25.414	0.056	29.52	0.11
9		25.443	0.062	29.513	0.068
		TIP4P/2005		TIP4P-1.1	
5		30.004	0.072	25.414	0.055
6		30.12	0.13	25.416	0.065
7		30.12	0.10	25.443	0.051
8		30.050	0.089	25.424	0.085
9		30.091	0.051	25.425	0.039
		TIP4P-1.2		SPC/E-1.7	
5		25.393	0.076	29.432	0.046
6		25.433	0.056	29.299	0.080
7		25.449	0.067	29.342	0.083
8		25.425	0.072	29.349	0.089
9		25.440	0.051	29.311	0.051

Gibbs free energy of transfer of water from water-rich liquid phase to vapor phase ($\Delta G^{W}_{wat\to vap}$) and 95% confidence interval (u).

Table S21. Gibbs Free Energy of Transfer for Water/n-Alkane Mixtures at $T = 298.15$ K and $p = 0.1013$ MPa

C_nH_{2n+2}	$\Delta G^{W}_{vap\to alk}$ /kJ·mol^{-1}	$\Delta G^{W}_{vap\to alk}$ /kJ·mol^{-1}	$u(\Delta G^{W}_{vap\to alk})$ /kJ·mol^{-1}	$\Delta G^{W}_{vap\to alk}$ /kJ·mol^{-1}	$u(\Delta G^{W}_{vap\to alk})$ /kJ·mol^{-1}
	Expt.[5,8]	TIP4P		SPC/E	
5	−2.50	2.256	0.025	2.2497	0.0074
6	−2.35	2.629	0.015	2.636	0.019
7	−2.19	2.930	0.028	2.940	0.026
8	−2.16	3.139	0.023	3.184	0.030
9	−2.14	3.346	0.019	3.366	0.013
		TIP4P/2005		TIP4P-1.1	
5		1.545	0.036	1.462	0.019
6		1.892	0.035	1.819	0.017
7		2.181	0.029	2.106	0.021
8		2.376	0.033	2.312	0.017
9		2.564	0.029	2.479	0.016
		TIP4P-1.2		SPC/E-1.7	
5		0.672	0.019	−3.202	0.037
6		0.984	0.034	−3.073	0.059
7		1.248	0.023	−2.920	0.033
8		1.467	0.017	−2.870	0.052
9		1.625	0.030	−2.734	0.043

Gibbs free energy of transfer of water from vapor phase to n-alkane-rich liquid phase ($\Delta G^{W}_{vap\to alk}$) and 95% confidence interval (u).

Table S22. Gibbs Free Energy of Transfer for Water/n-Alkane Mixtures at $T = 298.15$ K and $p = 0.1013$ MPa

C_nH_{2n+2}	$\Delta G^{A}_{vap\to wat}$ /kJ·mol^{-1}	$\Delta G^{A}_{vap\to wat}$ /kJ·mol^{-1}	$u(\Delta G^{A}_{vap\to wat})$ /kJ·mol^{-1}	$\Delta G^{A}_{vap\to wat}$ /kJ·mol^{-1}	$u(\Delta G^{A}_{vap\to wat})$ /kJ·mol^{-1}
	Expt.[7,8]	TIP4P		SPC/E	
5	9.72	11.76	0.30	11.05	0.64
6	10.7	12.85	0.44	12.12	0.65
7	11.7	13.89	0.56	13.13	0.58
8	13.1	14.94	0.70	14.19	0.51
9	13.6	15.90	0.85	15.30	0.59
		TIP4P/2005		TIP4P-1.1	
5		11.79	0.45	7.38	0.39
6		12.99	0.77	7.78	0.42
7		14.38	0.89	8.35	0.54
8		15.91	0.98	8.97	0.78
9		17.75	0.76	9.6	1.1
		TIP4P-1.2		SPC/E-1.7	
5		2.93	0.37	−9.972	0.084
6		2.67	0.55	−12.449	0.073
7		2.25	0.77	−14.734	0.073
8		1.74	0.89	−17.289	0.085
9		1.5	1.1	−19.508	0.071

Gibbs free energy of transfer of alkane from vapor phase to water-rich liquid phase ($\Delta G^{A}_{vap\to war}$) and 95% confidence interval (u).

Table S23. Gibbs Free Energy of Transfer for Water/n-Alkane Mixtures at $T = 298.15$ K and $p = 0.1013$ MPa

C_nH_{2n+2}	$\Delta G^{A}_{alk\to vap}$ /kJ·mol^{-1}	$\Delta G^{A}_{alk\to vap}$ /kJ·mol^{-1}	$u(\Delta G^{A}_{alk\to vap})$ /kJ·mol^{-1}	$\Delta G^{A}_{alk\to vap}$ /kJ·mol^{-1}	$u(\Delta G^{A}_{alk\to vap})$ /kJ·mol^{-1}
	Expt.[8]	TIP4P		SPC/E	
5	14.3	13.350	0.017	13.3382	0.0076
6	17.0	15.8356	0.0096	15.830	0.015
7	19.6	18.318	0.048	18.267	0.046
8	22.3	20.861	0.068	20.798	0.090
9	25.0	23.44	0.13	23.37	0.17
		TIP4P/2005		TIP4P-1.1	
5		13.340	0.025	13.333	0.010
6		15.800	0.018	15.837	0.022
7		18.307	0.041	18.283	0.067
8		20.851	0.097	20.789	0.084
9		23.41	0.14	23.17	0.19
		TIP4P-1.2		SPC/E-1.7	
5		13.329	0.014	13.336	0.019
6		15.851	0.019	15.820	0.033
7		18.331	0.053	18.298	0.042
8		20.812	0.086	20.799	0.045
9		23.39	0.14	23.39	0.19

Gibbs free energy of transfer of alkane from alkane-rich liquid phase to vapor phase ($\Delta G^{A}_{alk\to vap}$) and 95% confidence interval (u).

Table S24. Comparison of Data for Binary Water (1) + n-Alkane (2) Mixtures without/with Transfer of Alkanes at $T = 298.15$ K and $p = 0.1013$ MPa

Model	C_nH_{2n+2}	Without Transfer		With Transfer	
		$x_1^A/10^{-5}$	$u(x_1^A)/10^{-5}$	$x_1^A/10^{-5}$	$u(x_1^A)/10^{-5}$
SPC/E-1.7	5	15.48	0.57	13.54	0.37
	6	16.63	0.43	15.22	0.68
	7	18.00	0.61	15.84	0.62
	8	19.0	1.2	17.09	0.77
	9	20.68	0.74	18.00	0.72
		x_2^W	$u(x_2^W)$	$x_2^W/10^{-2}$	$u(x_2^W)/10^{-2}$
SPC/E-1.7	5			4.61	0.18
	6			4.13	0.16
	7			3.43	0.13
	8			3.10	0.12
	9			2.556	0.072
		$\Delta G^W_{wat\to vap}$	$u(\Delta G^W_{wat\to vap})$	$\Delta G^W_{wat\to vap}$	$u(\Delta G^W_{wat\to vap})$
SPC/E-1.7	5	29.573	0.064	29.432	0.046
	6	29.540	0.033	29.299	0.080
	7	29.493	0.058	29.342	0.083
	8	29.592	0.073	29.349	0.089
	9	29.504	0.054	29.311	0.051
		$\Delta G^W_{vap\to alk}$	$u(\Delta G^W_{vap\to alk})$	$\Delta G^W_{vap\to alk}$	$u(\Delta G^W_{vap\to alk})$
SPC/E-1.7	5	−3.214	0.056	−3.202	0.037
	6	−3.057	0.037	−3.073	0.059
	7	−2.930	0.047	−2.920	0.033
	8	−2.838	0.060	−2.870	0.052
	9	−2.773	0.070	−2.734	0.043
		$\Delta G^A_{vap\to wat}$	$u(\Delta G^A_{vap\to wat})$	$\Delta G^A_{vap\to wat}$	$u(\Delta G^A_{vap\to wat})$
SPC/E-1.7	5			−9.972	0.084
	6			−12.449	0.073
	7			−14.734	0.073
	8			−17.289	0.085
	9			−19.508	0.071

Mole fractions of water in n-alkane-rich liquid phase (x_1^A) and of n-alkane in water-rich liquid phase (x_2^W), transfer free energies of water from water-rich liquid phase to vapor phase ($\Delta G^W_{wat\to vap}$), of water from vapor phase to n-alkane-rich liquid phase ($\Delta G^W_{vap\to alk}$), and of n-alkane from vapor phase to water-rich liquid phase ($\Delta G^A_{vap\to wat}$), and 95% confidence interval (u). All transfer free energies are given in units of kJ·mol^{-1}.

Table S25. Water/n-Hexane Interfacial Tension at $T = 298$ K and $p = 1$ bar, $T = 323$ K and $p = 100$ bar, and $T = 473$ K and $p = 400$ bar

T /K	p /bar	Model	γ /(mN·m^{-1})	$u(\gamma)$ /(mN·m^{-1})	S	$u(S)$
298	1	Expt.[9]	49.96	0.71		
		TIP4P	46.0	1.6	0.091	0.037
		SPC/E	53.0	1.9	0.075	0.038
		TIP4P/2005	53.2	2.1	0.078	0.043
		TIP4P-1.1	41.1	1.7	0.198	0.045
		TIP4P-1.2	36.7	1.5	0.312	0.043
		SPC/E-1.7	15.4	1.6	1.19	0.10
323	100	Expt.[9]	45.90	0.54		
		TIP4P	44.6	1.3	0.048	0.032
		SPC/E	51.1	1.3	0.106	0.028
		TIP4P/2005	48.9	1.8	0.085	0.039
		TIP4P-1.1	38.3	1.0	0.183	0.029
		TIP4P-1.2	33.7	1.5	0.326	0.046
		SPC/E-1.7	14.1	1.4	1.20	0.10
473	400	Expt.[9]	29.22	0.74		
		TIP4P	24.34	0.74	0.185	0.040
		SPC/E	33.33	0.90	0.130	0.037
		TIP4P/2005	34.72	0.82	0.171	0.035
		TIP4P-1.1	21.28	0.83	0.320	0.046
		TIP4P-1.2	16.68	0.85	0.565	0.057
		SPC/E-1.7	5.74	0.91	1.68	0.16

Interfacial tension between water and n-hexane (γ), score (S) and 95% confidence interval (u).

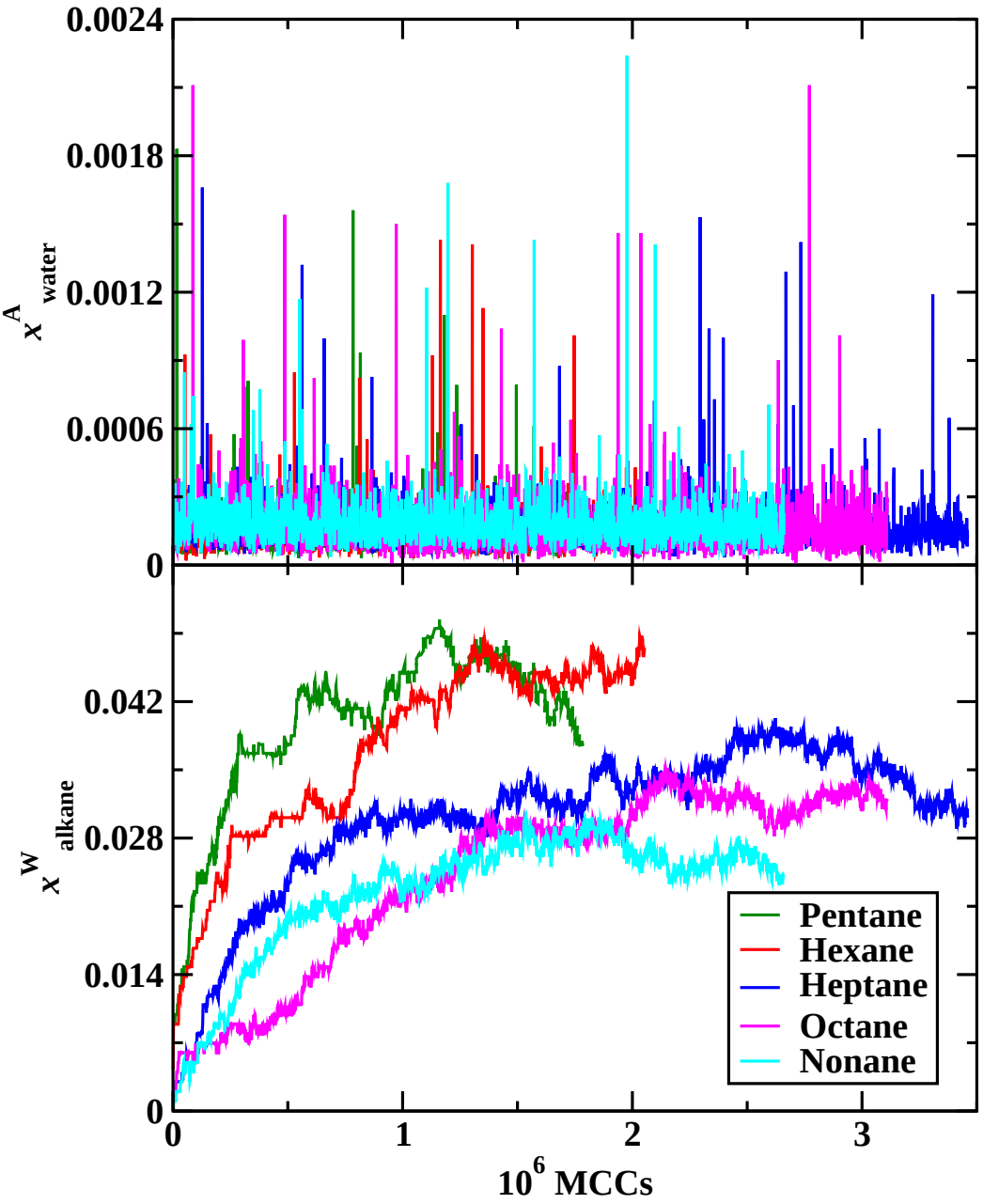

Figure S1. Evolution of the water mole fraction in the alkane-rich phase (top) and of the alkane mole fraction in the water-rich phase (bottom) observed for the water–alkane mixtures with the SPC/E-1.7 model at $T = 298.15$ K and $p = 0.1013$ MPa. The data show the instantaneous mole fractions for one of the eight independent trajectories for each system.

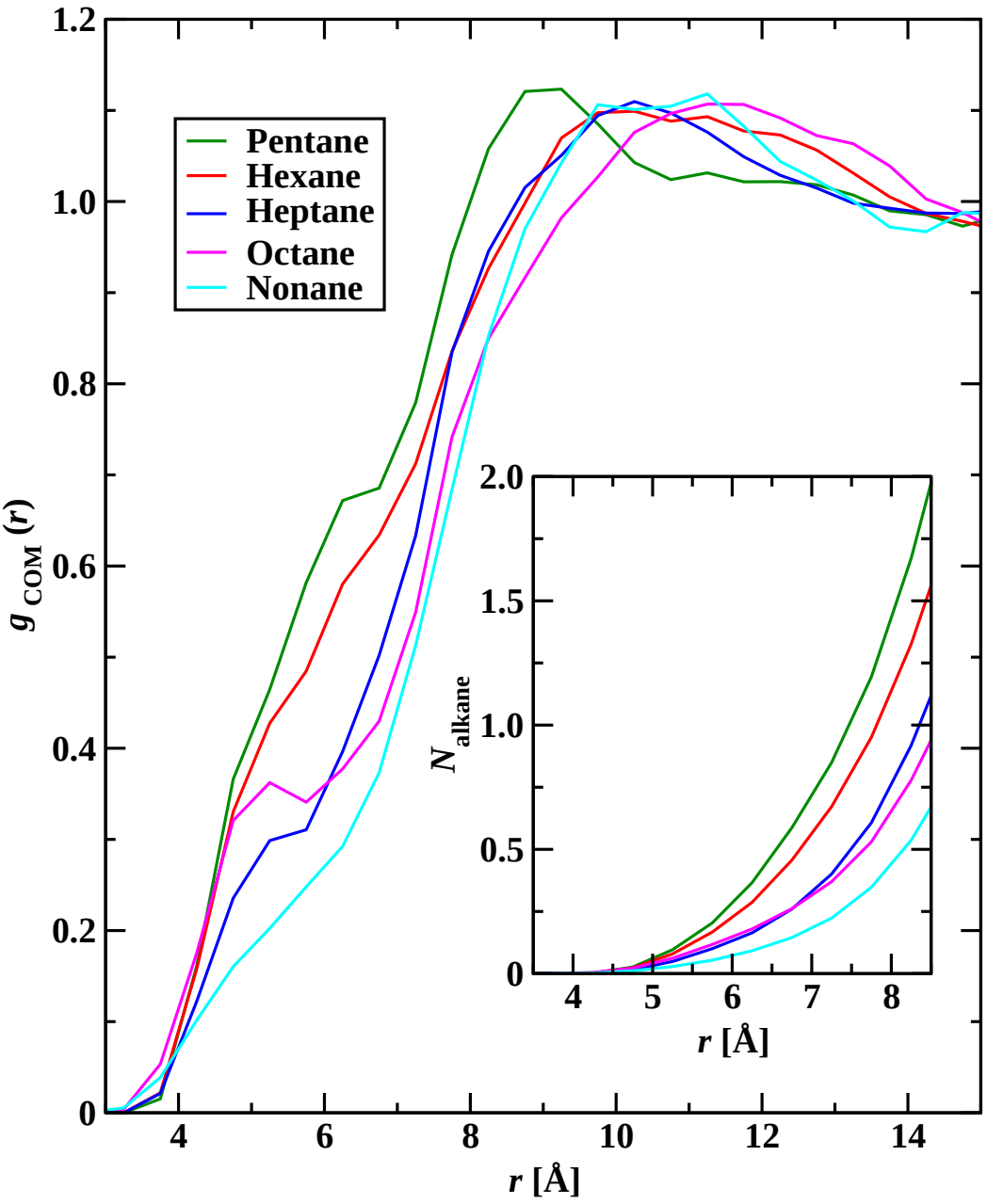

Figure S2. Center-of-mass radial distribution functions and corresponding number integrals for alkanes in the water-rich phase observed for the water–alkane mixtures with the SPC/E-1.7 model at $T = 298.15$ K and $p = 0.1013$ MPa. The data are averaged over the eight independent trajectories for each system.

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