

Predictions of water/oil interfacial tension at elevated temperatures and pressures: A molecular dynamics simulation study with biomolecular force fields

Supporting Information

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As described in the manuscript, the LJ-PME method was applied for the treatment of long-range Lennard-Jones interactions, as this has been shown to improve the description in inhomogeneous systems such as water/hydrocarbon mixtures [1]. However, it has been found recently that the combination of GAFF and LJ-PME leads to overestimations in the surface tension of organic liquids [2]. The source of this overestimation has been attributed to be the fact that the AMBER force fields, such as GAFF and Lipid14, have been parametrized for long-range Lennard-Jones (LJ) corrections using a simple cut-off approach [2]. Moreover, it has been reported that using the LJ-PME scheme led to an increase of the surface tension in lipid monolayers of almost 25% [3], which is close to the overestimation of IFT in our simulations. Therefore, utilizing the LJ-PME approach, even though it is computationally robust, has not been extensively tested in conjunction with force fields optimized for the cut-off approach [2]. This, however, contradicts the original argument of the LJ-PME developers, who claim that using this method is equivalent to imposing a 16 Å cut-off for the LJ potential [3]. In order to examine whether the IFT values are overestimated as a result of using the LJ-PME treatment, we have performed additional simulations on all systems by employing a 16 Å cut-off.

From the IFT data collected in Table S7, it is deduced that the IFT values are independent of the long-range treatment used for the LJ potential. We therefore chose the LJ-PME method for the simulations presented in the manuscript.

Table S1. Lipid14 and GAFF atom types.

GAFF	Lipid14	Description
c3	cD	sp3 carbon
ca	–	aromatic carbon
hc	hL	hydrogen bonded to aliphatic carbon without electron withdrawing group
ha	–	hydrogen bonded to aromatic carbon

Table S2. Toluene GAFF atom types and partial charges.

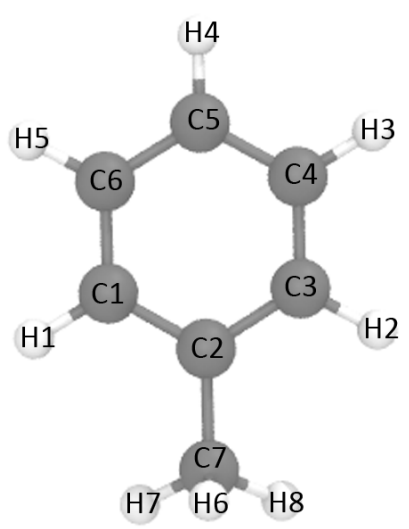
	Atom	Type	Charge
	C1	ca	-0.275155
	C2	ca	0.282982
	C3	ca	-0.275155
	C4	ca	-0.112135
	C5	ca	-0.172188
	C6	ca	-0.112135
	H1	ha	0.157026
	H2	ha	0.157026
	H3	ha	0.137677
	H4	ha	0.139105
	H5	ha	0.137677
	C7	c3	-0.384795
	H6	hc	0.106690
	H7	hc	0.106690
	H8	hc	0.106690

Table S3. *n*-dodecane Lipid14 atom types and partial charges.

	Atom	Type	Charge
	C1	cD	-0.218051
	H1	hL	0.043707
	H2	hL	0.043707
	H3	hL	0.043707
	C2	cD	0.184369
	H4	hL	-0.030719
	H5	hL	-0.030719
	C3	cD	-0.081636
	H6	hL	0.017473
	H7	hL	0.017473
	C4	cD	-0.000351
	H8	hL	0.010549
	H9	hL	0.010549
	C5	cD	-0.045994
	H10	hL	0.014082
	H11	hL	0.014082
	C6	cD	-0.016676
	H12	hL	0.012224
	H13	hL	0.012224
	C7	cD	-0.016676
	H14	hL	0.012224
	H15	hL	0.012224
	C8	cD	-0.045994
	H16	hL	0.014082
	H17	hL	0.014082
	C9	cD	-0.000351
H18	hL	0.010549	
H19	hL	0.010549	
C10	cD	-0.081636	
H20	hL	0.017473	
H21	hL	0.017473	
C11	cD	0.184369	
H22	hL	-0.030719	
H23	hL	-0.030719	
C12	cD	-0.218051	
H24	hL	0.043707	
H25	hL	0.043707	
H26	hL	0.043707	

Table S4. TIP4P/2005, TIP3P and SPC/E water atom types and partial charges.

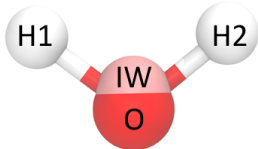
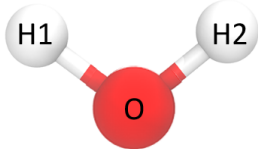
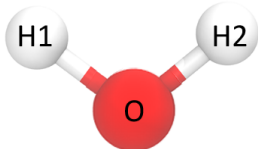
	Atom	Type	Charge
	TIP4P/2005		
	O	OWT4	0.0000
	H1	HW	0.5564
	H2	HW	0.5564
	IW	IW	-1.1128
	TIP3P		
	O	OW	-0.8340
	H1	HW	0.4170
	H2	HW	0.4170
	SPC/E		
	O	OW	-0.8476
	H1	HW	0.4238
	H2	HW	0.4238

Table S5. GAFF, Lipid14, TIP4P/2005, TIP3P, SPC/E force field parameters employed in the IFT simulations.

Type of interaction	Potential function and parameters			
Bond stretching	$V_b(r_{ij}) = \frac{1}{2} k_{ij}^b (r_{ij} - b_{ij})^2$			
	Bond	k_{ij}^b (kJ mol ⁻¹ nm ⁻²)	b_{ij} (nm)	
	c3-c3	2.5363e+05	0.15350	
	c3-hc	2.8225e+05	0.10920	
	cD-cD	2.5363e+05	0.15350	
	cD-hL	2.8225e+05	0.10920	
	ca-ca	4.0033e+05	0.13870	
	ca-c3	2.7070e+05	0.15130	
	ca-ha	2.8811e+05	0.10870	
	TIP4P/2005	HW-OWT4	4.6275e+05	0.09572
	IW-OWT4	–	0.01546	
TIP3P	HW-OW	4.6275e+05	0.09572	
SPC/E	HW-OW	3.4500e+05	0.10000	
Bond angle bending	$V_a(\theta_{ijk}) = \frac{1}{2} k_{ijk}^\theta (\theta_{ijk} - \theta_{ijk}^0)^2$			
	Bond angle	k_{ijk}^θ (kJ mol ⁻¹ rad ⁻²)	θ_{ijk}^0 (°)	
	cD-cD-hL	3.8802e+02	110.05	
	cD-cD-cD	5.2894e+02	110.63	
	hL-cD-hL	3.2995e+02	108.35	
	ca-ca-ca	5.6216e+02	119.97	
	c3-ca-ca	5.3421e+02	120.63	
	ca-ca-ha	4.0551e+02	120.01	
	ca-c3-hc	3.2995e+02	108.35	
	TIP4P/2005	HW-OWT4-HW	8.3680e+02	104.52
	HW-OWT4-IW	–	52.26	
TIP3P	HW-OW-HW	8.3680e+02	104.52	
SPC/E	HW-OW-HW	3.8300e+02	109.47	
Dihedral angles	$V_d(\varphi_{ijkl}) = k_\varphi (1 + \cos(n\varphi - \varphi_s))$			
	Angle	k_φ (kJ mol ⁻¹)	φ_s (°)	n
	cD-cD-cD-cD	1.30206	180.0	1
	cD-cD-cD-cD	-0.51589	180.0	2
	cD-cD-cD-cD	0.48074	0.0	3
	cD-cD-cD-cD	-0.92006	0.0	4
	cD-cD-cD-cD	0.90793	0.0	5

Table S5. Cont.

Dihedral angles	hL-cD-cD-hL	0.62760	0.0	3			
	cD-cD-cD-hL	0.66944	0.0	3			
$V_d(\varphi_{ijkl}) = \sum_{n=0}^5 C_n (\cos(\psi))^n, \psi = \varphi - 180, C_n \text{ (kJ mol}^{-1}\text{)}$							
	Angle	C_0	C_1	C_2	C_3	C_4	C_5
	ca-ca-ca-ca	30.334	0.000	-30.334	0.000	0.000	0.000
	ca-ca-ca-ha	30.334	0.000	-30.334	0.000	0.000	0.000
	hc-c3-ca-ca	0.000	0.000	0.000	0.000	0.000	0.000
	c3-ca-ca-ca	30.334	0.000	-30.334	0.000	0.000	0.000
	c3-ca-ca-ha	30.334	0.000	-30.334	0.000	0.000	0.000
	ha-ca-ca-ha	30.334	0.000	-30.334	0.000	0.000	0.000
Improper dihedral angles	$V_d(\varphi_{ijkl}) = k_\varphi (1 + \cos(n\varphi - \varphi_s))$						
	Angle	$k_\varphi \text{ (kJ mol}^{-1}\text{)}$		$\varphi_s \text{ (}^\circ\text{)}$		n	
	ca-ca-ca-ha	4.60240		180.0		2	
	c3-ca-ca-ca	4.60240		180.0		2	
Non bonded Lennard-Jones	$V_{LJ} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$						
			$\sigma \text{ (nm)}$		$\varepsilon \text{ (kJ mol}^{-1}\text{)}$		
	ca	0.339970		0.35982			
	ha	0.259960		0.06276			
	c3	0.339970		0.45773			
	hc	0.264950		0.06569			
	cD	0.339970		0.45773			
	hL	0.260140		0.04184			
TIP4P/2005	OWT4	0.315890		0.77491			
	HW	0.000000		0.00000			
	IW	0.000000		0.00000			
TIP3P	OW	0.315066		0.63627			
	HW	0.000000		0.00000			
SPC/E	OW	0.316600		0.65000			
	HW	0.000000		0.00000			
Non bonded electrostatic	$V_c(r_{ij}) = \frac{1}{4\pi\varepsilon_o} \frac{q_i q_j}{\varepsilon_r r_{ij}}$						
	Partial charge values are provided in Tables S2-S4.						

Table S6. Calculated IFT values of our contest entry and benchmark experimental values. The water model used is TIP4P/2005.

T (K)	γ (mN/m)				Difference (%)
	water/toluene				
383.15	simulation	32.3 ± 0.4	Experiment	28.6	12.9
403.15		29.1 ± 0.6		26.4	10.2
423.15		27.5 ± 0.6		23.8	15.5
443.15		26.1 ± 0.6		20.2	29.2
	water/ <i>n</i> -dodecane				
383.15	simulation	47.4 ± 0.8	Experiment	40.0	18.5
403.15		44.7 ± 0.5		36.5	22.5
423.15		41.7 ± 0.5		32.9	26.7
443.15		38.4 ± 0.9		28.5	34.7
	water/toluene/ <i>n</i> -dodecane				
383.15	simulation	38.5 ± 1.0	Experiment	31.4	22.6
403.15		36.4 ± 0.9		29.0	25.5
423.15		33.9 ± 0.7		26.1	29.9
443.15		31.9 ± 0.8		22.6	41.2

Table S7. Calculated IFT values with the LJ-PME approach and 16 Å cut-off treatment of the tail of Lennard-Jones potential. The water model used is TIP4P/2005.

T (K)	γ (mN/m)							
	water/toluene							
383.15	LJ-PME 5 ns (contest entry)	32.3 ± 0.4	LJ-PME 10 ns	33.1 ± 0.7	16 Å cut-off 10 ns	32.0 ± 0.6	Experiment	28.6
403.15		29.1 ± 0.6		31.2 ± 1.0		30.3 ± 0.6		26.4
423.15		27.5 ± 0.6		29.0 ± 0.6		28.6 ± 1.0		23.8
443.15		26.1 ± 0.6		25.6 ± 0.7		25.5 ± 0.4		20.2
	water/ <i>n</i> -dodecane							
383.15	LJ-PME 5 ns (contest entry)	47.4 ± 0.8	LJ-PME 10 ns	47.5 ± 0.8	16 Å cut-off 10 ns	47.8 ± 1.3	Experiment	40.0
403.15		44.7 ± 0.5		45.4 ± 0.8		45.3 ± 2.1		36.5
423.15		41.7 ± 0.5		42.4 ± 0.8		42.1 ± 1.4		32.9
443.15		38.4 ± 0.9		39.8 ± 1.1		38.4 ± 0.8		28.5
	water/toluene/ <i>n</i> -dodecane							
383.15	LJ-PME 5 ns (contest entry)	38.5 ± 1.0	LJ-PME 10 ns	38.7 ± 0.8	16 Å cut-off 10 ns	38.0 ± 0.7	Experiment	31.4
403.15		36.4 ± 0.9		36.4 ± 0.3		36.0 ± 0.6		29.0
423.15		33.9 ± 0.7		34.7 ± 0.4		33.9 ± 0.4		26.1
443.15		31.9 ± 0.8		31.6 ± 0.9		30.9 ± 0.6		22.6

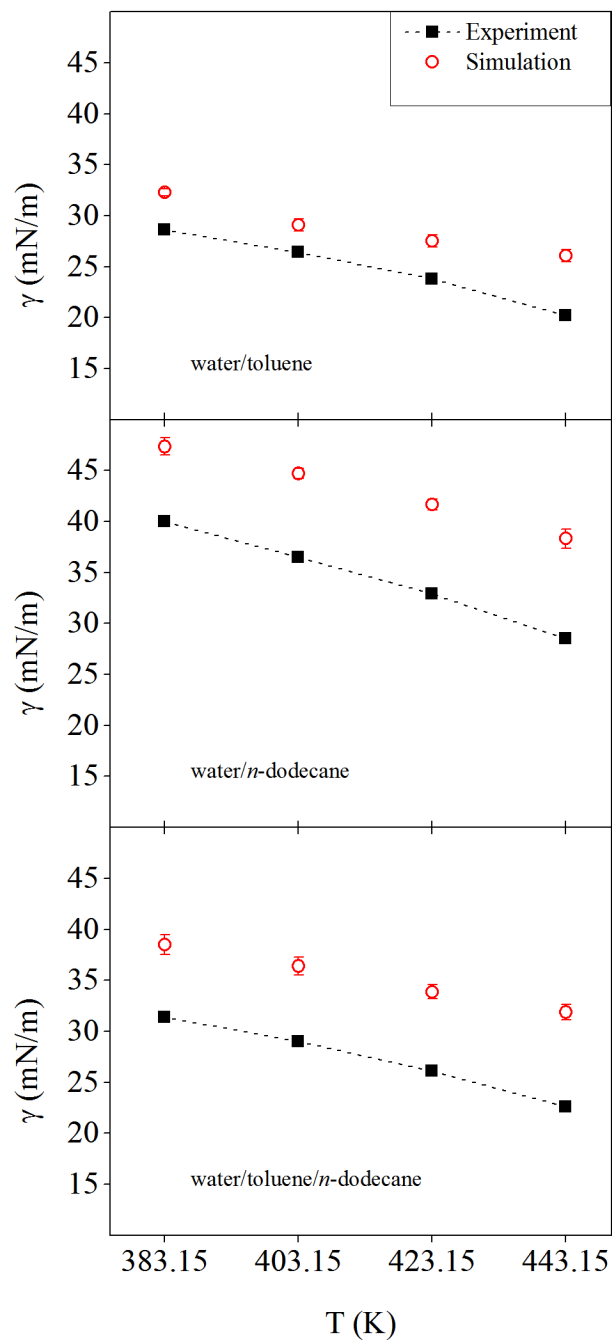


Figure S1. Experimental and calculated interfacial tension values (contest entry) of water/toluene, water/*n*-dodecane and 50:50 (wt/wt) water/toluene/*n*-dodecane mixtures with the GAFF (toluene), Lipid14 (*n*-dodecane) and TIP5P/2005 (water) force fields.

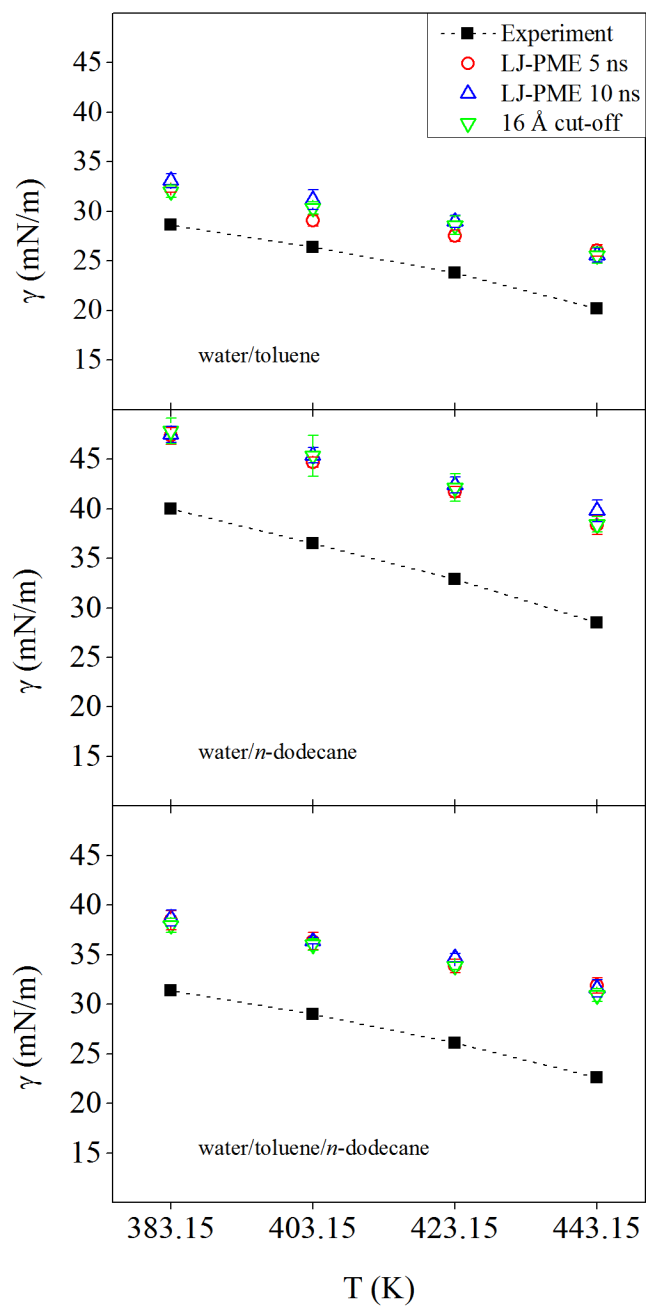


Figure S2. Calculated interfacial tension of water/toluene, water/*n*-dodecane and 50:50 (wt/wt) water/toluene/*n*-dodecane mixtures obtained from longer runs (maybe add how many ns) and different treatments of the Lennard-Jones potential.

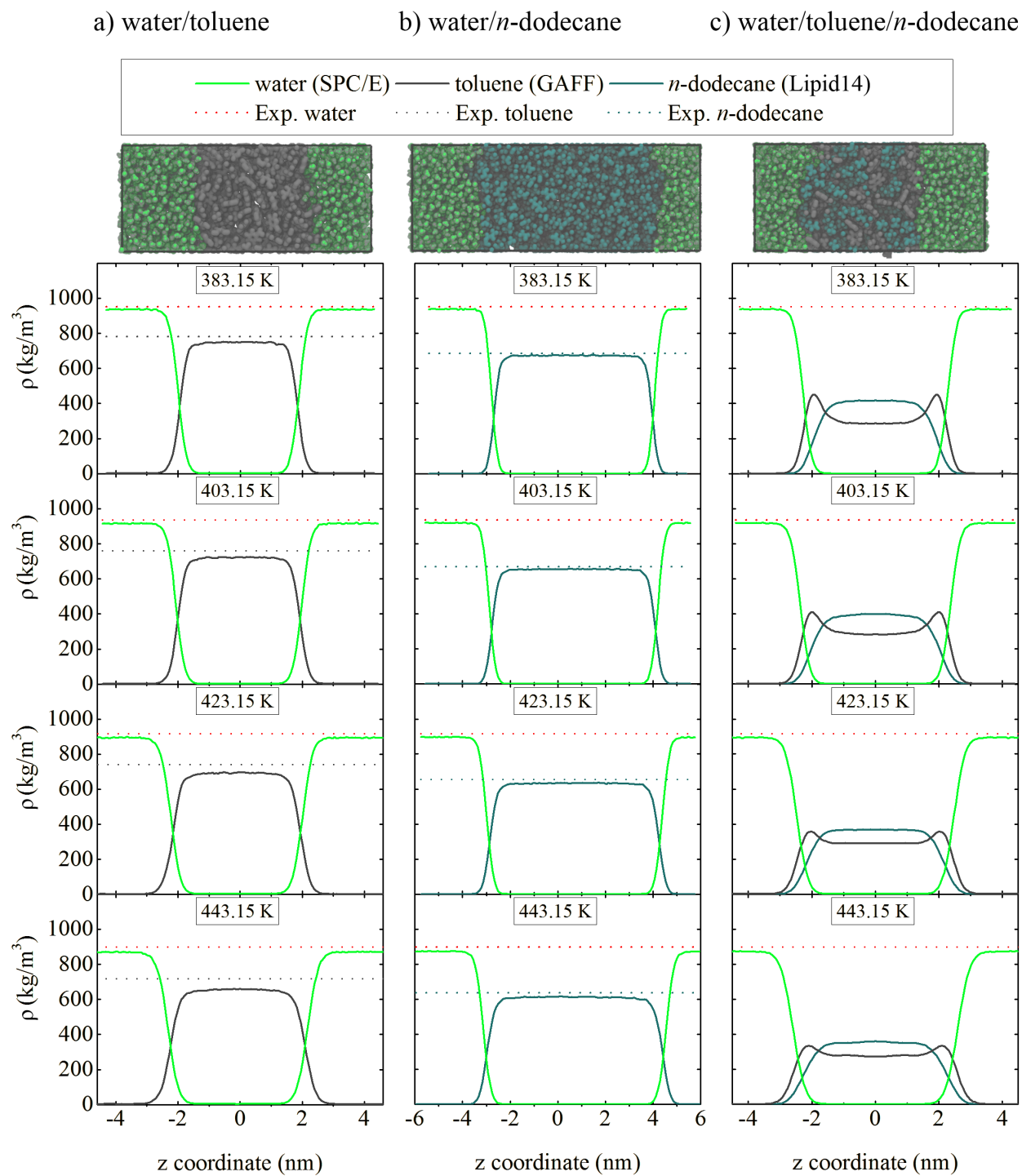


Figure S3. Equilibrated structures and partial densities of all systems studied using the SPC/E model for water, at different temperatures and pressure 1.83 MPa. Water, toluene and *n*-dodecane molecules are illustrated in green, gray and cyan colors, respectively.

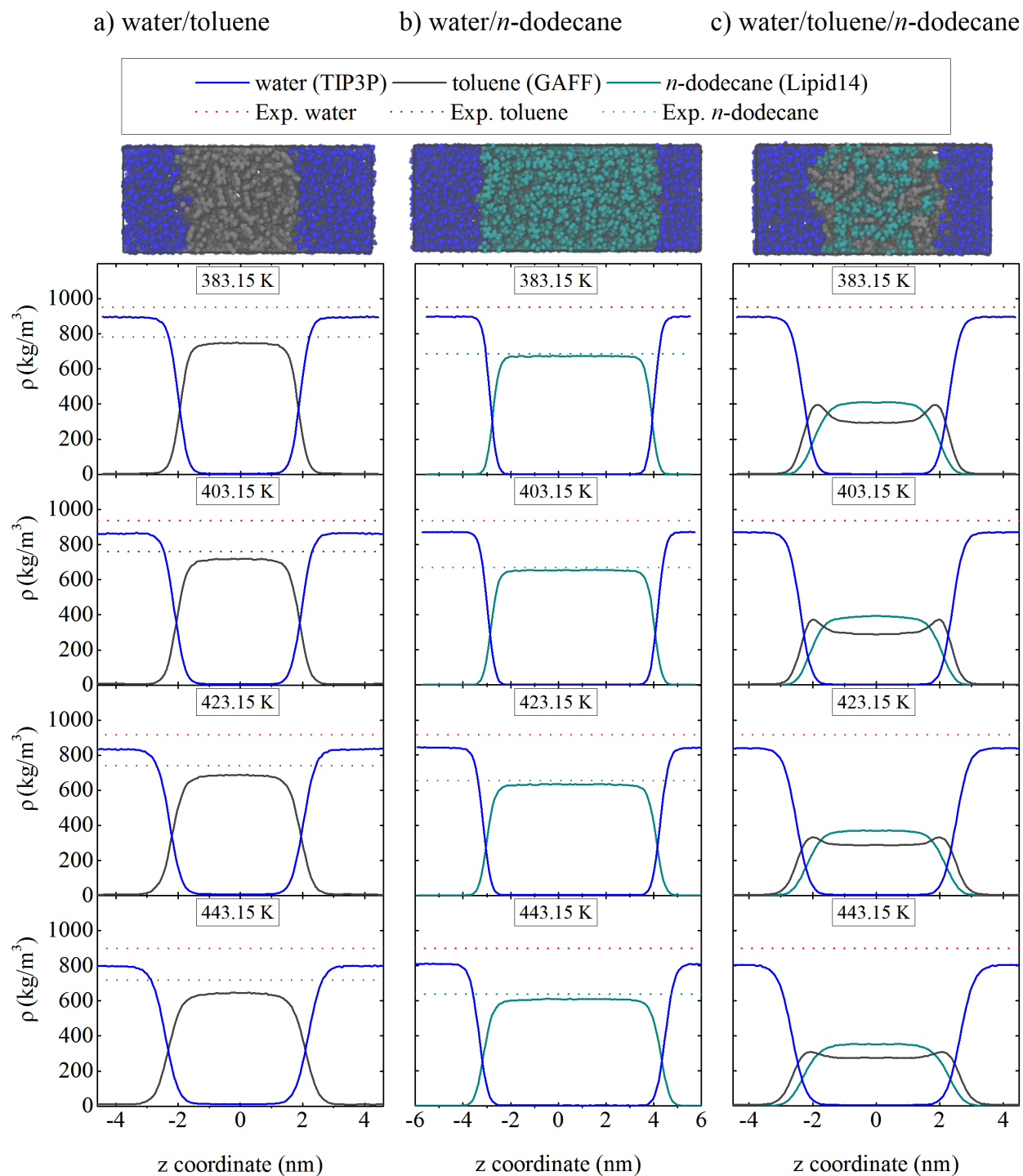


Figure S4. Equilibrated structures and partial densities of all systems studied using the TIP3P model for water, at different temperatures and pressure 1.83 MPa. Water, toluene and *n*-dodecane molecules are illustrated in blue, gray and cyan colors, respectively.

References

- [1] L. Lundberg, O. Edholm, Dispersion corrections to the surface tension at planar surfaces, *J. Chem. Theory Comput.*, 12 (2016) 4025-4032.
- [2] N.M. Fischer, P.J. van Maaren, J.C. Ditz, A. Yildirim, D. van der Spoel, Properties of organic liquids when simulated with long-range Lennard-Jones interactions, *J. Chem. Theory Comput.*, 11 (2015) 2938-2944.
- [3] C.L. Wennberg, T. Murtola, B. Hess, E. Lindahl, Lennard-Jones lattice summation in bilayer simulations has critical effects on surface tension and lipid properties, *J. Chem. Theory Comput.*, 9 (2013) 3527-3537.