Supplementary Information for:

Intermolecular Network Analysis of the Liquid and Vapor Interfaces of Pentane and Water: Microsolvation Does Not Trend with Interfacial Properties

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Table S1. Bonded potential parameters for C_5H_{12} and H_2O.[a-c]

Type	r_0 (Å)	Type	θ_0 (°)	k_θ (kcal/mol/rad)²	Type	k_1 (kcal/mol)	k_2 (kcal/mol)	k_3 (kcal/mol)
O-H	0.9572	C-C-C	112.7	58.35	H-C-C-H	0.0	0.0	0.3
C-C	1.529	H-C-H	107.8	33.00	H-C-C-C	0.0	0.0	0.3
C-H	1.090	C-C-H	110.7	37.50	C-C-C-C	1.3	-0.05	0.2
		H-O-H	104.52	55.0				

[a]Form of the bonded potential: $u = k(r - r_0)^2$

[b]Form of the angular potential: $u = k_\theta(\theta - \theta_0)^2$

[c]Form of the torsional potential: $u = \frac{1}{2}k_1(1 + \cos\phi) + \frac{1}{2}k_2(1 - \cos 2\phi) + \frac{1}{2}k_3(1 + \cos 3\phi)$

Table S2. Lennard-Jones parameters and charges for C_5H_{12} and H_2O.[a,b]

C_5H_{12}			
Atom	**σ(Å)**	**ε (kcal/mol)**	**q**
H	2.4	0.015	0.06
C1(methyl)	3.75	0.097	-0.18
C2(methylene)	3.75	0.0665	-0.12
C3(tertiary)	3.75	0.032	-0.06
C4(quaternary)	3.75	0.003	0.00
H_2O			
Atom	**σ(Å)**	**ε (kcal/mol)**	**q**
H	0.0	0.0	0.415
O	3.188	0.102	-0.830

[a]Using the form $u = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$

[b]Mixing rules $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \varepsilon_{ij} = \sqrt{\varepsilon_i \times \varepsilon_j}$

Table S3. Gibbs dividing surface position for water and alkane in different systems in Å.

System	Z_{water}(Å)	Z_{alkane}(Å)
Water:Vapor@273 K	±28.55	
Water:Vapor@298K	±37.00	
Water:Neopentane@273K	±37.73	±36.05
Water:*n*-Pentane@273K	±31.03	±32.15
Water:Neopentane@298K	±38.27	±37.14
Water:*n*-Pentane@298K	±33.73	±31.73
n-Pentane:Vapor@298K		±32.97
Neopentane:Vapor@273K		±31.48

Table S4. Density in g/cm^3 and diffusion coefficient, D, in cm^2/sec for H_2O and C_5H_{12} at different temperatures.

Liquid bulk T(K)	ρ(g/cm^3)	D×(10^{-5} cm^2/sec)
H_2O(TIP3P/Ew) @ 273K	0.99	1.16
H_2O(TIP3P/Ew) @ 298K	1.04	4.16
n-Pentane @ 298K	0.63	5.60
Neopentane @ 273K	0.63	3.30

Table S5. Hydrogen bond distribution and its statistical error for bulk water as well as vapor and organic interfaces for both 273 and 298K.

System	1H-Bond	2H-Bond	3H-bond	4H-Bond	5H-Bond
Water at 273K	1.92±0.01	12.23±0.04	36.44±0.6	47.04±0.12	2.35±0.01
Water at 298K	3.95±0.02	18.40±0.05	39.47±0.01	36.05±0.09	2.10±0.01
Water:Vapor at 273K	27.23±0.37	28.43±0.24	28.33±0.20	15.26±0.07	0.73±0.00
Water:Vapor at 298K	40.29±0.39	31.39±0.26	20.50±0.34	7.33±0.06	0.46±0.14
Water:Neopentane at 273K	23.028±2.06	26.28±0.54	30.83±1.07	17.89±1.44	0.96±0.09
Water:Pentane at 298K	29.69±2.73	29.42±0.45	26.90±1.53	13.29±1.51	0.68±0.13

Table S6. Cross correlation of each instance of hydrogen bond breakage and formation with the change in O..O distance in H_2O:vapor at 298K.

$\Delta r_{O....O}$(Å)	% Occurrence at the interface	% Occurrence at bulk
0.00--0.05	27.92	24.80
0.05--0.10	22.66	20.82
0.10--0.15	16.99	16.12
0.15--0.20	11.26	11.14
0.20--0.25	6.75	7.22
0.25--0.30	3.90	4.69
0.30--0.35	2.36	3.16
0.35--0.40	1.55	2.30
0.40--0.45	1.14	1.77
0.45--0.50	0.90	1.41
0.50--0.55	4.55	6.53

Table S7. Liquid density (ρ_L) and vapor density (ρ_V) of C_5H_{12}:vapor and H_2O:vapor interfaces studies in g/cm^3.

Liquid-Vapor/ T(K)	ρ_L (g/cm^3)	ρ_V (g/cm^3)
TIP3P/Ew: vapor@273	0.963	0.022
TIP3P/Ew : vapor@298	0.998	0.015
Neopentane : vapor@273	0.492	0.005
n-Pentane : vapor@ 298	0.560	0.009

Table S8. Complete list of surface tensions and interfacial widths for all vapor systems using all fitting methods.

Liquid-Vapor/ T(K)	γ_p	γ_e	γ_t	w_t	w_e	Δ_t	Δ_e	Δ_t^2	Δ_e^2
TIP3P/Ew: vapor 273K	64.81	63.17	63.76	2.65	2.81	1.20	1.12	1.44	1.26
TIP3P/Ew : vapor 298K	45.67	44.28	73.57	2.66	3.1	1.21	1.24	1.46	1.53
Neopentane : vapor 273K	16.59	22.9	23.59	5.50	5.97	2.49	2.38	6.22	5.67
n-Pentane : vapor 298K	20.35	19.6	23.23	8.79	3.02	3.99	1.21	15.89	1.45

Table S9. Diffusion coefficients in ($10^{-5}cm^2/sec$) and liquid density densities of H_2O:C_5H_{12} in this work in g/cm^3.

Liquid:Liquid/ T(K)	D×($10^{-5}cm^2/sec$)	$\rho_{water}(g/cm^3)$	$\rho_{alkane}(g/cm^3)$
TIP3P/Ew:n-Pentane@ 298K	3.1:5.8	1.0	0.623
TIP3P/Ew:Neopentane @273 K	1.8:3.0	1.03	0.629

Table S10. Cross correlation of each instance of hydrogen bond breakage and formation with the change in O..O distance in H_2O:pentane at 298K.

$\Delta r_{O....O}$(Å)	% Occurrence at the interface	$\Delta r_{O....O}$(Å)	% Occurrence at bulk
0.00--0.05	27.182276	0.00--0.05	24.150045
0.05--0.10	22.051653	0.05--0.10	20.775272
0.10--0.15	17.086611	0.10--0.15	16.384352
0.15--0.20	11.656017	0.15--0.20	11.663977
0.20--0.25	7.2889738	0.20--0.25	7.808403
0.25--0.30	4.3214912	0.25--0.30	5.0737596
0.30--0.35	2.6190484	0.30--0.35	3.385426
0.35--0.40	1.6891139	0.35--0.40	2.4102104
0.40--0.45	1.2073233	0.40--0.45	1.8390678
0.45--0.50	0.91524667	0.45--0.50	1.4396348
0.50--0.55	3.9822452	0.50--0.55	5.0698533

Figure S1. Order parameter, S_z, as a function of θ in degrees, defined by the three vectors of *n*-pentane.

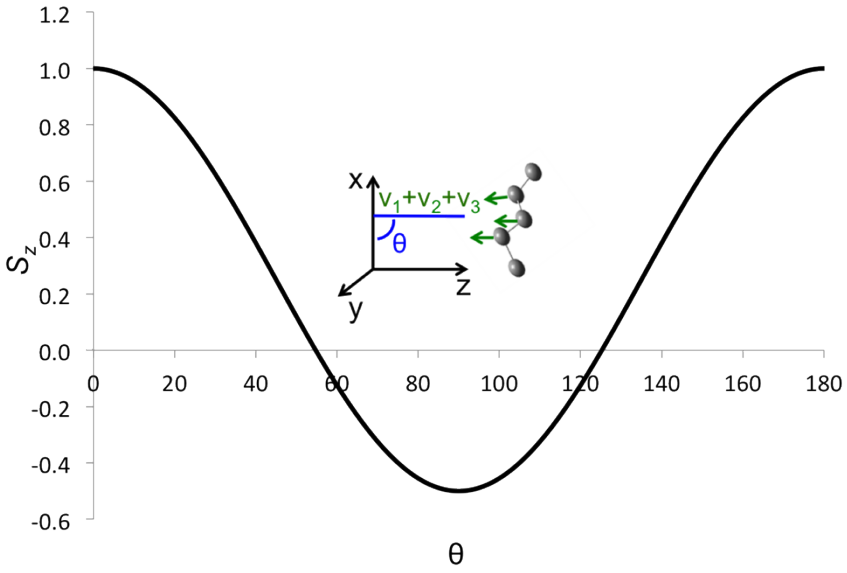

Figure S2. Geometric criterion that defines a hydrogen bond.

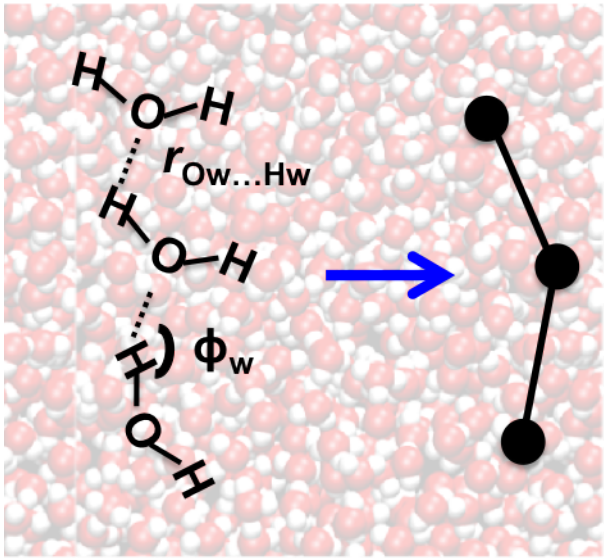

Figure S3. (A) Definition of dipole moment orientation of H_2O with respect to a solute. (B) The special case where the solute is a water molecule (reference H_2O). For the water molecule donating a H-bond to the reference H_2O, the angle is called alpha (α) wherein a value of 180° indicates alignment of the dipole moment vector along the axis of the hydrogen bond. For a water molecule accepting a H-bond from the reference H_2O, the angle is referred to as (β) wherein a value of 0° indicates perfect alignment of the dipole moment vector along the H-bond.

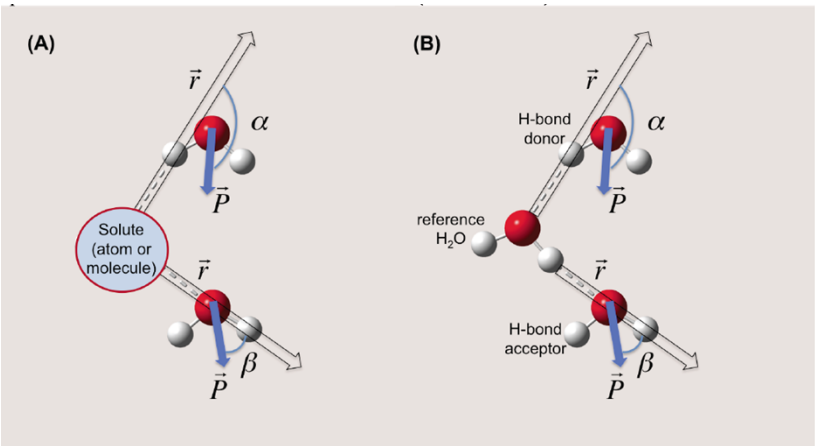

Figure S4. Radial distribution functions ($\rho_{O\text{-}O}$ and $\rho_{O\text{-}H}$) of TIP3P/Ew H_2O at 273 K and 298 K.

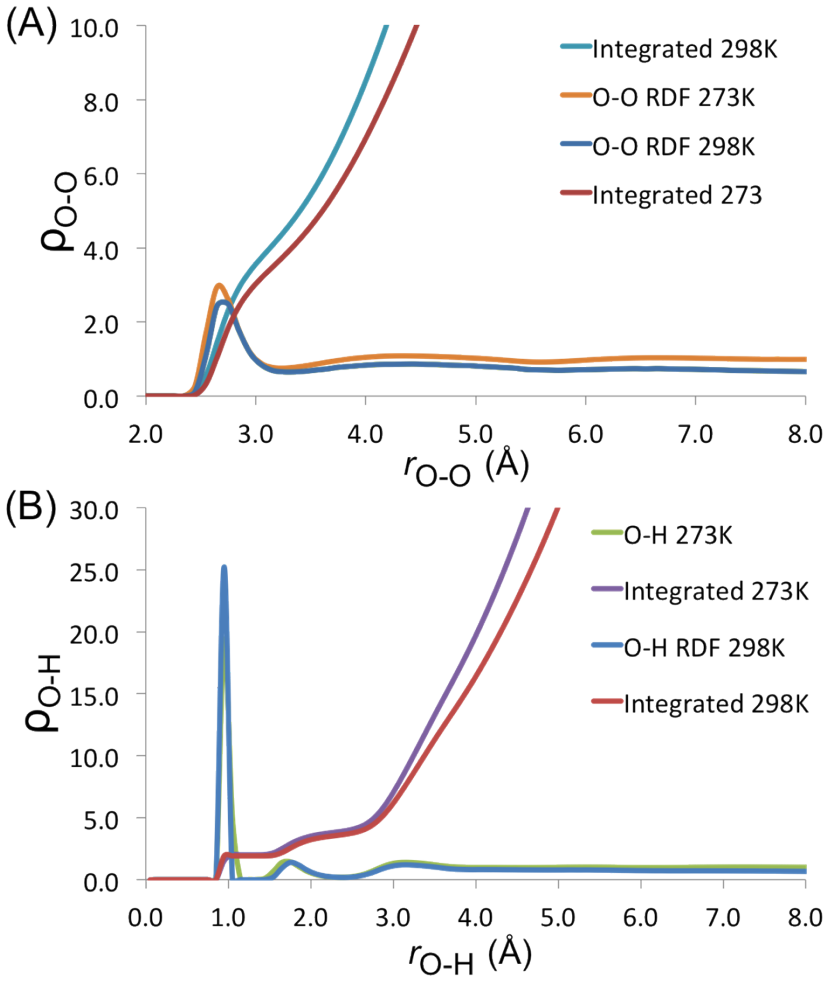

Figure S5. Radial distribution functions between C-atoms in n-pentane at 298K. Labeling of atomic centers is C_1-C_2-C_3-C_4-C_5.

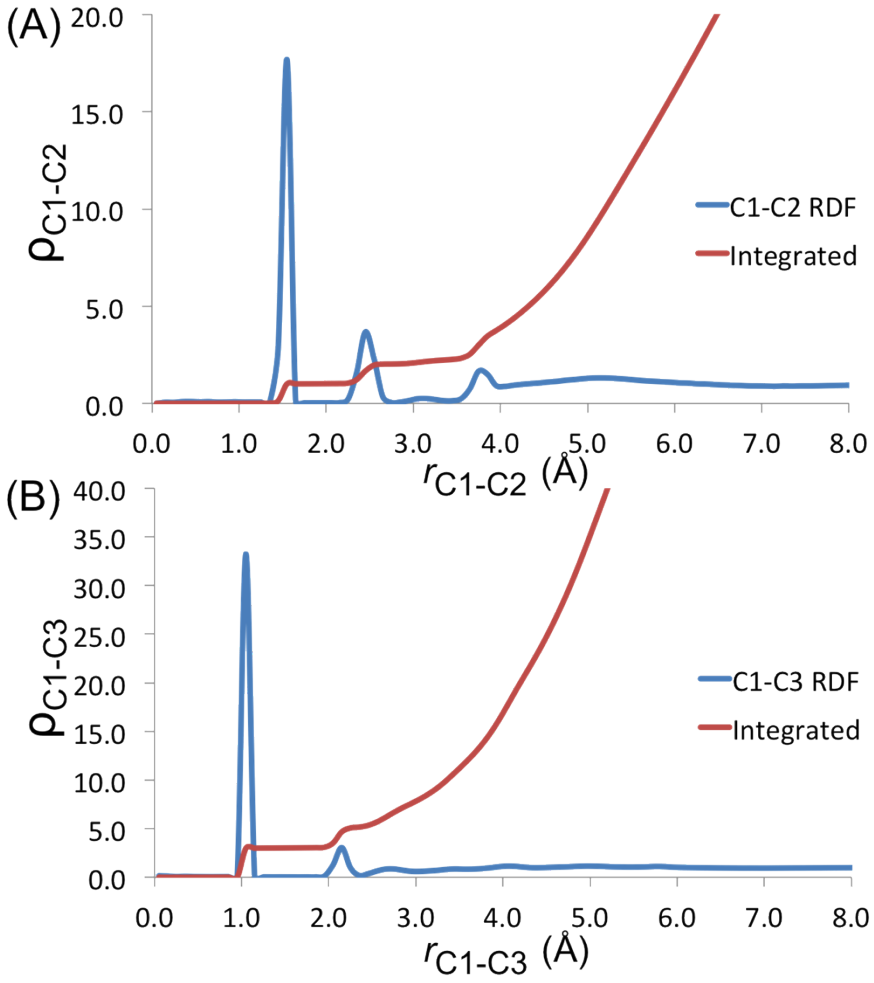

Figure S6. Radial distribution functions between central C-atoms in neopentane at 298K.[7]

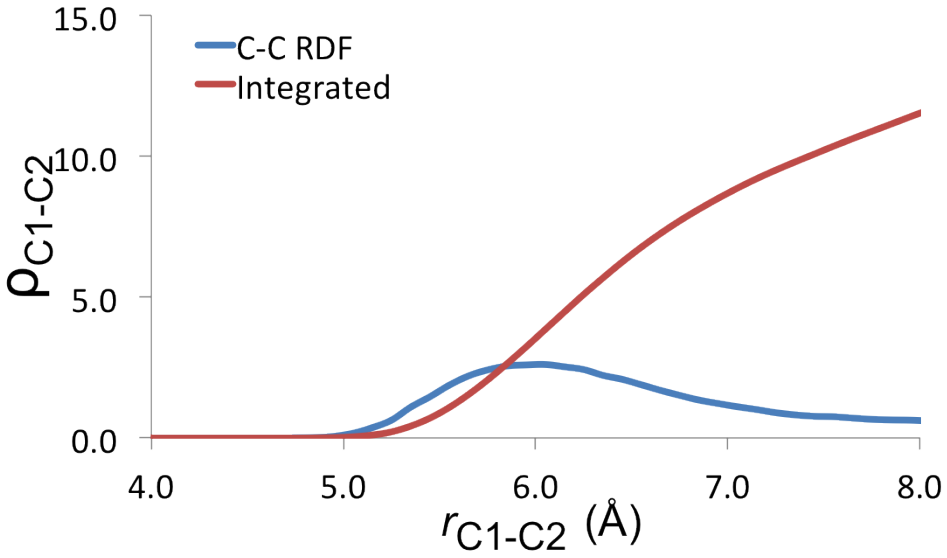

Figure S7. Density profile of water:vapor systems at 273 K and 298 K.

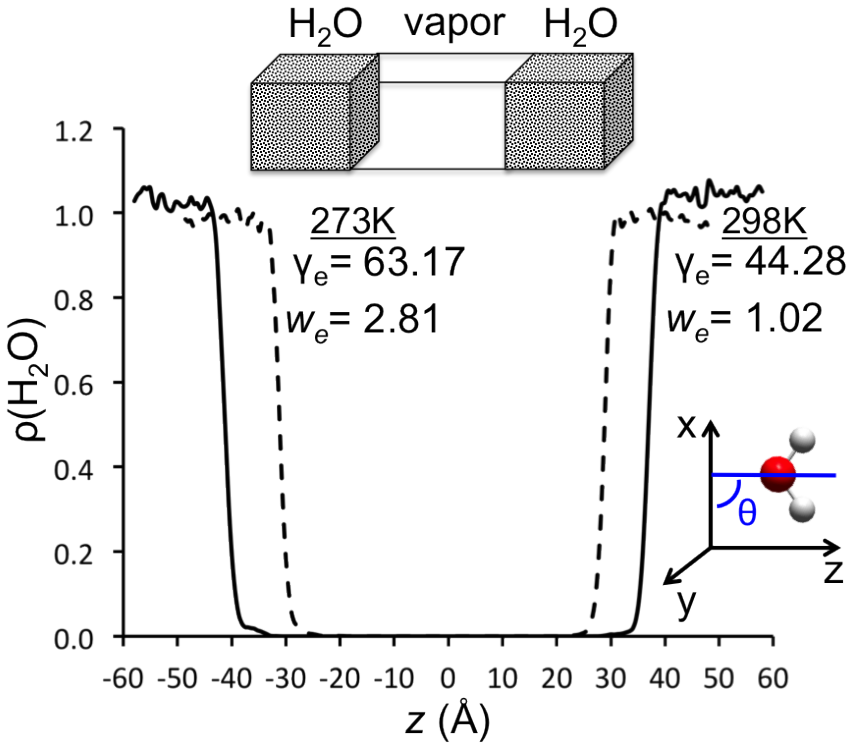

Figure S8. Density profiles of (A) water:*n*-pentane at 298 K, and (B) water:neopentane at 2173 K.

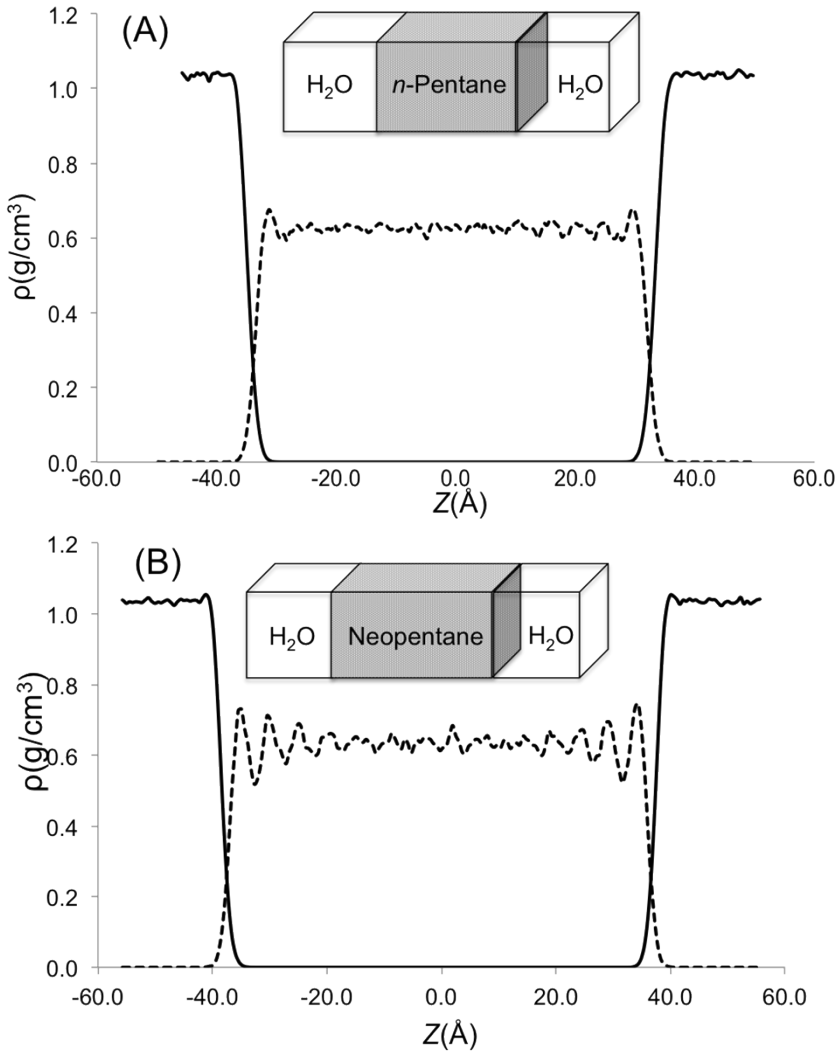

Figure S9. A) Potential of mean force for water migration across the water:pentane or water:vapor interfaces and b) pentane traveling across the water:pentane and pentane:vapor interfaces in kcal/mol.

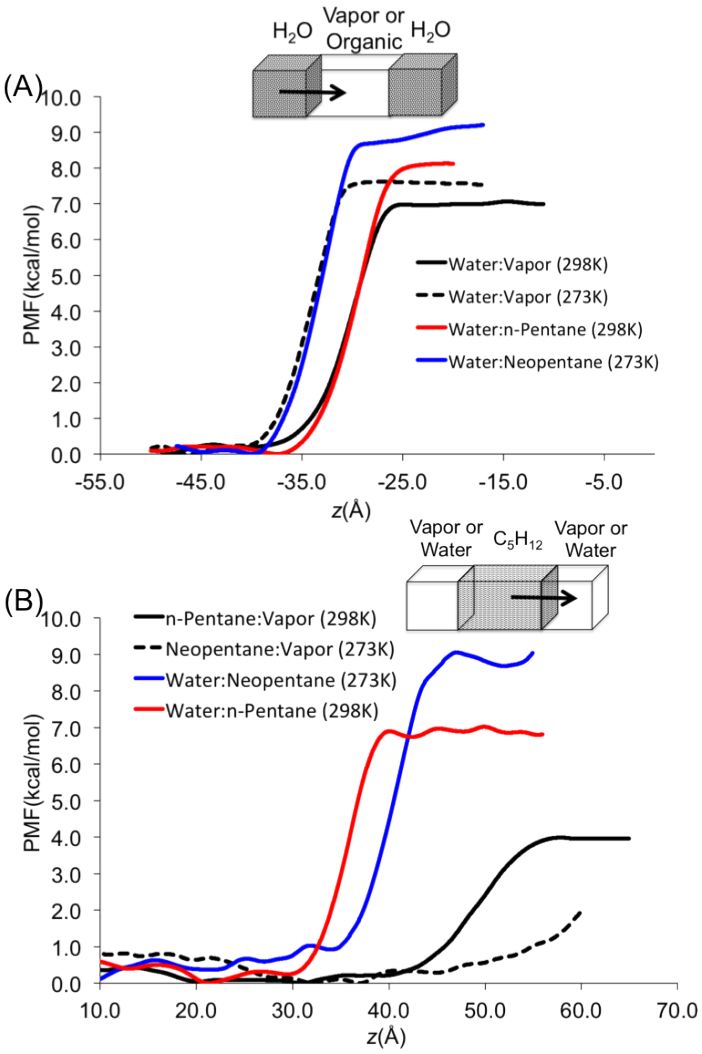

Figure S10. Distributions of (A) the number of neopentane molecules that solvate individual H_2O, and (B) the number of water molecules that solvate individual neopentane at 273 K and 298 K.