Supporting Information

Temperature Effect on the Interactions between Oil Droplet and Kerogen Surface at Reservoir Temperatures

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List of Contents

Supporting Text 1. Parameterization of SPC/F water model.

Supporting Text 2. Tcl/tk script for VMD

Supporting Text 3. Equation derivation.

Figure S1. Comparison between the free energy of a single polar oil molecule desorption from a fixed (rigid) kerogen surface and from an unrestricted (flexible) kerogen surface under different temperatures.

Figure S2. The free energy profiles of a single polar oil molecule on a rigid kerogen surfaces wetted with different water models.

Figure S3. Fraction of number of atoms in oil droplets affected by the kerogen surface.

Figure S4. Surface areas of different contact regions on adsorbed oil droplets.

Table S1. Description and performance of water models SPC/F, SPC, SPC/E, TIP3P, TIP4P-Ew, and TIP5P-E.

Table S2. Molecular dipole moment of water, octane, octanethiol, and kerogen.

Table S3. Contact angles of polar and non-polar oil droplets at different temperatures.

Table S4. System average pressures of free oil droplet simulations and adsorbed oil droplet simulations at different temperatures.

Table S5. Surface areas of different contact regions on oil droplets.

Supporting Information

Supporting Text 1. Parameterization of SPC/F water model.

[moleculetype]

; molname nrexcl

SOL 2

[atoms]

;	nr	type re	snr	residue	atom	cgnr	charge	mass
	1	OW	1	SOL	OW	1	-0.820	15.99940
	2	HW	1	SOL	HW1	1	0.410	1.00800
	3	HW	1	SOL	HW2	1	0.410	1.00800

[bonds]

; i	j	funct	length force.c.
1	2	1	0.09572 502080.0 ; OW HW
1	3	1	0.09572 502080.0 ; OW HW

[angles]

- ; i j k funct angle force.c.
- 2 1 3 1 109.50 627.600 ; HW-OW-HW

Supporting Information

Supporting Text 2. Tcl/tk script for VMD

Scripts and instruction are available at https://github.com/er1czz/vmd

Supporting Text 3. Equation derivation.

Free energy (*F*) can be expressed as a function of surface tension (γ) and surface area (*a*), which can be applied for both the Helmholtz and the Gibbs free energy. In the equation below, "_o" denotes oil; "_s", surface; "_w", water; and "_v", vacuum. And " ^o" and " [']"stand for a system with the free oil droplet and a system with the adsorbed oil droplet, respectively.

For both systems, $dF = \gamma_{i-j} \cdot da_{i-j}$ can be expanded as

$$dF = \gamma_{s-v} \cdot da_{s-v} + \gamma_{w-v} \cdot da_{w-v} + \gamma_{o-w} \cdot da_{o-w} + \gamma_{s-w} \cdot da_{s-w} + \gamma_{o-s} \cdot da_{o-s}$$
(s1)

For systems in steady/equilibrium state, the surface areas of water-vacuum and surface-vacuum contact regions should be unchanged. Therefore

$$0 = da_{w-v} = da_{s-v} \tag{s2}$$

Given that the free energy of desorption

$$\Delta F = F^{\circ} - F^{\prime} \tag{s3}$$

Combine s1, s2, and s3 to obtain

$$\Delta F = (\gamma_{o-w} \cdot a^{o}_{o-w} + \gamma_{s-w} \cdot a^{o}_{s-w}) - (\gamma_{o-w} \cdot a^{'}_{o-w} + \gamma_{s-w} \cdot a^{'}_{s-w} + \gamma_{o-s} \cdot a^{'}_{o-s})$$
(s4)

Since kerogen surface is rigid, its total surface area should be a constant value

$$a^{\circ}_{s-w} = a'_{s-w} + a'_{o-s}$$
 (s5)

Substituting for a°_{s-w} in s4 gives

$$\Delta F = \gamma_{\text{o-w}} \cdot (a^{\circ}_{\text{o-w}} - a'_{\text{o-w}}) + (\gamma_{\text{s-w}} - \gamma_{\text{o-s}}) \cdot a'_{\text{o-s}}$$
(s6)

According to the Young's equation

$$\gamma_{s-w} - \gamma_{o-s} = \gamma_{o-w} \cdot \cos\theta \tag{s7}$$

Now substitute for $\gamma_{s-w} - \gamma_{o-s}$ in s6 we obtain

$$\Delta F = \gamma_{\text{o-w}} \cdot (a^{\circ}_{\text{o-w}} - a'_{\text{o-w}} + a'_{\text{o-s}} \cdot \cos\theta) \quad \text{QED.}$$
(s8)





Figure S1. Comparison between the free energy of a single polar oil molecule desorption from a fixed (rigid) kerogen surface and from an unrestricted (flexible) kerogen surface under different temperatures. The energies of oil desorption from unrestricted kerogen surfaces are systematically lower than those from fixed kerogen surfaces. Standard errors are illustrated with error bars.



Figure S2. The free energy profiles of a single polar oil molecule on a rigid kerogen surfaces wetted with different water models. The distance is measured from the center of mass of the oil molecule to that of the kerogen slab. These free energy profiles are qualitatively identical. The deviation in energy minimum position is reasonable, and is attributed to the heterogeneity of kerogen surfaces and the asymmetric geometry of the polar oil molecule.



Figure S3. An example of a set of data on fraction of number of atoms in oil droplets affected by the kerogen surface. The fraction is the percentage of oil atoms within 0.36 nm of the surface out of the total number of atoms in the oil droplet. The orange bars represent polar oil droplets, while the blue bars (with stripe pattern) denote the non-polar oil droplets. Standard errors are illustrated with error bars.



Figure S4. Surface areas of different contact regions on adsorbed oil droplets. Orange, yellow, sky blue, and blue squares denote contact areas between polar oil and water, polar oil and kerogen surface, non-polar oil and water, and non-polar oil and kerogen surface, respectively. Standard errors are illustrated with error bars.

Table S1. Description and performance of water models SPC/F, SPC, SPC/E, TIP3P, TIP4P-Ew, and TIP5P-E. The benchmark tests were conducted at NERSC using 64 cores on Cori Intel Xeon Phi (KNL) node. Each calculation computed a free energy surface at 350 K of a single polar oil molecule interacting with a fixed kerogen surface in the presence of 3950 water molecules. Each free energy surface was derived from 121 configurations. 200 ps umbrella sampling was performed on each configuration.

Model	Description	Dipole	Hours	Efficienc	$\Delta G (kJ / mol)$
				у %	
SPC/F	Flexible Simple Charge Point, 3 sites	$2.39 - 2.46^{1,2}$	48	100	19.08 (3.57)
SPC	Simple Charge Point, 3 sites	2.27^{3}	49	98	27.99 (3.36)
SPC/E	Extended Simple Charge Point, 3 sites	2.35^{4}	49	98	27.85 (2.70)
TIP3P	Transferable Intermolecular Potential, 3 sites	2.35^{5}	49	98	24.85 (2.61)
TIP4P-Ew	4 sites, Ewald summation	2.32^{6}	54	89	30.41 (3.21)
TIP5P-E	5 sites, Ewald summation	2.29^{7}	62.5	77	29.60 (3.00)

Table S2. Molecular dipole moment of water, octane, octanethiol, and kerogen. Molecular dynamics simulation (MD) were carried out by Avogadro.^{8,9} Semi-empirical calculations were conducted by MOPAC with PM7 Hamiltonian.^{10,11} Density function theory (DFT) calculations were performed by GAMESS with 6-31G* basis set,^{12,13} B3LYP functional,^{14,15} and a SCF convergence of 10⁻⁵ of the density matrix. Please note that all these calculations are based on single molecule models in vacuum. The optimized kerogen structure can be downloaded from https://github.com/er1czz/md

Compound		Dipole Moment (I	Debye)
Compound	MD	PM7	DFT
water	1.13	2.130	2.094514
octane	0.00	0.003	0.000161
octanethiol	1.05	2.218	2.025873
kerogen	1.27	0.490	0.645501

Table S3. Contact angles of polar and non-polar oil droplets at different temperatures. "()" denotes standard error.

Tomporatura (V)	Contact a	Contact angle (degree)				
Temperature (K)	Polar oil	Non-polar oil				
300	48.27 (2.26)	50.37 (1.62)				
350	56.35 (3.12)	59.05 (3.27)				
400	54.38 (2.42)	61.33 (2.10)				
450	67.29 (1.27)	65.24 (1.98)				
500	63.72 (2.92)	74.12 (2.42)				

Temperature	Polar oil droplet s	ystem pressure (bar)	Non-polar oil droplet system pressure (bar)		
(K)	Free	Adsorbed	Free	Adsorbed	
300	2.00E+03	1.98E+03	2.03E+03	2.01E+03	
350	2.08E+03	2.04E+03	2.14E+03	2.13E+03	
400	2.18E+03	2.15E+03	2.21E+03	2.19E+03	
450	2.32E+03	2.28E+03	2.34E+03	2.31E+03	
500	2.49E+03	2.45E+03	2.51E+03	2.48E+03	

Table S4. System average pressures of free oil droplet simulations and adsorbed oil droplet simulations at different temperatures.

Table S5. An example of a set of the surface areas of different contact regions on oil droplets based on solvent-accessible surface area (SASA) algorithm. "()" denotes standard error.

		Polar oil (nm ²)		Non-polar oil (nm ²)		
Temperature	Free droplet	Adsorbed droplet		Free droplet	Adsorbed droplet	
	Oil-water	Oil-water	Oil-kerogen	Oil-water	Oil-water	Oil-kerogen
300 K	36.27 (0.44)	28.66 (0.30)	22.18 (0.37)	34.84 (0.49)	28.71 (0.18)	21.71 (0.35)
350 K	37.66 (1.14)	29.86 (0.37)	22.59 (0.48)	35.66 (0.35)	28.76 (0.24)	20.49 (0.43)
400 K	43.39 (1.02)	32.06 (0.73)	24.98 (0.90)	40.14 (1.00)	31.63 (0.49)	24.32 (0.96)
450 K	45.48 (1.02)	32.86 (0.64)	22.36 (0.78)	45.24 (1.22)	32.51 (1.25)	22.20 (0.99)
500 K	55.77 (1.06)	40.39 (0.91)	25.48 (0.95)	49.42 (1.59)	35.40 (0.66)	21.46 (1.16)

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