

Computational Insights into Selective Water–Methanol Transport in PSS/rGO Composite Films

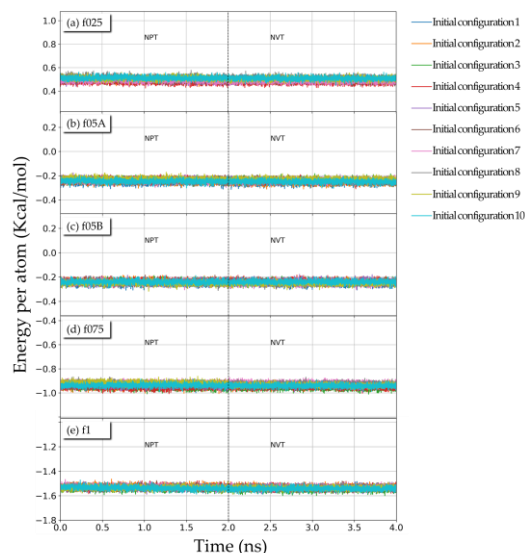


Figure S1. Total energy per atom over the course of the simulation for each rGO/PSS composition during the thermalization stage in the NPT ensemble and the production stage in the NVT ensemble.

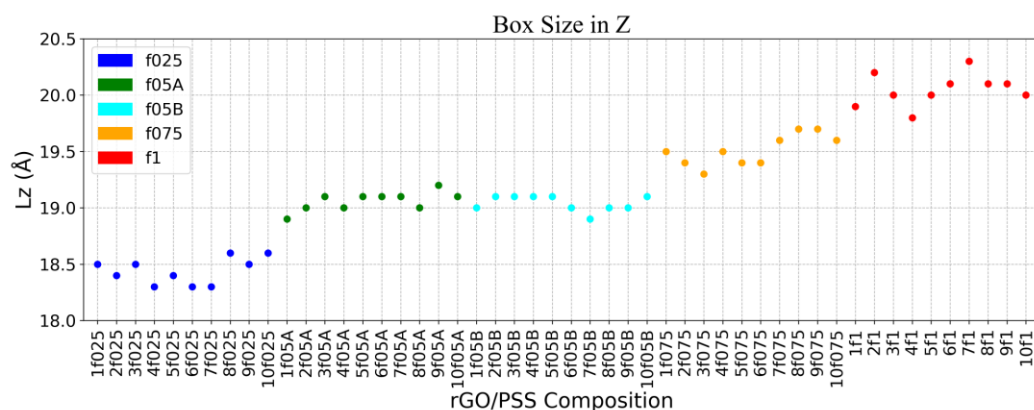


Figure S2. Box size in the Z-direction for each rGO/PSS composition.

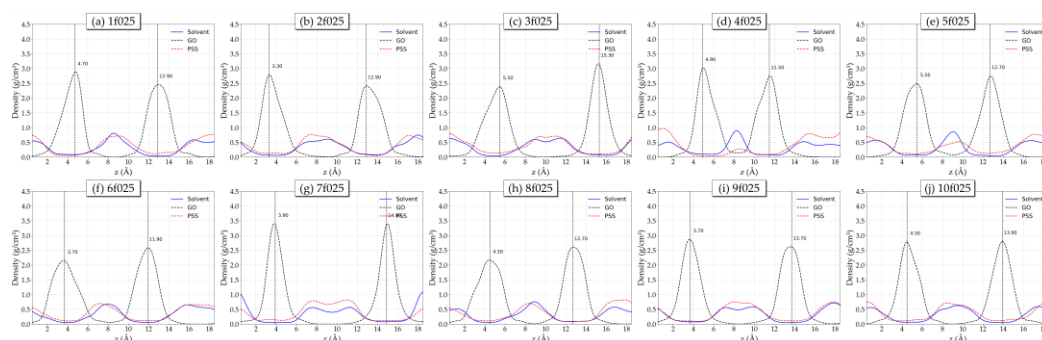


Figure S3. Mass density for each initial configuration for the rGO/PSS f025 composition.

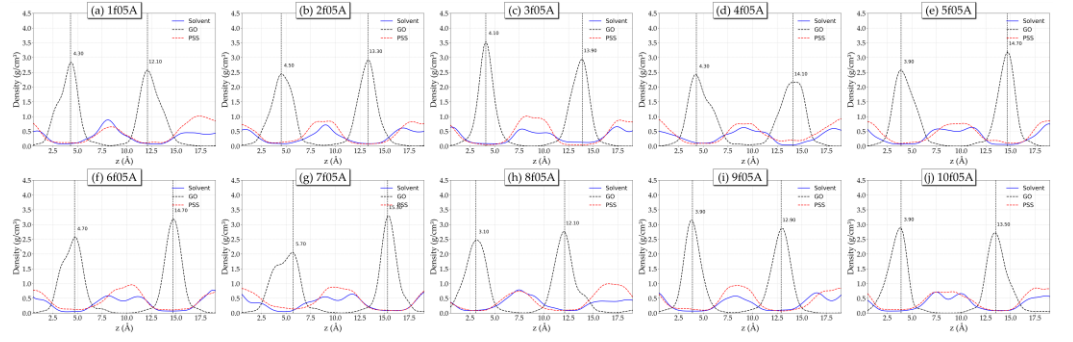


Figure S4. Mass density for each initial configuration for the rGO/PSS f05A composition.

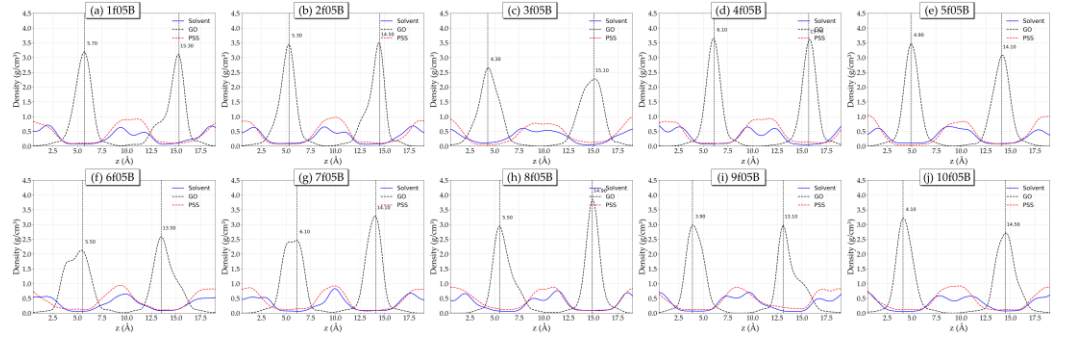


Figure S5. Mass density for each initial configuration for the rGO/PSS f05B composition.

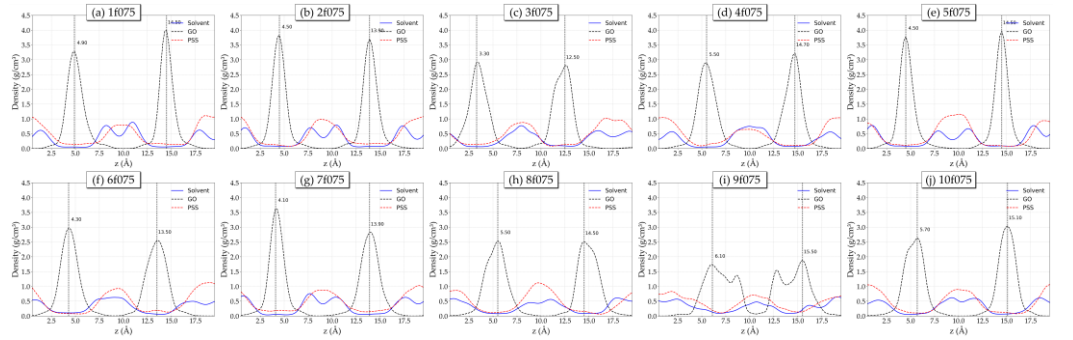


Figure S6. Mass density for each initial configuration for the rGO/PSS f075 composition.

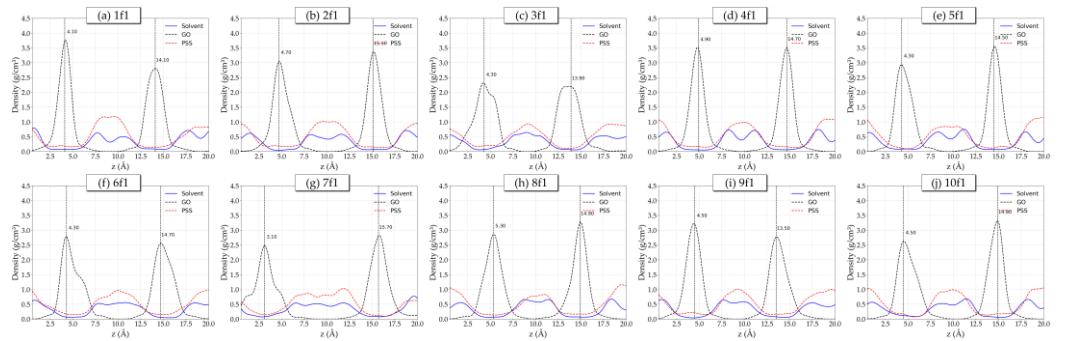


Figure S7. Mass density for each initial configuration for the rGO/PSS f1 composition.

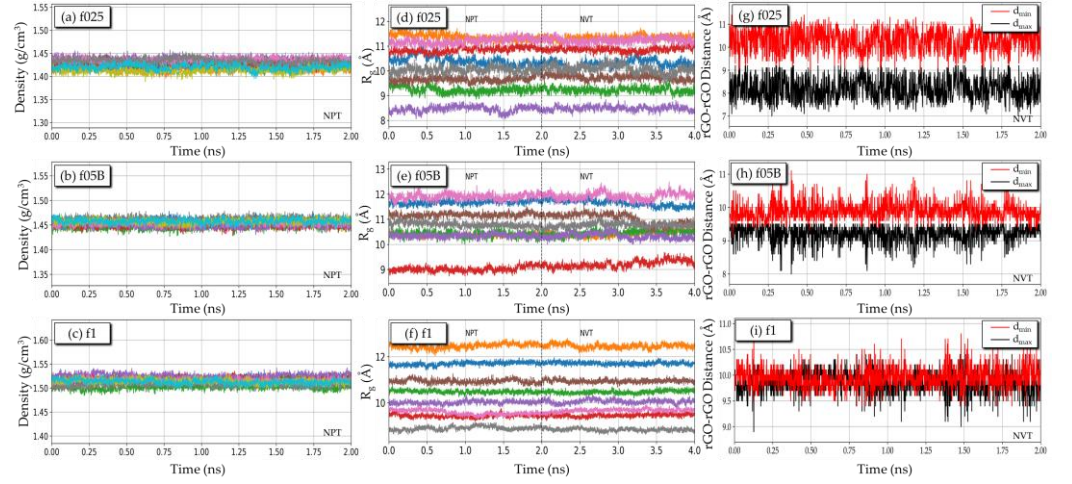


Figure S8. (a–c) Density, (d–f) radius of gyration, and (g–i) rGO–rGO distance as a function of time for the systems f025, f05B, and f1. These profiles confirm that the system does not undergo significant structural changes over the time interval encompassing both the NPT equilibration and subsequent NVT production phases.

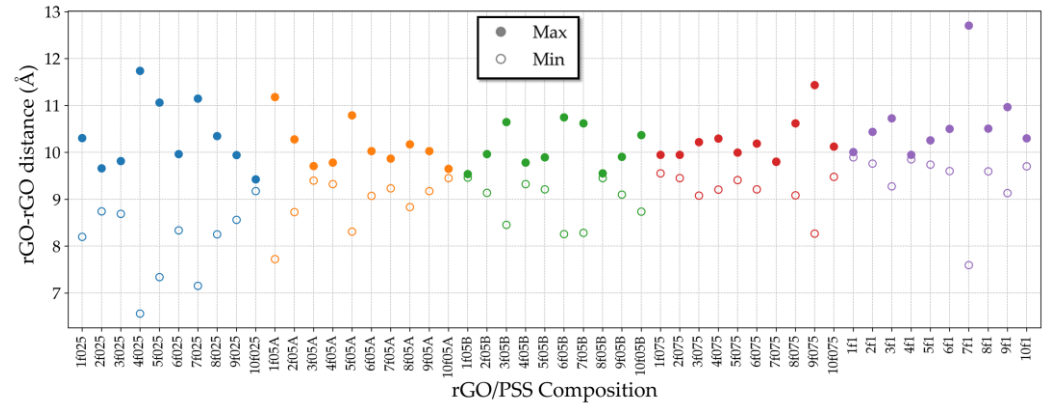


Figure S9. Maximum and minimum average rGO distance for each composition.

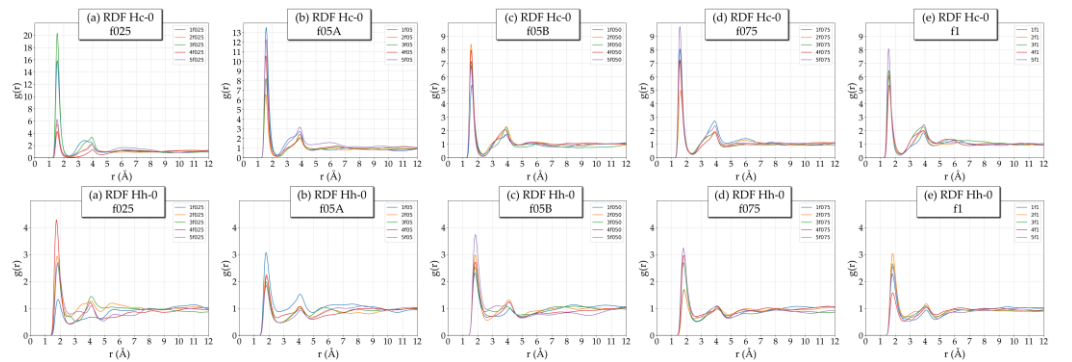


Figure S10. Radial distribution function between the carboxyl and hydroxyl groups of the rGO sheet with the oxygen atoms of PSS.

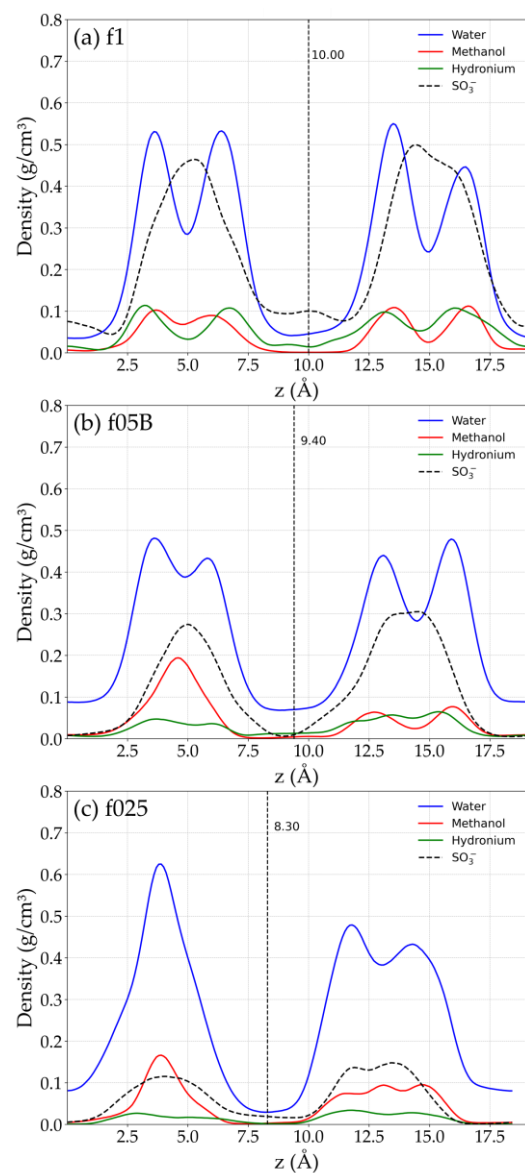


Figure S11. The mass profiles of water (blue), methanol (red), hydronium (green), and SO₃⁻ (black) for films with sulfonate fraction (a) f1 and (b) f05B and (c) f025, representing typical distribution of the components along the z-direction.

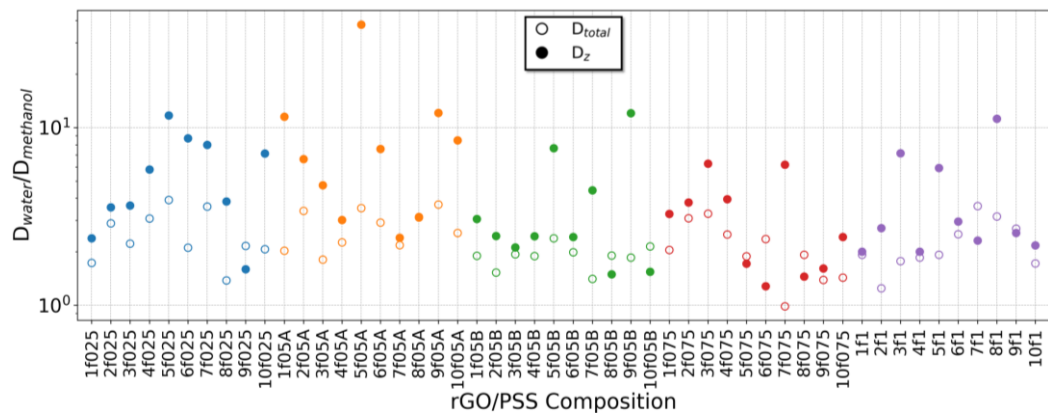


Figure S12. $D(\text{water})/D(\text{methanol})$ ratio.

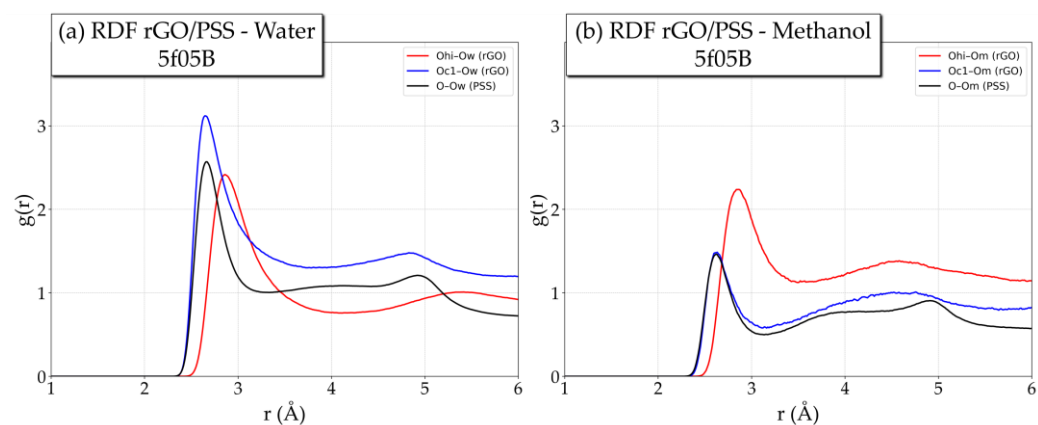


Figure S13. Radial distribution function between oxygen atoms of the carboxyl and hydroxyl groups of the rGO sheet and (a) water oxygen atoms and (b) methanol oxygen atoms.

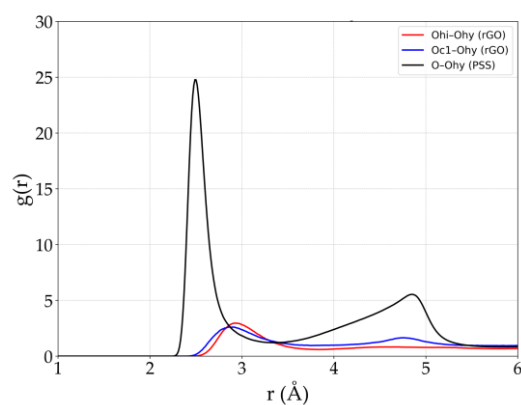


Figure S14. Radial distribution function between oxygen atoms of the carboxyl and hydroxyl groups of the rGO sheet and hydronium oxygen atoms.

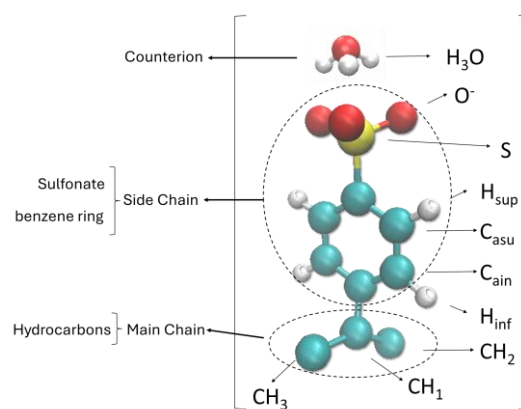


Figure S15. Diagram of the PSS monomer with hydronium counterion.

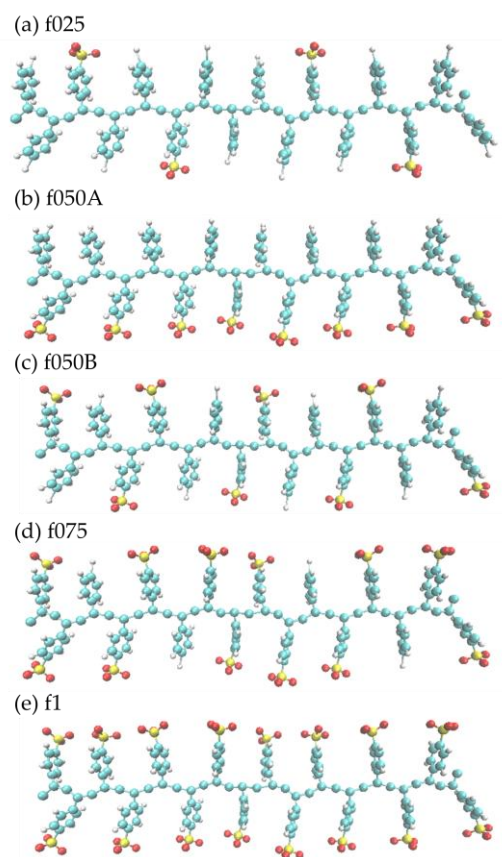


Figure S16. PSS configurations with different degrees of sulfonation.

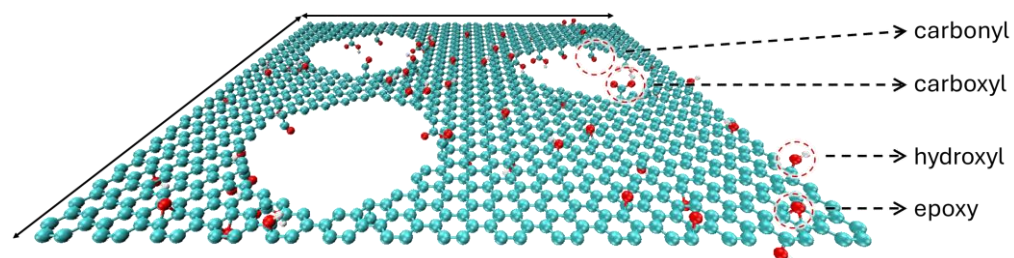


Figure S17. rGO sheet with oxygen-containing groups.

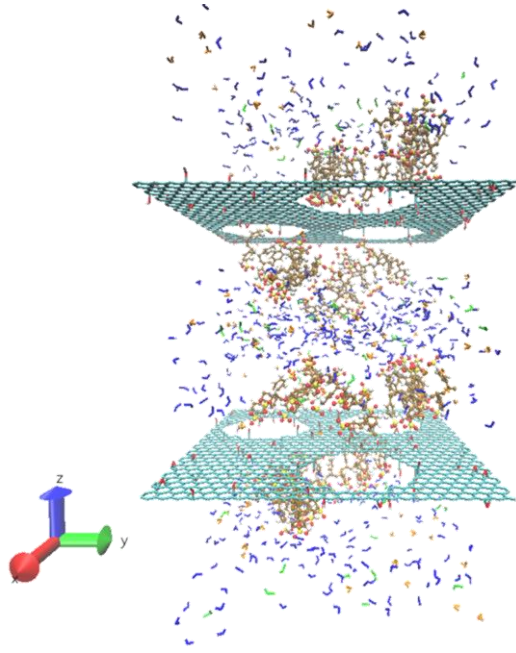


Figure S18. Initial configuration of GPSS (GPSS1F1). PSS carbon atoms are shown in ochre, water molecules in blue, methanol in green, hydronium in orange, and rGO carbon atoms in cyan.

Table S1. Lennard-Jones parameters and partial charges for PSS ($U_{LJ} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$).

LJ	ϵ (kcal/mol)	σ (Å)	Charge (e)
$\mathcal{C}_{ach}$	0.0860	3.3997	-0.0556
$\mathcal{C}_{ao}$	0.0860	3.3997	-0.1438
$\mathcal{C}_{ain}$	0.0860	3.3997	-0.1133
$\mathcal{C}_{asu}$	0.0860	3.3997	-0.0905
$\mathcal{CH}_1$	0.0994	3.4887	0.0000
$\mathcal{CH}_2$	0.1094	3.6669	0.0000
$\mathcal{CH}_3$	0.1494	3.6669	0.0000
H	0.0150	2.5996	0.2670
H_{inf}	0.0150	2.5996	0.0631
H_{sup}	0.0150	2.5996	0.1069
$\mathcal{S}$	0.3440	3.5903	1.1063
$\mathcal{O}$	0.0957	3.0331	-0.6131
$\mathcal{O}_{hy}$	0.1553	3.1600	-0.2480

Table S2. PSS bond parameters($U_b = K_b(r - r_o)^2$).

Bond	k_b (kcal/mol*Å ²)	r_0 (Å)
$\mathcal{C}_{ach}-\mathcal{C}_{ain}$	469	1.400
$\mathcal{C}_{ach}-\mathcal{CH}_1$	317	1.510
$\mathcal{C}_{ao}-\mathcal{C}_{asu}$	469	1.400
$\mathcal{C}_{ao}-H$	367	1.080
$\mathcal{C}_{ao}-\mathcal{S}$	350	1.740

$C_{air}-C_{asu}$	469	1.400
$C_{air}-C_{ain}$	367	1.080
$C_{air}-H_{sup}$	367	1.080
CH_1-CH_2	310	1.526
CH_1-CH_3	310	1.526
$O-S$	350	1.480
$O_{hy}-H_{hy}$	553.2	0.970

Table S3. PSS angle parameters ($U_\theta = K_\theta(\theta - \theta_o)^2$).

Angle	K_θ (kcal/mol · rad ²)	θ_o (degrees)
$C_{ach}-C_{air}-C_{asu}$	63.000	120.000
$C_{ach}-C_{air}-H_{inf}$	35.000	120.000
$C_{ach}-CH_1-CH_2$	60.000	109.470
$C_{ach}-CH_1-CH_3$	60.000	109.470
$C_{ao}-C_{asu}-C_{ain}$	63.000	120.000
$C_{ao}-C_{asu}-H_{sup}$	35.000	120.000
$C_{ao}-S-O$	56.160	103.800
$C_{air}-C_{ach}-C_{ain}$	63.000	120.000
$C_{air}-C_{ach}-CH_1$	70.000	120.000
$C_{air}-C_{asu}-H_{sup}$	35.000	120.000
$C_{asu}-C_{ao}-C_{asu}$	63.000	120.000
$C_{asu}-C_{ao}-H$	35.000	120.000

Table S4. PSS dihedral parameters ($U_\varphi = K_\varphi[1 + \cos(n\varphi - d)]$).

Dihedral	$k\varphi$ (cal/mol)	n	d (degrees)
$C_{ach}-C_{air}-C_{asu}-C_{ao}$	3.1	2	180
$C_{ach}-C_{air}-C_{asu}-H_{sup}$	3.1	2	180
$C_{ach}-CH_1-CH_2-CH_1$	1.4	3	0
$C_{air}-C_{ach}-C_{air}-C_{asu}$	3.1	2	180
$C_{air}-C_{ach}-C_{air}-H_{inf}$	3.1	2	180
$C_{air}-C_{ach}-CH_1-CH_2$	0	0	0
$C_{air}-C_{ach}-CH_1-CH_3$	0	0	0
$C_{asu}-C_{ao}-C_{asu}-C_{ain}$	3.1	2	180
$C_{asu}-C_{ao}-C_{asu}-H_{sup}$	3.1	2	180
$C_{asu}-C_{ao}-S-O$	1.3	2	180
$CH_1-C_{ach}-C_{air}-C_{asu}$	3.1	2	180
$CH_1-C_{ach}-C_{air}-H_{inf}$	1.4	3	0
$CH_2-CH_1-CH_2-CH_1$	1.4	3	0
$CH_3-CH_1-CH_2-CH_1$	1.4	3	0
$H-C_{ao}-C_{asu}-C_{ain}$	3.1	2	180
$H-C_{ao}-C_{asu}-H_{sup}$	3.1	2	180
$H_{inf}-C_{air}-C_{asu}-C_{ao}$	3.1	2	180
$H_{inf}-C_{air}-C_{asu}-H_{sup}$	3.1	2	180

$\mathcal{S}-\mathcal{C}_{ao}-\mathcal{C}_{asu}-\mathcal{C}_{ain}$	3.1	2	180
$\mathcal{S}-\mathcal{C}_{ao}-\mathcal{C}_{asu}-H_{sup}$	0	0	0

Table S5. PSS improper dihedral parameters ($U_x = K_x(x - x_o)^2$).

Improper	$K_x(Kcal.rad^{-2}.mol^{-1})$	$x (degrees)$
$\mathcal{CH}_1 - \mathcal{C}_{ach} - \mathcal{C}_{ain} - \mathcal{C}_{ain}$	2	180

Table S6. Lennard-Jones parameters and partial charges for rGO ($U_{LJ} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$).

LJ	ϵ (kcal/mol)	σ (Å)	Charge (e)
$\mathcal{C}$	0.0860	3.3997	0.0000
$\mathcal{C}_{ca1}$	0.1066	3.7500	0.5500
$\mathcal{C}_{ca2}$	0.0693	3.3997	0.0800
$\mathcal{C}_{ep}$	0.0694	3.3997	0.2000
$\mathcal{C}_{hi}$	0.0694	3.3997	0.1966
$\mathcal{C}_k$	0.1050	3.7500	0.4610
H_{ca}	0.0000	0.0000	0.4500
H_{hi}	0.0000	0.0000	0.3294
$\mathcal{O}_{1ca}$	0.1726	3.0000	-0.5800
$\mathcal{O}_{2ca}$	0.2132	2.9600	-0.5000
$\mathcal{O}_{ep}$	0.1422	3.0330	-0.4000
$\mathcal{O}_{hi}$	0.1399	3.1660	-0.5260
$\mathcal{O}_k$	0.2100	2.9600	-0.4610

Table S7. rGO bond parameters ($U_b = K_b(r - r_o)^2$).

Bond	k_b (kcal/mol*Å ²)	r_0 (Å)
$\mathcal{C}-\mathcal{C}$	469.000	1.400
$\mathcal{C}-\mathcal{C}_{2c}$	469.000	1.400
$\mathcal{C}-\mathcal{C}_e$	365.000	1.502
$\mathcal{C}-\mathcal{C}_h$	365.000	1.502
$\mathcal{C}-\mathcal{C}_k$	254.000	1.460
$\mathcal{C}1c-\mathcal{C}2c$	300.000	1.480
$\mathcal{C}1c-\mathcal{O}1c$	230.000	1.400
$\mathcal{C}1c-\mathcal{O}2c$	750.000	1.220
$\mathcal{C}_e-\mathcal{C}_e$	222.500	1.523
$\mathcal{C}_e-\mathcal{O}_e$	220.000	1.450
$\mathcal{C}_h-\mathcal{O}_h$	428.000	1.420
$\mathcal{C}_k-\mathcal{O}_k$	700.000	1.230
$\mathcal{C}_m-\mathcal{O}_m$	1000.000	1.430
$H_c-\mathcal{O}1c$	545.000	0.960
$H_h-\mathcal{O}_h$	545.000	0.960
$H_{hy}-\mathcal{O}_{hy}$	553.285	0.970

H_m-O_m	1000.000	0.945
H_w-O_w	1000.000	1.000
$O-S$	350.000	1.480

Table S8. rGO angle parameters ($U_\theta = K_\theta(\theta - \theta_o)^2$).

Angle	K_θ (kcal/mol · rad ²)	θ_o (degrees)
$C-C-C$	63.000	120.000
$C-C-C_{2c}$	63.000	120.000
$C-C-C_e$	70.000	120.000
$C-C-C_h$	70.000	120.000
$C-C-C_k$	63.000	120.000
$C-C_{2c}-C$	63.000	120.000
$C-C_{2c}-C_{1c}$	85.000	120.000
$C-C_e-C$	40.000	109.500
$C-C_e-C_e$	63.000	114.000
$C-C_e-O_e$	50.000	109.500
$C-C_h-C$	40.000	109.500
$C-C_h-O_h$	50.000	109.500
$C-C_k-O_k$	70.000	121.300
$C_{1c}-O_{1c}-H_c$	35.000	113.000
$C_{2c}-C-C_h$	63.000	120.000
$C_{2c}-C_{1c}-O_{1c}$	70.000	120.000
$C_{2c}-C_{1c}-O_{2c}$	80.000	120.400
C_e-C-C_e	63.000	120.000
C_e-C-C_h	63.000	120.000
$C_e-C_e-O_e$	50.000	109.500
$C_e-O_e-C_e$	60.000	109.500
C_h-C-C_h	63.000	120.000
$C_h-O_h-H_h$	55.000	108.500
$O_{1c}-C_{1c}-O_{2c}$	80.000	121.000

Table S9. rGO dihedral parameters ($U_\varphi = K_\varphi[1 + \cos(n\varphi - d)]$).

Dihedral	$k\varphi$ (cal/mol)	n	d (degrees)
$C-C-C-C$	3.100	2	180
$C-C-C-C_{2c}$	0.500	1	180
$C-C-C-C_e$	3.100	2	180
$C-C-C-C_h$	3.100	2	180
$C-C-C-C_k$	3.100	2	180
$C-C-C_{2c}-C$	0.560	1	180
$C-C-C_{2c}-C_{1c}$	0.560	1	180
$C-C-C_e-C$	0.230	2	180

$\mathcal{C}-\mathcal{C}-\mathcal{C}_e-\mathcal{C}_e$	0.230	2	180
$\mathcal{C}-\mathcal{C}-\mathcal{C}_h-\mathcal{C}$	0.230	2	180
$\mathcal{C}-\mathcal{C}-\mathcal{C}_k-\mathcal{O}_k$	1.400	2	180
$\mathcal{C}_{2c}-\mathcal{C}-\mathcal{C}-\mathcal{C}_e$	3.100	2	180
$\mathcal{C}_{2c}-\mathcal{C}-\mathcal{C}-\mathcal{C}_h$	3.100	2	180
$\mathcal{C}_{2c}-\mathcal{C}-\mathcal{C}_h-\mathcal{C}$	3.100	2	180
$\mathcal{C}_{2c}-\mathcal{C}-\mathcal{C}_h-\mathcal{O}_h$	3.100	2	180
$\mathcal{C}_{2c}-\mathcal{C}_{1c}-\mathcal{O}_{1c}-H_C$	0.975	1	180
$\mathcal{C}_e-\mathcal{C}-\mathcal{C}-\mathcal{C}_e$	3.100	2	180
$\mathcal{C}_e-\mathcal{C}-\mathcal{C}-\mathcal{C}_h$	3.100	2	180
$\mathcal{C}_e-\mathcal{C}-\mathcal{C}-\mathcal{C}_k$	3.100	2	180
$\mathcal{C}_e-\mathcal{C}-\mathcal{C}_e-\mathcal{C}$	3.100	2	180
$\mathcal{C}_e-\mathcal{C}-\mathcal{C}_e-\mathcal{C}_e$	3.100	2	180
$\mathcal{C}_e-\mathcal{C}-\mathcal{C}_h-\mathcal{C}$	3.100	2	180
$\mathcal{C}_h-\mathcal{C}-\mathcal{C}-\mathcal{C}_h$	3.100	2	180
$\mathcal{C}_h-\mathcal{C}-\mathcal{C}-\mathcal{C}_k$	3.100	2	180
$\mathcal{C}_h-\mathcal{C}-\mathcal{C}_{2c}-\mathcal{C}$	3.100	2	180
$\mathcal{C}_h-\mathcal{C}-\mathcal{C}_{2c}-\mathcal{C}_{1c}$	0.560	1	180
$\mathcal{C}_h-\mathcal{C}-\mathcal{C}_e-\mathcal{C}$	3.100	2	180
$\mathcal{C}_h-\mathcal{C}-\mathcal{C}_e-\mathcal{C}_e$	3.100	2	180
$\mathcal{C}_h-\mathcal{C}-\mathcal{C}_h-\mathcal{C}$	3.100	2	180
$\mathcal{O}_{1c}-\mathcal{C}_{1c}-\mathcal{C}_{2c}-\mathcal{C}$	1.400	2	180
$\mathcal{O}_{2c}-\mathcal{C}_{1c}-\mathcal{C}_{2c}-\mathcal{C}$	1.400	2	180
$\mathcal{O}_{2c}-\mathcal{C}_{1c}-\mathcal{O}_{1c}-H_C$	2.050	2	180
