Electronic Supplementary Information (ESI) for

Multiscale Molecular Thermodynamics of Graphene-oxide Liquid-phase Exfoliation

Amir A. Farajian[1]*, Reza Mortezaee[1], Tim H. Osborn[1,†], Olga V. Pupysheva[1], Michael Wang[2], Aruna Zhamu[2], and Bor Z. Jang[2]

[1]*Department of Mechanical and Materials Engineering, Wright State University, 3640 Colonel Glenn Highway, Dayton, Ohio 45435, U.S.A.*

[2]*Angstron Materials LLC, 1240 McCook Avenue, Dayton, Ohio 45404, U.S.A.*

Figure S1

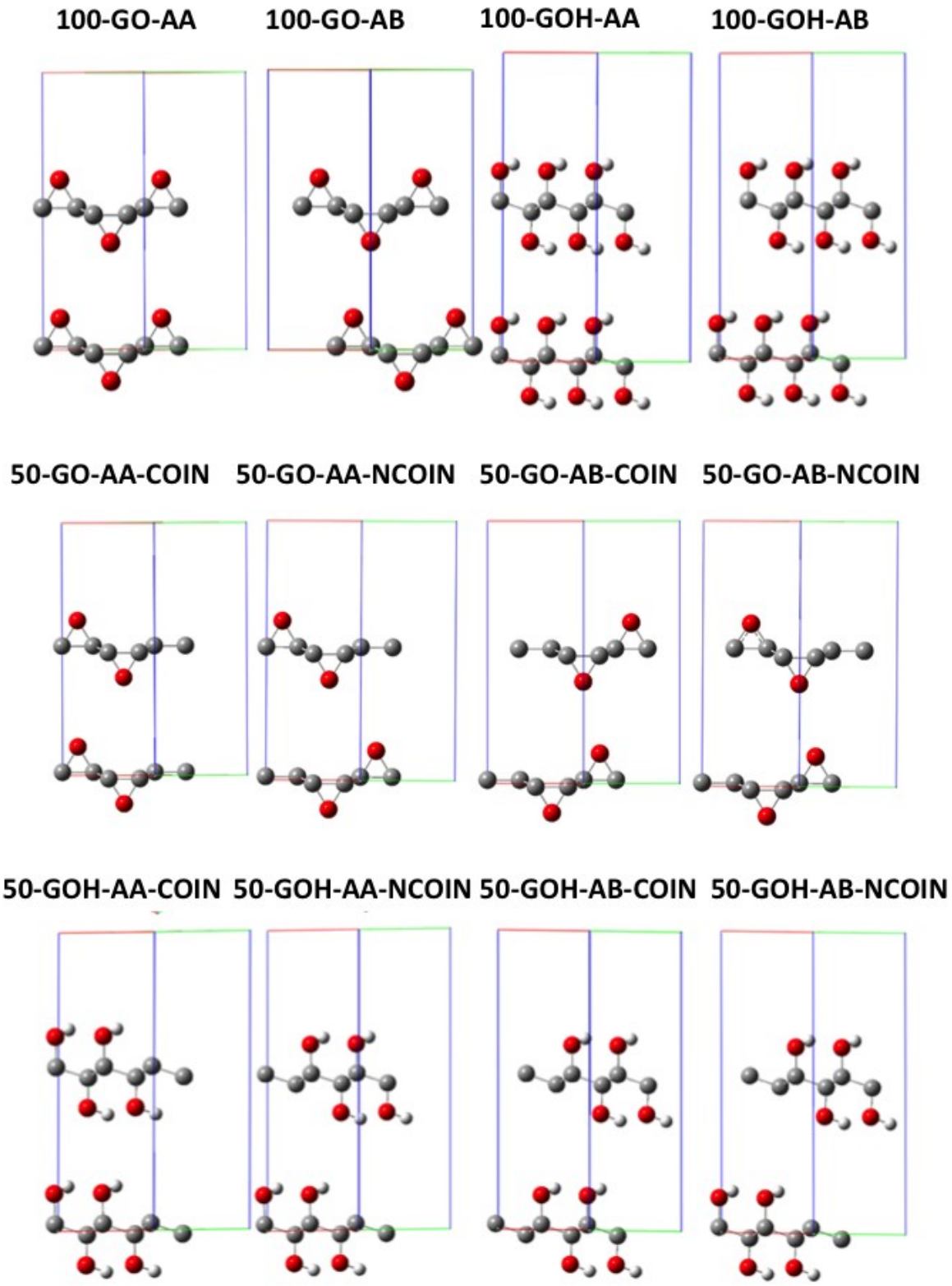
100-GO-AA
100-GO-AB
100-GOH-AA
100-GOH-AB
50-GO-AA-COIN
50-GO-AA-NCOIN
50-GO-AB-COIN
50-GO-AB-NCOIN
50-GOH-AA-COIN
50-GOH-AA-NCOIN
50-GOH-AB-COIN
50-GOH-AB-NCOIN

Figure S1: Side views (i.e., parallel to the GO planes) of unit cells containing various bilayer GO structures with one-type coverage (either epoxy or hydroxyl group) for periodic DFT-LDA calculations. AA and AB refer to graphene bilayer stacking, 100 and 50 denote coverage percentage, GO is for epoxy- and GOH is for hydroxyl-group: 100% epoxy- and hydroxyl-group coverage in AA and AB arrangements (100-GO-AA, 100-GO-AB, 100-GOH-AA, and 100-GOH-AB); 50% epoxy-group coverage in AA and AB arrangements with coinciding and non-coinciding bilayer configurations (50-GO-AA-COIN, 50-GO-AA-NCOIN, 50-GO-AB-COIN, and 50-GO-AB-NCOIN); 50% hydroxyl-group coverage in AA and AB arrangements with coinciding and non-coinciding bilayer configurations (50-GOH-AA-COIN, 50-GOH-AA-NCOIN, 50-GOH-AB-COIN, and 50-GOH-AB-NCOIN). For 50% coverages, coinciding (COIN) and non-coinciding (NCOIN) denote relative location of functional groups of the top and bottom layers.

Table S1

Structure	100-GO-OPT	100-GOH-OPT	50-GO-OPT	50-GOH-OPT	75-GO-GOH-OPT
$k_{sh,x}$ (J/m^2)	874.9	162.3	402.9	635.5	112.1
$k_{sh,y}$ (J/m^2)	206.4	74.6	108.1	1829.9	384.8
$k_{sh,z}$ (J/m^2)	1942.4	4020.9	1665.0	1393.7	1784.7
$k_{t,x}$ (10^{-15}J/rad^2)	264	509	217	169	3.8
$k_{t,y}$ (10^{-15}J/rad^2)	256	537	216	163	3.4
$k_{t,z}$ (10^{-15}J/rad^2)	1.5	0.0	0.8	3.0	0.1

Table S1: Effective inter-layer force constants $k_{sh,i}$ (in units of J/m^2) for shifts and $k_{t,i}$ (in units of 10^{-15}J/rad^2) for tilts, of bilayer GO square sheets with 40 Å side lengths. The effective force constants are calculated by parabolic fits to the UFF energy variation upon small shift/tilt values around minimum energy configurations of bilayer GO. *x* and *y* are in-plane coordinates, i.e. parallel to the edges of the square sheets of bilayer GO, and *z* is perpendicular to the GO plane.

Figure S2

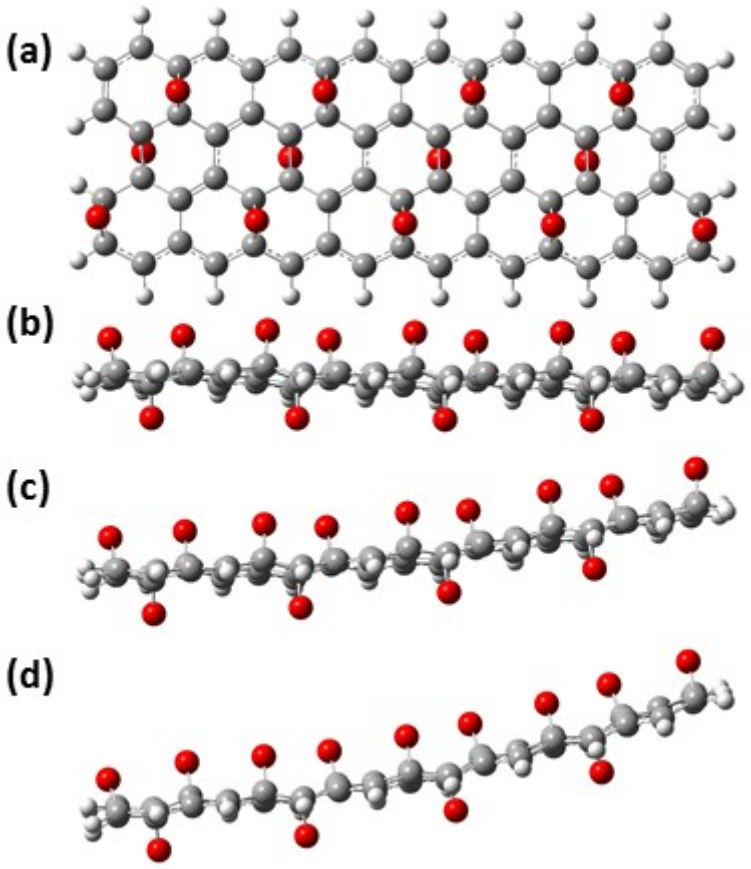

Figure S2: Top (a) and side (b) views of optimized GO nanoribbon with zigzag edge and 50% epoxy coverage, as well as side views of its constrained optimization results with bent right edge to accommodate one (c) and two (d) water molecules.

Figure S3

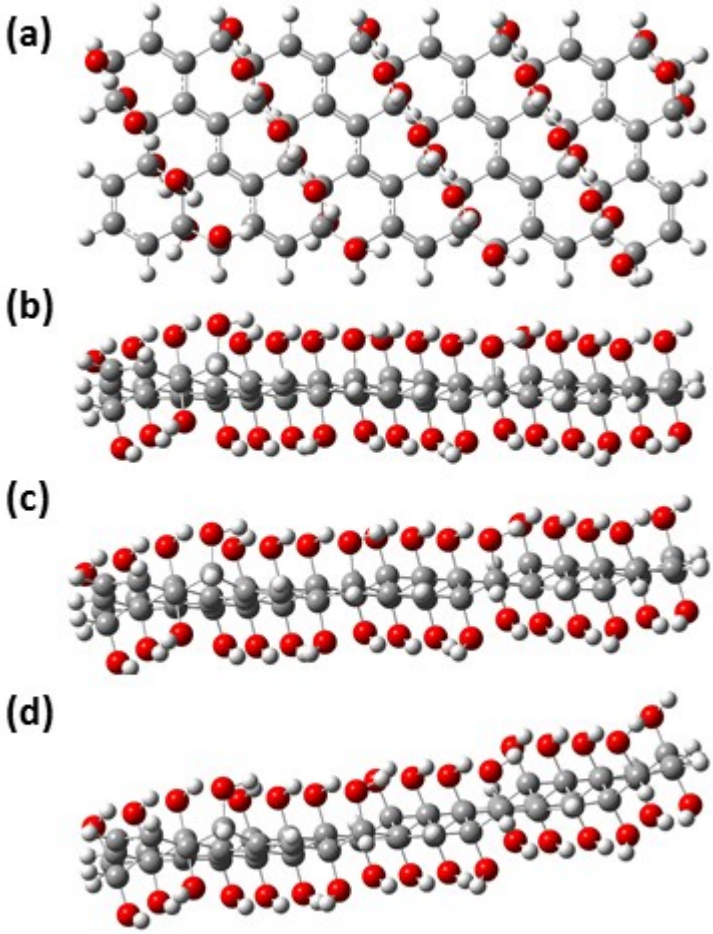

Figure S3: Top (a) and side (b) views of optimized GO nanoribbon with zigzag edge and 50% hydroxyl coverage, as well as side views of its constrained optimization results with bent right edge to accommodate one (c) and two (d) water molecules.

Figure S4

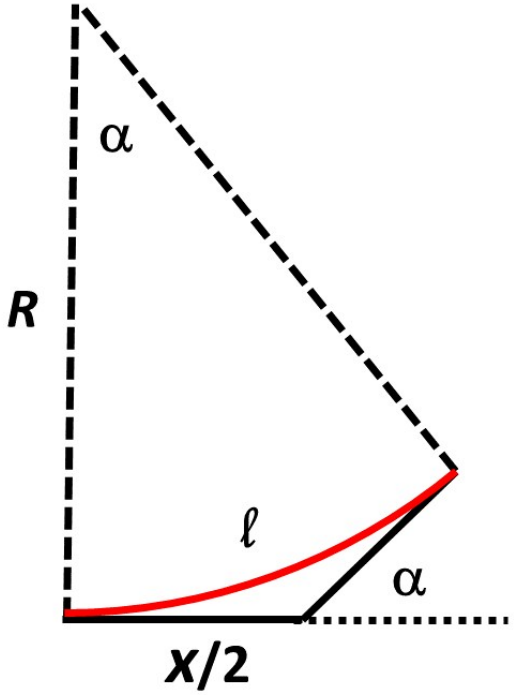

Figure S4: The difference between the lengths of initial nanoribbon structure with abrupt bent at the middle (x) and that of nanoribbon with smooth curvature after constrained optimization (l) is $x - l = \left(2 - \frac{\alpha[rad]}{\tan(\alpha/2)}\right)\frac{x}{2}$ This difference is added to the length of the nanoribbon (with abrupt bent) before constrained optimization to make the optimized arc's length equal to that of flat nanoribbon optimized without any constraint, and hence avoid unrealistic stress buildup that affects energetics.

Table S2

Structure	Coverage	Bent 1 energy (eV)	Bent 2 energy (eV)
GO-A	50%	-0.014	-0.008
GO-Z	50%	0.040	0.064
GOH-A	50%	-0.007	-0.028
GOH-Z	50%	0.005	0.047
GM-A	75%	0.054	0.143
GM-Z	75%	0.038	0.113
GO-A	100%	-0.013	-0.012
GO-Z	100%	0.638	-0.017
GOH-A	100%	0.067	0.123
GOH-Z	100%	0.063	0.119

Table S2: Energy change after constrained optimization upon bending of different nanoribbon structures. GO, GOH, and GM represent graphene oxide with epoxy functional groups, graphene oxide with hydroxyl functional groups, and graphene oxide with mixed functional groups (as introduced in the text). A and Z refer to armchair and zigzag edge geometry, respectively. Bent 1 and Bent 2 refer to bending to accommodate one and 2 water molecules, respectively.

Table S3

Structure	100-GO-OPT	100-GOH-OPT	50-GO-OPT	50-GOH-OPT	75-GO-GOH-OPT
σ (Å)	3.97	5.59	3.83	4.75	5.16
ε_{L-J} (eV)	41.275	39.587	34.574	38.003	35.025

Table S3: Lennard-Jones parameters for modeling interlayer energy rise upon bending of square nanoplatelets with various coverages and 40 Å side length.