

# Supporting Information

## Properties of Nanographene in Polymer Nanocomposites through Molecular Simulations: Dynamics and Anisotropic Brownian Motion

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## Atomistic Force Field

Simulations were performed with the GROMACS simulation package.<sup>1</sup> United atom models are applied for both polymers, PE and PEO based on the TraPPE force field,<sup>2</sup> which has been slightly modified in the case of PEO.<sup>3</sup> Non-bonded interactions between polymer atoms, as well as between the carbons of graphene and polymer atoms, are described by a spherically truncated 6-12 Lennard-Jones potential. Standard Lorentz- Berthelot mixing rules were used. Concerning the model graphene sheets we applied a force field previously used for various carbon structures<sup>4,5</sup> whereas, for the functional groups grafted on the graphene edges, the OPLS-AA force field was utilized.<sup>6</sup> Note that the OPLS force field uses scaling factors 0.5 for the 1-4 interactions, which is not the case of the graphene force field. Therefore, the parameters for this type of interaction were adapted in the way as it was done for the proteins in ref.<sup>7</sup> Table SI-1 contains  $\epsilon$  and  $\sigma$  parameters for all atoms of the systems whereas, all bonded parameters are included in Table SI-2.

**Table SI-1.** Model parameters and functional forms of all non-bonded interactions of the atomistic force field used here.

<b>Non-Bonded Interactions</b>				
$V_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], r \leq R_c$				
<b>Atom Types</b>	<b>mass (g/mol)</b>	<b><math>\sigma</math> (nm)</b>	<b><math>\epsilon</math> (kJoule/mol)</b>	<b>Atom Description</b>
CH2	14.027	0.395	0.382465	united atom of polymer
CH3	15.035	0.375	0.814818	terminal united atom of polymer
OM	15.9994	0.28	0.457296	oxygen of PEO
CGR	12.011	0.347	0.275	carbon of graphene
CGRC	12.011	0.355	0.29288	functionalized carbon atom
CX	12.011	0.375	0.43932	carbon of carboxyl group
O	15.9994	0.296	0.87864	Oxygen
OH	15.9994	0.3	0.71128	oxygen of carboxyl group
HO	1.008	0.0	0.0	hydrogen of carboxyl group
H	1.008	0.242	0.12552	hydrogen

**Table SI-2.** Model parameters and functional forms of all bonded interactions of the atomistic force field used here.

<b>Bonded Interactions</b>		
$V_b(r_{ij}) = \frac{1}{2} k_{ij}^b (r_{ij} - b_{ij})^2$		
<b>Bond</b>	<b>b (nm)</b>	<b>k<sup>b</sup> (kJ/mol·nm<sup>2</sup>)</b>
CH2 -CH2	0.154	217700
CH2-OM	0.141	267900
CH3-OM	0.141	267900
CGR-CGR	0.1418	478.9
CGRC-CGR	0.1418	478.9
CGRC-CGRC	0.1418	478.9
CX-CGRC	0.149	334720
CX-O	0.1229	476976
CX-OH	0.1364	376560
HO-OH	0.0945	462750.4
CGRC-H	0.108	307105.6
$V_\alpha(\theta_{ijk}) = \frac{1}{2} k_{ijk}^\theta (\theta_{ijk} - \theta_{ijk}^0)^2$		
<b>Angle</b>	<b><math>\theta^0</math> (deg)</b>	<b>k<sup>0</sup> (kJ/mol*rad<sup>2</sup>)</b>
CH2-CH2-OM	112	418.218
CH2-OM-CH2	112	502.194
CH3-OM-CH2	112	502.194
CGR-CGR-CGR	120	562.2
CGR-CGR-CGRC	120	562.2
CGR-CGRC-CGR	120	562.2
CGRC-CGR-CGRC	120	562.2
CGRC-CGRC-CGR	120	562.2
CGRC-CGRC-CGRC	120	562.2
CX-OH-HO	113	292.88
CGRC-CX-OH	120	585.76
CGRC-CX-O	120.4	669.44
CX-CGRC-CGR	120	711.28
CX-CGRC-CGRC	120	711.28
O-CX-OH	121	669.44
CGR-CGRC-H	120	292.88
CGRC-CGRC-H	120	292.88

$$V_{rb}(\varphi_{ijkl}) = \sum_{n=0}^5 C_n (\cos(\psi))^n$$

Dihedral	C <sub>0</sub> (KJ/mol)	C <sub>1</sub> (KJ/mol)	C <sub>2</sub> (KJ/mol)	C <sub>3</sub> (KJ/mol)	C <sub>4</sub> (KJ/mol)	C <sub>5</sub> (KJ/mol)
OM-CH2-CH2-OM	2.22267	17.03651	8.29835	-31.2451	5.13025	-1.91522
CH2-CH2-OM-CH2	1.60941	19.79231	-7.82474	-15.7247	6.43215	-4.5435
CH2-CH2-OM-CH3	1.60941	19.79231	-7.82474	-15.7247	6.43215	-4.5435
CGR-CGR-CGR-CGR	25.12	0	-25.12	0	0	0
CGR-CGR-CGRC-CGRC	25.12	0	-25.12	0	0	0
CGR-CGRC-CGR-CGR	25.12	0	-25.12	0	0	0
CGR-CGRC-CGRC-CGR	25.12	0	-25.12	0	0	0
CGRC-CGR-CGRC-CGR	25.12	0	-25.12	0	0	0
CGR-CGRC-CGR- CGRC	25.12	0	-25.12	0	0	0
CGRC-CGR-CGR- CGRC	25.12	0	-25.12	0	0	0
CGRC-CGR-CGR- CGR	25.12	0	-25.12	0	0	0
CGRC-CGRC-CGRC-CGR	25.12	0	-25.12	0	0	0
CGRC-CGRC-CGR-CGRC	25.12	0	-25.12	0	0	0
CGRC-CX-OH-HO	29.288	-8.368	-20.92	0	0	0
CGR-CGRC-CX-OH	8.7864	0	-8.7864	0	0	0
CGR-CGRC-CX-O	8.7864	0	-8.7864	0	0	0
CGRC-CGRC-CX-OH	8.7864	0	-8.7864	0	0	0
CGRC-CGRC-CX-O	8.7864	0	-8.7864	0	0	0
HO-OH-CX-O	20.92	0	-20.92	0	0	0
H-CGRC-CGRC-H	25.12	0	-25.12	0	0	0
CX-CGRC-CGRC-H	25.12	0	-25.12	0	0	0
CX-CGRC-CGRC-CX	25.12	0	-25.12	0	0	0
CX-CGRC-CGR-CGR	25.12	0	-25.12	0	0	0
CX-CGRC-CGRC-CGR	25.12	0	-25.12	0	0	0
CX-CGRC-CGR-CGRC	25.12	0	-25.12	0	0	0
CX-CGRC-CGRC-CGRC	25.12	0	-25.12	0	0	0
H-CGRC-CGR-CGR	25.12	0	-25.12	0	0	0
H-CGRC-CGRC-CGR	25.12	0	-25.12	0	0	0
H-CGRC-CGR-CGRC	25.12	0	-25.12	0	0	0
H-CGRC-CGRC-CGRC	25.12	0	-25.12	0	0	0

## Generation and Equilibration of Model Systems

For the construction of an initial configuration of a graphene-based polymer nanocomposite model system the following procedure is used: Having an equilibrated configuration of the corresponding bulk polymer we enlarge the simulation box in one dimension such that free space is created. Then we move the coordinates of the polymer melt in the same direction such that almost half of it is placed out of the simulation box. In the following a graphene sheet is put in the free space in a distance which ensures no overlaps with the polymer atoms and an *NPT* simulation run starts till the system reaches the desired density. Due to the application of periodic boundary conditions, this procedure results in a configuration of the nanocomposite where the graphene flake is surrounded by polymer chains, which is used as an initial configuration for our simulation run.

## Shape Analysis

The shape of the graphene layer can be characterized through the asphericity ( $a$ ) and prolateness ( $p$ ) parameters, which are obtained from the radius of gyration tensor.

In more detail, the asphericity ( $a$ ) is given by :  $a = \frac{(L_y - L_x)^2 + (L_z - L_x)^2 + (L_z - L_y)^2}{2(L_x + L_y + L_z)^2}$ , where  $L_c$

( $c=x,y,z$ ) are the three principal moments of the gyration tensor. The asphericity parameter attains values between 0 and 1, for a perfectly spherical object  $a=0$  and  $L_x=L_y=L_z$ .

The prolateness ( $p$ ) is given by:  $p = \frac{(2L_x - L_y - L_z)(2L_y - L_x - L_z)(2L_z - L_x - L_y)}{2(L_x^2 + L_y^2 + L_z^2 - L_xL_y - L_xL_z - L_yL_z)^{3/2}}$  and its values are in

the range  $-1 \leq p \leq 1$ ; for perfectly oblate objects  $p=-1$  and  $L_x < L_y = L_z$ , whereas for perfectly prolate objects  $p=1$  and  $L_x = L_y < L_z$ . Values for  $a$  and  $p$  for the pristine and functionalized nanographene flakes at  $T = 450K$  are presented in Table SI-3

**Table SI-3:** Asphericity ( $a$ ), prolateness ( $p$ ) and the average second moment of the out of plane displacement, spatially averaged over all the atoms of the sheet (amplitude of rippling), for various simulated systems.

System	$A$	$P$	$d_{mean} = \sqrt{\langle d^2 \rangle}$ (Å)
$G_{20}/PE$	$0.19 \pm 0.07$	$-0.61 \pm 0.50$	0.610
$G_{50}/PE$	$0.23 \pm 0.01$	$-0.87 \pm 0.24$	0.892
$G_{80}/PE$	$0.24 \pm 0.008$	$-0.90 \pm 0.14$	1.236
$G_H/PE$	$0.23 \pm 0.02$	$-0.85 \pm 0.26$	0.624
$G_{COOH}/PE$	$0.24 \pm 0.02$	$-0.61 \pm 0.32$	0.622
$G_H/PEO$	$0.23 \pm 0.01$	$-0.88 \pm 0.18$	0.626
$G_{COOH}/PEO$	$0.23 \pm 0.01$	$-0.76 \pm 0.24$	0.639

Although rippling of the nanographene flakes in the nanocomposites, induce continuous changes in their shape, values of Table SI-3 predict a shape closely described by an oblate ellipsoid (in the limit of a thin disk).

### Amplitude of rippling

In the fourth column of Table SI-3 the data for the average amplitude of the out of plane displacement of all C atoms in the nanographene layer are reported. Comparing nanographene flakes of the same dimensions (i.e.,  $(4.9 \times 5.1) \text{ nm}^2$ ) there is an obvious suppress of rippling in functionalized sheets. Furthermore bigger ripples are formed in the bigger graphene flakes.

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