

Properties of Nanographene in Polymer Nanocomposites through All-atom Simulations

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ABSTRACT - SUMMARY:

Nanographene sheets embedded in polymer matrices are studied through all-atom Molecular Dynamics simulations. Conformational and morphological transitions (rippling) of graphene sheets are presented in atomistic detail. The dynamics of graphene sheets in the polymer matrices is also investigated in atomic scale, as a function of the host matrix, the type of the graphene sheet and the temperature.

INTRODUCTION:

The morphology of graphene and the response of rippling under external stimuli (i.e, strain) have been studied both through simulations [1] and experiments [2]. On top of that, functionalization of graphene sheets was found to be crucial for its conformational transitions, such as rippling and wrinkling [3]. Structural defects can also affect the performance of the various graphene-based devices. Despite the fact that graphene based polymer nanocomposites have been extensively studied through experimental techniques, detailed investigations at the atomistic level, of the conformational and morphological transitions, as well as the dynamical behavior, of graphene sheets with nm dimensions (nanographene) dispersed in a polymer matrix are still missing. This is exactly the main topic of the present work.

SIMULATION METHOD:

We have performed detailed atomistic MD simulations of graphene/polymer nanocomposites. Pristine graphene sheets of various sizes have been modeled. Nanographene sheets were dispersed in two different polymer matrices, a non-polar (polyethylene, PE) and a polar (polyethylene oxide, PEO) one. In addition, functionalized graphene sheets were simulated, with two types of functional groups, which are attached to the edge carbon atoms: (a) hydrogenated (G_H) and (b) carboxylated graphene (G_{COOH}). Details about the all-atom force field as well as the MD simulations are given elsewhere [4]. Moreover a thorough description of the analysis methods is presented in our extended papers.[5]

RESULTS AND DISCUSSION:

In order to compare the behavior of the nanographene sheets dispersed into two different polymer matrices (PE and PEO), we initially provide some information about the polymers. First, in Figure 1 polymer density profiles are presented. More

specifically, monomer density profiles, $\rho(r)$, are depicted as a function of the radial distance from the central atom of graphene for PE and PEO at $T=450K$. Both curves are normalized with the density of the bulk polymer respectively, at the same temperature. We observe a slightly higher peak for PE at distances very close to the graphene sheet which denotes slightly stronger attraction of PE from the surface compared to PEO. At longer distances differences are eliminated. This feature is reflected in the dynamics of polymer chains in the vicinity of the polymer/nanographene interface as well.

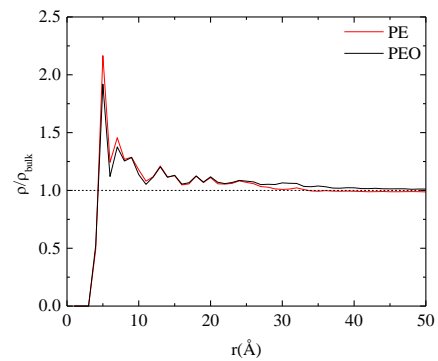


Fig. 1: Monomer mass radial density profiles for PE and PEO normalized with the corresponding bulk density values in systems G_{COOH}/PE and G_{COOH}/PEO , at $T = 450K$, as a function of distance r from the central atom of the graphene layer (Figure from ref. 5).

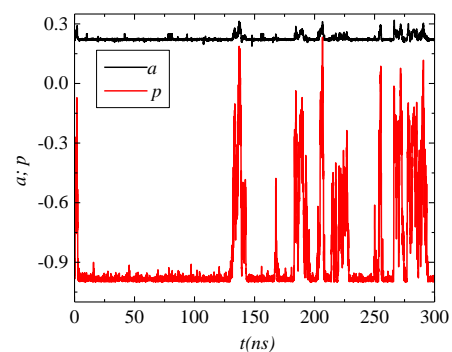
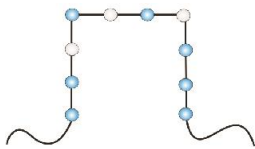


Fig. 2: Graphene's overall shape fluctuations in time asphericity (a) and prolateness (p) as a function of time for G_{50}/PE system at $T = 450K$ (Figure from ref. 5).



In the following we study the morphological transitions of graphene sheets through a detailed shape analysis of the overall shape of the graphene layers. All graphene flakes that have been used in the simulations are almost quadratic. In the initial state a nanographene sheet is very closely described as an oblate object whereas, in a nanocomposite a shape deformation is observed.

The existence of strong fluctuations in the overall shape of the nanographene is obvious in Figure 2 through the calculation of two shape parameters named, prolateness,

$$p = \frac{(2L_x - L_y - L_z)(2L_y - L_x - L_z)(2L_z - L_x - L_y)}{2(L_x^2 + L_y^2 + L_z^2 - L_x L_y - L_x L_z - L_y L_z)^{3/2}}$$

and asphericity,

$$a = \frac{(L_y - L_x)^2 + (L_z - L_x)^2 + (L_z - L_y)^2}{2(L_x + L_y + L_z)^2},$$

which are presented as a function of time for pristine graphene in polyethylene (G_{50}/PE). L_c ($c=x,y,z$) are the three principal moments of the gyration tensor. For perfectly oblate objects $p=-1$ and $a>0$. We observe that fluctuations in the overall shape exhibit long time behavior.

The conformational-morphological transitions of the graphene layers (rippling) in the local/atomistic level are presented in the following. A characteristic snapshot of a graphene flake, where crests and troughs are observed, is presented in Figure 3a. These are determined by thermal fluctuations, functionalization of the sheet and interactions with the polymer matrix. The average amplitude of rippling for every atom of the sheet has been calculated and depicted in Figure 3b for G_{50}/PE . Color code represents the amplitude of the out of plane displacement in nm. An enhanced amplitude is observed at the edge atoms compared to the central ones.

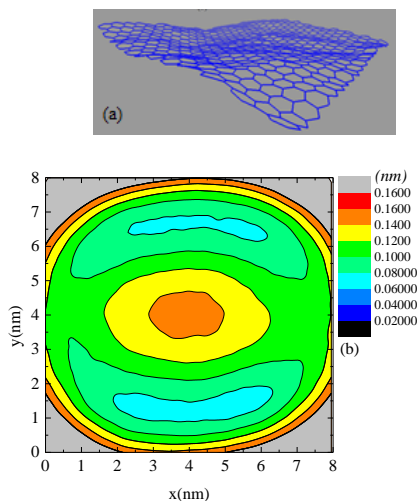


Fig. 3: (a) Characteristic snapshot of G_{50}/PE pristine graphene flake with fluctuations. (b) The average amplitude for every atom of the sheet for the G_{50}/PE system (Figure from ref. 5).

Since graphene sheet is a non-spherical object its diffusion in a medium is expected to be anisotropic with

respect to its plane, at least at short times. In order to investigate this, we analyze graphene's center-of-mass motion in the body frame. Two components of MSD are calculated: the parallel to the plane $X'Y'$, and the perpendicular one (along direction Z'). Results for MSDs of systems with two different graphene flakes (pristine and carboxylated) are presented in Figure 4. Anisotropy is apparent in both systems. There is a clear difference between the two components of MSD at short times which is eliminated for longer times, rendering the diffusion of the sheet isotropic. The motion parallel to the $X'Y'$ plane is always faster compared to the one perpendicular to the plane (Z' -component).

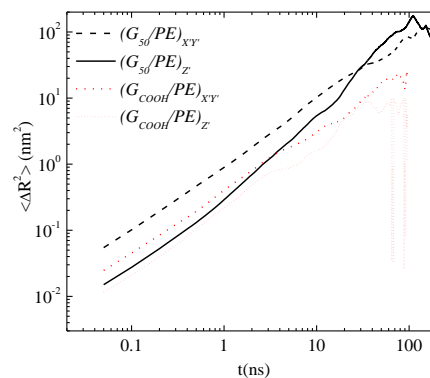


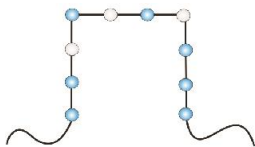
Fig. 4: The $X'Y'$ and Z' components, defined on the body frame, of the mean squared displacement of the center of mass of graphene as a function of time for G_{50}/PE and G_{COOH}/PE systems (Figure from ref. 5).

CONCLUSIONS:

In the present work we explore structural – conformational and dynamical properties of nanographene sheets in polymer/graphene nanocomposites through all-atom Molecular Dynamics simulations. Our results for all systems show that the initially undeformed (almost quadrangular) graphene flakes, which are very closely described by a perfect oblate, bear strong fluctuations which affect their overall shape. A detailed analysis, observing ripples of both small and big width, has been performed and show that thermally induced rippling of graphene flakes, do not exhibit any systematic spatial correlation. Inhomogeneity is observed in Brownian motion of graphene in terms of anisotropy between two directions, the parallel and the perpendicular to its plane. The motion along the plane is faster than the one vertical to the plane.

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11th Hellenic Polymer Society International Conference
Heraklion Crete, November 3-5, 2016

Acknowledgements: This work was partially supported by the European Union's Seventh Framework Programme (FP7-REGPOT-2012-2013-1) under Grant agreement No. 316165