

STUDY OF THE DYNAMICS OF POLYMER/GRAPHENE NANOCOMPOSITES THROUGH DETAILED ATOMISTIC SIMULATIONS

Anastassia N. Rissanou^{1,2}, Petra Bacova¹ and Vagelis Harmandaris^{1,2}

¹Institute of Applied and Computational Mathematics, Foundation for Research and Technology Hellas, GR-71110 Heraklion, Crete, Greece.

²Department of Mathematics and Applied Mathematics, University of Crete, GR-71409, Heraklion, Greece.
e-mail: rissanou@iesl.forth.gr

Keywords: Atomistic Simulations, Polymer/Graphene Nanocomposites, Dynamical properties.

Abstract. *Polymer/graphene nanocomposites are hybrid materials with a broad range of technological applications. In the current work hybrid polymer/graphene systems are studied using four different polymers (Polyethylene (PE), Polystyrene (PS), Poly(methyl methacrylate) (PMMA) and Poly(ethylene oxide) (PEO)) and graphene sheets, which are either frozen or flexible to move in the polymer matrix. We study the way that the various properties of the polymers are affected by the graphene, using detailed atomistic Molecular Dynamics simulations. The current study is focused on the dynamical properties of the hybrid systems which are compared with the corresponding properties of the bulk systems respectively.*

1 INTRODUCTION

Polymer/graphene nanocomposites have remarkable physical properties with a broad range of potential applications in many different areas. In the current study we present results which are part of a general computational approach based on a methodology of hierarchical simulations for the study of real polymer/graphene systems. Our primary goal is the study of the effect of the graphene sheets on the structural and dynamical properties of polymers. In more details we study three hybrid polymer/graphene systems: PE/graphene, PS/graphene and PMMA/graphene using a periodic graphene sheet (infinite graphene) which remains frozen during the simulation. These are thin polymer films confined between two graphene layers. Furthermore we study systems of PE/graphene and PEO/graphene where a flexible graphene sheet of finite size is used. In the last case the graphene sheet is of three different types: a) with a partial charge distribution at the edges¹, b) with edge atoms functionalized with hydrogens and c) with edge atoms functionalized with carboxyl groups (reduced graphene).

Various properties have been studied like the density profile, structural characteristics of the polymer chains as well as dynamical properties which are the focus of the current work. We study the dynamics of polymer chains both in the monomer level and the entire chain level (center of mass of the chain), recording the time evolution of the mean squared displacement, as well as through time autocorrelation functions for a vector which is defined along the polymer chain. All the examined properties are studied as a function of the distance from the graphene sheet defining in this way a series of “adsorption layers”. Moreover all the examined properties are compared to the corresponding properties of the respective bulk systems at the same conditions.

Preliminary results based on the study of the wrinkling of the graphene sheet during its motion in the polymer matrix are also presented.

2 SIMULATION METHOD

The current study was based on detailed atomistic Molecular Dynamics simulations. For the case of thin polymer films, details about the force field which was used for each different polymer are given in our previous publications.^{2,3,4} For the case of the systems with flexible graphene sheets of finite size, an all atom model was used. In this model which has been described by Bellido et al.¹ partial charges are placed on all the terminal atoms of the graphene sheet (type a). For graphene flakes with hydrogen or carboxyl groups at the end atoms (types b and c), the corresponding force fields are described in references 5 and 6. The concentration of graphene in the polymer matrix is 3% wt. Simulations are carried out at constant pressure of $P=1\text{atm}$ and temperature $T=450\text{K}$ for PE, $T=500\text{K}$ for PS and PMMA and $T=318\text{K}$ for PEO. A different analysis scheme has been used for the case of the periodic graphene sheet (“infinite graphene”) and the systems with the finite graphene layers. In the first case the various properties have been studied as a function of the distance from the graphene flake using the definition of layers parallel to the sheet of specific thickness (binning), which can have

a different value depending on the property under investigation. In the second case the analysis has been performed in radial distances measured from the center of mass of the graphene. In this way spherical shells of increasing radius are created. Again the thickness of the spherical shell diversifies according to the studied property.

3 RESULTS AND DISCUSSION

In the following we present results of dynamics for the systems that we study, dividing into two general categories: a) Confined polymer films where we use periodic graphene sheets (“infinite size”), which remain frozen during the simulations^{2,3,4} and b) Finite size graphene sheets which move freely in the polymer matrix.^{7,8}

3.1 Confined Polymer Films

Three systems of thin polymer films of the same thickness were studied: PE/graphene, PS/graphene and PMMA/graphene.^{2,4} A comparison among the three different polymers is based on a vector which is defined along the backbone of the polymer chain and connects two non-consecutive carbon atoms (\mathbf{v}_{BB}). We observe a time autocorrelation function of this vector expressed by the second Legendre polynomial: $P_2(t) = 3(\langle \cos^2\theta(t) \rangle - 1)/2$ as a function of the distance from the graphene sheet (adsorption layers). Then we fit each curve with a Kohlrausch-Williams-Watts (KWW) function: $P_2(t) = A \exp(-t/t_{KWW})^\beta$ from which the segmental relaxation time is extracted through the relation: $\tau_{seg} = (t_{KWW}/\beta)\Gamma(1/\beta)$, where $\Gamma()$ is the gamma function. Furthermore the values of the β -exponent provide important information for the distribution of the relaxation times, or in other words the deviation of the behavior of the system from the ideal Debye behavior which stands for $\beta=1$. Segmental relaxation times (τ_{seg}) as a function of the distance from the graphene layer, for the three different polymers, are depicted in Figure 1a. A qualitative similar behavior is observed for all three systems though, clear quantitative differences are detected. The monomers which are very close to the graphene sheet are much slower compared to the more distant monomers. Therefore graphene sheet induced a retardation of dynamics which results in very large values of the relaxation times at short distances. In the following relaxation times are reduced gradually and attain the values of the corresponding bulk systems at long distances from graphene (dashed horizontal lines in Figure 1a). Quantitative comparisons among the three polymers reveal PE the fastest of the three systems, which reaches the corresponding bulk value after almost $2nm$ from the surface, PS follows at almost $3nm$, while PMMA is the slowest one, it attains its bulk value at about $4nm$ from the graphene sheet. The values for the corresponding β -exponents, which are depicted in Figure 1b, do not present any specific quantitative difference among the three systems. However, the values are lower close to the interface and higher at longer distances, where the corresponding bulk values are almost attained within statistical uncertainties (± 0.05). This behavior is indicative of a broader distribution of relaxation times close to the graphene layer.

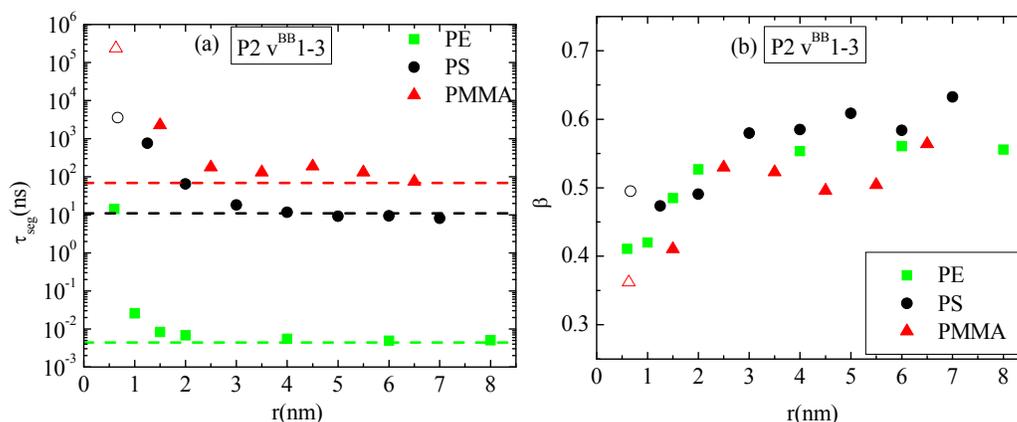


Figure 1. (a) Segmental relaxation time for the characteristic vector \mathbf{v}_{BB} , based on the time autocorrelation function $P_2(t)$ for PS, PMMA and PE polymer/graphene hybrid systems, as a function of the distance from the graphene sheet. (b) The exponent β , as it is extracted from the fit with KWW functions for all three systems.

3.2 Finite Size Graphene Sheets

In the following we study the dynamics for a polymer/graphene system, where one graphene sheet of type (a) and of finite size (49×51) \AA^2 , is moving in a PE matrix. Calculation of the segmental relaxation time for the same vector (\mathbf{v}_{BB}) as in the previous subsection leads to Figure 2a,b. Values of the corresponding bulk system are also included in Figure 2 with dashed lines. It is also obvious in this case that polymer chains close to graphene (up to almost 0.5nm) have slower dynamics compared to the rest of the film. At these distances τ_{seg} is almost 10 times larger than the bulk value. At longer distances monomers move more freely leading to an almost constant value of τ_{seg} beyond $4.0\text{-}5.0\text{nm}$. This is a similar qualitative behavior to that of the confined thin PE film, though the quantitative comparison of the two curves, shown in Figure 2a reveals a faster dynamics at short distances for the system with the finite graphene sheet (nanocomposite). Moreover the values for the exponent β are smaller compared to the bulk polymer at any distance from graphene (Figure 2b). This shows a broader distribution of the segmental relaxation times even at long distances from the graphene layer where the values for the times have reached the corresponding bulk value. This aspect of dynamical heterogeneities existing in the nanocomposite polymer systems seem to be even more complex than that in the case of the confined between two graphene layers polymer chains for which the behavior at long distances from the surface is similar to bulk.

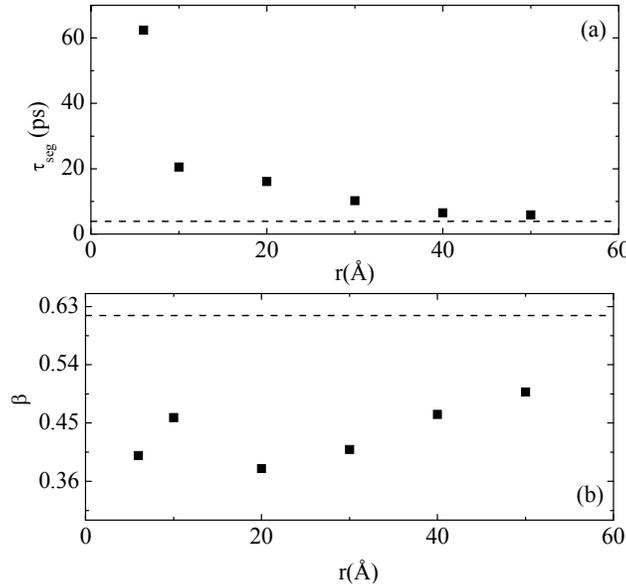


Figure 2. (a) Segmental relaxation time for the characteristic vector \mathbf{v}_{BB} , based on the time autocorrelation function $P_2(t)$ for PE as a function of the radial distance from the center of mass of the graphene sheet. (b) The exponent β , as it is extracted from the fit with KWW functions. Dashed horizontal lines correspond to the bulk PE values for τ_{seg} and β at the same conditions.

The dynamical heterogeneity of polymer atoms discussed above can be examined in greater detail through the calculation of the translational segmental dynamics of PE chains, based on the average mean-square displacement (msd) defined as: $g^j(\tau) = \langle [\mathbf{r}_i(t+\tau) - \mathbf{r}_i(t)]^2 \rangle$, which is calculated for different distances from graphene flake. The probability distributions of segmental $g^j(\tau)$ msd's for a specific time period $\tau=5\text{ps}$ are depicted as bars in Figures 3a-3c for three different radial regimes: $[0-6]\text{\AA}$, $[20-25]\text{\AA}$ and $[45-50]\text{\AA}$. An important aspect is related to the disturbance of such a distribution, compared to the bulk polymer system. In all cases the distribution of a bulk system is shown with a solid line. First, a broad distribution is shown for all regimes, especially for the second and third regime shown here (Figures 3b and 3c), for which msd's have been found in the range $[0-80]\text{\AA}^2$ similar to the one of the bulk system. Segments in the first regime (atoms closest to the graphene sheet) show a more narrow distribution, with msd's in a $[0-40]\text{\AA}^2$ range. Second, the probability distribution of $g^j(\tau)$ msd's, of atoms belonging in the first adsorption regime (Figure 3a), is larger than the bulk one for small displacements, up to about 10\AA^2 . On the contrary, the probability to find larger msd's, above about

10\AA^2 is smaller than the bulk one. As we move far away from the graphene sheet the probability distribution of the $g^i(\tau)$ msd's data approaches the bulk one, i.e. probability of finding small msd's decreases, whereas the probability to find larger msd's increases. This is particular clear for the longer distances $[45-50]\text{\AA}$, which exhibit very similar distribution to the bulk PE atoms.

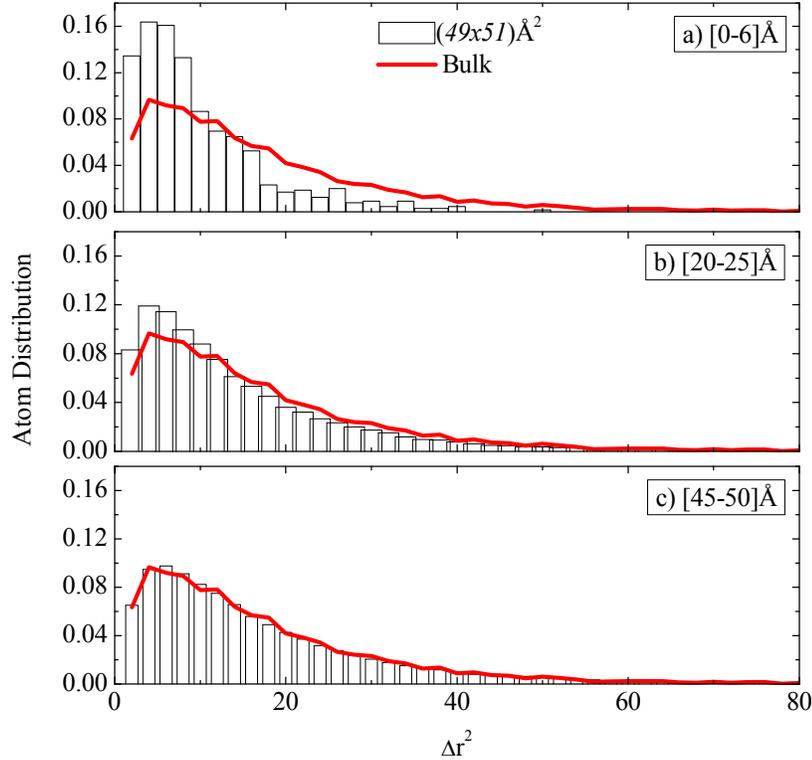


Figure 3. Probability distribution of the mean squared displacements, $g^i(\tau)$, for a PE/graphene system where the size of the graphene sheet is $(49 \times 51) \text{\AA}^2$, at a specific time period ($\tau=5\text{ps}$) for three different radial regimes: (a) $[0-6]\text{\AA}$, (b) $[20-25]\text{\AA}$ and (c) $[45-50]\text{\AA}$. In all cases the distribution of a bulk system is shown with a solid line.

Finally for the case of the nanocomposites where the graphene sheets have hydrogens or carboxyl groups at the terminal atoms (cases b and c) we study the effect of the terminal groups on the dynamics of the polymer chains as a function of the distance from the graphene layer. More specifically the following results correspond to hybrid PEO/graphene systems. An interesting observation is depicted in Figure 4 where a qualitative different behavior of the dynamics of the monomers is observed between the two systems. For the case of graphene sheets functionalized with hydrogen atoms (b) the slower monomers (those with the shortest displacement from the closest to them atom of graphene) are observed to be above and below the graphene layer in parallel to the graphene planes. Moreover there is a gradual increase of their dynamics with the increasing distance from the graphene. This behavior is qualitative similar with the one of the confined polymer films as well as the nanocomposites with graphene flakes of type (a). On the contrary for the systems with graphene flakes of type (c) the slowest monomers are observed around the edges of the graphene due to their electrostatic interactions with the carboxyl groups.

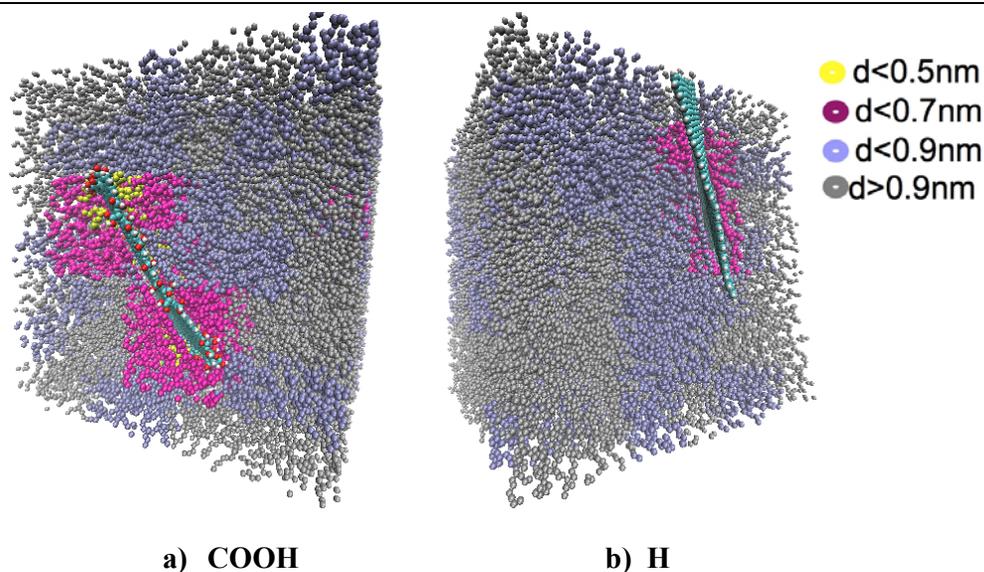


Figure 4. Configurations of systems of Poly(ethylene oxide) (PEO)/graphene (a) functionalized graphene with carboxyl groups. (b) functionalized graphene with hydrogen atoms. d : is the displacement of the PEO monomers from the closest to them atom of graphene.

3.3 Wrinkling of Graphene

Finally, some preliminary results, concerning conformational characteristics of the graphene sheets in terms of fluctuations – wrinkling behavior, are presented. For this purpose we define one cross line on the sheet, parallel to the y -direction (Figure 5B) and observe its motion during the simulation starting from a completely straight line (i.e., a planar conformation of the graphene sheet).

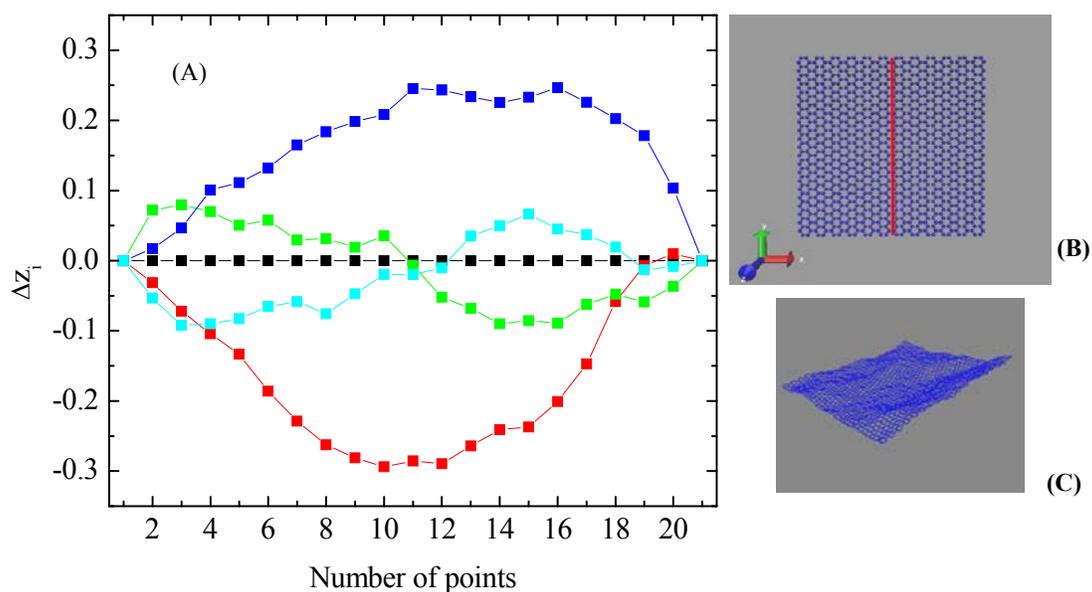


Figure 5. (A) The out of plane motion of the cross line defined on the graphene sheet for all the atoms of the line at four different time spots (colored symbols), together with the initial snapshot (black symbols, $t=0$) for the system with is $(49 \times 51) \text{ \AA}^2$ graphene sheet. (B) A schematic representation for the conformational analysis of graphene sheets. (C) A characteristic snapshot of a graphene layer with fluctuations.

A “wavy” motion is observed with crests and troughs, as it is observed in the characteristic snapshot of Figure 5C. This is a combinatory result of thermal fluctuations as well as fluctuations imposed by the (attractive) energetic interactions between the graphene and the polymer matrix. The motion of this line at different times is presented for the system with a graphene sheet of $(49 \times 51) \text{ \AA}^2$ area in Figure 5A, where we have chosen four time points together with the initial snapshot ($t=0$). This is only a qualitative picture in which various shapes of the line are observed. It is interesting to see that there are cases where only crests or only troughs are detected and cases where crests and troughs exist in the same line. This analysis is in progress.

4. CONCLUSIONS

In the current study we present results concerning the way that graphene affects the dynamical properties of various hybrid polymer/graphene systems using detailed atomistic Molecular Dynamics simulations. The systems under investigation were: a) confined thin polymer films (PE, PS, PMMA) with periodic graphene sheets which were frozen during the simulation and b) Graphene flakes of finite size moving freely in a polymer matrix (PE, PEO). In the second case the graphene sheet is of three different types: a) with a partial charge distribution at the edges, b) functionalized with hydrogens and c) functionalized with carboxyl groups.

In all cases a heterogeneous dynamics of the polymer is observed due to the presence of the graphene flake. At close to the graphene distances a retardation of the dynamics of the polymer chains is observed whereas at longer distances polymer dynamics approaches the one of the corresponding bulk system. Quantitative differences among the different polymers are found.

In the second case the effect of the terminal groups at the edges of the graphene flake is revealed. Among the three types of functionalized graphene that we study only in the case of the reduced graphene (c) (carboxyl groups at the edges) a qualitative differentiation in polymer dynamics is observed, in terms of the distribution of the monomers according to their distance from graphene. More specifically, for the case of a hybrid PEO/graphene system with graphene sheets of type (c), the slowest monomers (the ones with the shortest displacement from the closest to them graphene atom) are those which are close to the edges of graphene due to the electrostatic interactions of polymer with the carboxyl groups. On the contrary for the rest of the systems the slowest monomers are above and below the graphene sheet in parallel planes.

Acknowledgements: This research has been co-financed by the European Union (European Social Fund – ESF) and Greek national funds through the Operational Program "Education and Lifelong Learning" of the National Strategic Reference Framework (NSRF) - Research Funding Program: KRHPIS.

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