Mathematical Modeling and Molecular Dynamics Simulations of Polymeric Nanocomposite Materials

by

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Abstract

The study of Polymeric Complex Materials is an intense research area due to the broad spectrum of systems, applications, length and time scales. For example, concerning hybrid Polymeric nanocomposite systems, nanoparticles are used to modify/enhance the thermodynamics, the mechanical properties and the dynamical/rheological behavior of the entire system. The aim of this work is to predict the heterogeneous behavior and properties of such complex systems. Detailed atomistic (united atoms) molecular dynamics simulations of several graphene based polymer (polyethylene, PE) nanocomposite systems have been performed. Systems with graphene sheets of different sizes have been simulated at the same graphene concentration (~3%). In addition, a periodic graphene layer ("infinite sheet") has been studied. Results concerning structural and dynamical properties of PE chains are presented for the various systems and compared to data from a corresponding bulk system. The final properties of the material are the result of a complex effect of the graphene's sheet size, mobility and fluctuations. A detailed investigation of density, structure and dynamics of the hybrid systems has been conducted. Particular emphasis has been given in spatial heterogeneities due to the PE/graphene interfaces, which were studied through a detailed analysis based on radial distances form the graphene's center-of-mass. Chain segmental dynamics is found to be slower, compared to the bulk one, at the PE/graphene interface by a factor of 5 to 10. Furthermore, an analysis on the graphene sheets characteristics is presented in terms of conformational properties (i.e., wrinkling) and mobility. Moreover, we study the properties of polymer/gold nanoparticle (NP) nanocomposites through atomistic molecular dynamics, MD, simulations. We probe the structural, conformational and dynamical properties of polymer chains at the vicinity of a gold (Au) NP and a functionalized (core/shell) Au NP, and compare them against the behavior of bulk polyethylene (PE). The bare Au NPs were constructed via a systematic methodology starting from abinitio calculations and an atomistic Wulff construction algorithm resulting in the crystal shape with the minimum surface energy. For the functionalized NPs the interactions between gold atoms and chemically adsorbed functional groups change their shape. As a model polymer matrix we consider polyethylene of different molecular lengths, from the oligomer to unentangled Rouse like systems. The PE/Au interaction is parametrized via DFT calculations. By computing the different properties the concept of the interface, and the interphase as well, in polymer nanocomposites with metal NPs are critically examined. Results concerning polymer density profiles, bond order parameter, segmental and terminal dynamics show clearly that the size of the interface/interphase, depends on the actual property under study. In addition, the anchored polymeric chains change the behavior/properties, and especially the chain density profile and the dynamics, of the polymer chain at the vicinity of the Au NP. In addition, the dynamics of polymer chains in poly(ethylene oxide) / silica nanoparticles, PEO/SiO2, nanohybrids has been investigated via atomistic molecular dynamics simulations. We study the effect of spatial confinement, induced by the nanoparticles, and of chain adsorption on the polymer structure and dynamics. Investigation of the static properties of the nanocomposites via detailed atomistic simulations reveals a heterogeneous polymer density layer at the vicinity of the PEO/SiO₂ interface, which exhibits an intense maximum close to the inorganic surface with the bulk density reached for distances ~1-1.2nm away from the nanoparticle. For small volume fraction of nanoparticles, the polymer dynamics, probed by the atomistic simulations of low molecular weight chains at high temperatures, is consistent with the presence of a thin adsorbed layer that shows slow dynamics with the dynamics far away from the nanoparticle being similar to that in the bulk. However, for high volume fraction of nanoparticles (strong confinement) the dynamics of all polymer chains are predicted slower than that in the bulk.

1. Introduction

The study of model polymer nanocomposite systems [1-9], as well as general polymer–solid interfaces, at the molecular level is a very intense research area due to the development of hybrid materials, polymer coatings and lubricant films [10-13]. It is now accepted that the behavior of polymer melts close to a solid surface is rather different to the bulk behavior. For example, concerning the segmental dynamics of the macromolecules, a distribution of relaxation rates was found that depended largely on the strength of the polymer–surface interactions [14] whereas in some cases new dynamical modes appeared [15].

A lot of achievements both in basic research and in different industrial fields have been made on hybrid polymer/solid nanoparticle systems [16]. The most important concern the modification of the electrochemical behavior [17] and the improvement of the thermal degradation of the nanocomposites [18]. Moreover, enhancement of hardness, solvent resistance and glossiness of nanocomposites have been reported [19]. The improvement of the tensile strengths of nanocomposite films [20] and the enhancement of the interfacial adhesion between nanoparticle and polymer matrix are also of high importance [21]. Furthermore, nanoparticles modify the mechanical properties of a polymer matrix in the case of hybrid polymer/solid nanoparticle systems [22].

A range of simulations have been also employed to study the effect of the interface [6, 7], including dynamic Monte Carlo simulations for generic bead spring models [23, 24], united atom molecular dynamics (MD) simulations for alkanes [3, 25, 26], atomistic MD simulations [27, 28] and stochastic dynamics simulations of alkanes [29]. Bead–spring models using dynamic Monte Carlo simulations [30] and molecular dynamics [31] observed that segmental packing and orientation returned to bulk values within only a couple of segment lengths from the surface and chain dimensions returned to the bulk values after 1–2 times the radius of gyration R_g [32].

The study of polymer-based hybrid materials is a field of immense interest as it involves a broad spectrum of systems, applications, and spatiotemporal scales. On polymer/solid nanostructured systems in particular, the solid phase can strongly modify the properties of the entire hybrid system, such as its mechanical and electrical ones, as well as its dynamical/rheological behavior [33-39]. Therefore, the investigation of model polymer/solid interfacial systems, at the molecular level, is an intense research area, since such interfaces play a crucial role on the behavior of polymer-based systems with important technological applications, including for example polymer nanocomposites, polymer coatings, lubricants and thin films [9, 10, 16, 40, 41]. Examples include the modification of the electrochemical behavior [17] and the amelioration of the thermal degradation of the nanocomposites [18]. Moreover, there have been reports of enhancement of hardness, solvent resistance and glossiness of nanocomposites [19]. The improvement of the tensile strengths of nanocomposite films [20] and the enhancement of the interfacial adhesion between nanoparticle and polymer matrix are also very important [21]. Furthermore, nanoparticles modify the mechanical properties of a polymer matrix [22, 42].

The investigation of the structure, chain conformation and dynamics in polymer nanocomposites (PNCs) constitutes a very active research area due to the innovative properties of these materials that make them candidates for a broad range of applications. [43-54] The properties of polymer chains are different close to the surface of a nanoadditive or under confinement, when compared to those in the bulk, affecting the overall behavior of the systems. [10, 55-66] Important advances both in basic research [44, 46, 48, 53, 67, 68] and in different industrial fields have been made on hybrid polymer/nanoparticle systems [69-71]. Moreover, a number of computational [2, 3, 46, 72-87], experimental [10, 59, 60, 62, 63, 65, 67, 68, 88-98] or combined studies [55, 99] have been employed to investigate the effects of the presence of the interfaces on the properties of the polymer providing a measure of the interphase length. [2, 55, 57, 86, 100-104]

The present thesis is organized as follows:

- Chapter 2 gives a rather detailed presentation of the molecular dynamics method, with particular emphasis in its implementation for polymeric systems and the molecular model.
- Chapter 3, 4 and 5 consists of a description for the simulated systems that we used, the simulation method and analysis that we followed. On those chapters the results of the thesis are presented. Data concerning polymer density profiles, bond order parameter, end to end distance, dihedral distribution,

segmental and terminal dynamics, orientational and translational dynamics are reported. The polymer properties are examined as a function of distance from the Au NP and as an average value of the entire system.

• Chapter 6 presents the conclusions of the work of this thesis and recommendations for future plans.

2. Molecular Dynamics Simulations

2.1 The Molecular Dynamics Algorithm

Molecular dynamics (MD) is a powerful technique for computing the equilibrium and dynamical properties of classical many-body systems. Over the last twenty years, due to the rapid development of computers, polymeric systems have been the subject of intense study with MD simulations [23].



Figure 1: Multiscale modeling of polymer–solid interfaces from the electronic structure level, through the atomistic level, to the mesoscopic coarse-grained level and beyond [105].

There are several simulation methods that describe different length and time scales (see Figure 1):

• In quantum level we use the Density Functional Theory which take into account the electronic structure of the atoms. DFT calculations can be used for modeling the interaction of a few atoms with the solid surface.

- In microscopic level we use the atomistic molecular dynamics or the Monte Carlo Molecular Dynamics.
- In mesoscopic level we use the Coarse Grained Molecular Dynamics, where we compose a group of atoms in a super atom.
- And finally, in continuum level we solve Navier-Stokes or Burger's like equations.

In this work we used the Atomistic Molecular Dynamics simulations. At the heart of the MD technique is the solution of the classical equations of motion which are integrated numerically to give information for the positions and velocities of atoms in the system [7, 8, 106]. The description of a physical system with the classical equations of motion rather than quantum-mechanically is a satisfactory approximation as long as the spacing hv between successive energy levels described is $hv < k_BT$. For a typical system at room temperature this holds for $< 0.6 \times 10^{13}$ Hz, i.e. for motions of time periods of about t $> 1.6 \times 10^{-13}$ sec or 0.16 ps.

A flow diagram of a standard MD algorithm is shown in Figure 2 and includes the following steps [107, 108].

- First, a model configuration representing a molecular-level snapshot of the corresponding physical system is chosen or constructed, and is initialized (initial positions, velocities of each particle within the system).
- Then the total force acting on each particle within the system is computed. For polymer systems such a force has two components: intermolecular (from atoms belonging to different polymer chains) and intramolecular (from atoms belonging to the same chain).
- The integration of the equations of motion follows with an appropriate method (like Verlet).
- Actual measurements are performed (positions, velocities, energies, etc., are stored) after the system has reached equilibration, periodically every N_k steps.
- After completion of the central loop (N steps), averages of the measured quantities and of the desired properties are calculated and printed.



Figure 2: Diagram of a standard MD algorithm.

2.2 Classical Equations of Motion

As stated above, at the heart of an MD simulation is the solution of the classical equations of motion. Let us consider a system consisting of N interacting atoms described by a potential energy function V. Let us also denote as q_k and \dot{q}_k the generalized coordinates describing the molecular configuration and their time derivatives of particle k, respectively. The classical equations of motion for this system can be formulated in various ways [109]. In the Lagrangian formulation, the trajectory $q(t)(=q_1(t), q_2(t), ..., q_N(t))$ satisfies the following set of differential equations:

$$\frac{\partial \mathbf{L}}{\partial \mathbf{q}_{\mathbf{k}}} = \frac{\mathbf{d}}{\mathbf{dt}} \left(\frac{\partial \mathbf{L}}{\partial \dot{\mathbf{q}}_{\mathbf{k}}} \right) \tag{1}$$

where k=1,2,..., N and L is the Lagrangian of the system. This is defined in terms of the kinetic, K and potential energy, V as

$$\mathbf{L} = \mathbf{L}(\mathbf{q}, \dot{\mathbf{q}}, \mathbf{t}) \equiv \mathbf{K}(\dot{\mathbf{q}}(\mathbf{t})) - \mathbf{V}(\mathbf{q}(\mathbf{t}))$$
(2)

The generalized momenta p_k conjugate to the generalized coordinates q_k are defined as

$$p_{k} = \frac{\partial L}{\partial \dot{q}_{k}}$$
(3)

Alternatively, one can adopt the Hamiltonian formalism, which is cast in terms of the generalized coordinates and momenta. These obey Hamilton's equations

$$\dot{\mathbf{q}}_{\mathbf{k}} = \frac{\partial \mathbf{H}}{\partial \mathbf{p}_{\mathbf{k}}}, \dot{\mathbf{p}}_{\mathbf{k}} = -\frac{\partial \mathbf{H}}{\partial \mathbf{q}_{\mathbf{k}}}$$
 (4)

where H is the Hamiltonian of the system, defined through the equation

$$H(p,q) = \sum_{k} \dot{q}_{k} p_{k} - L$$
(5)

If the potential V is independent of velocities and time, then *H* becomes equal to the total energy of the system [109]:

$$H(p,q) = K(p) + V(q)$$
(6)

In Cartesian coordinates, Hamilton's equation of motion read:

$$\dot{\mathbf{r}}_i \equiv \mathbf{v}_i = \frac{\mathbf{p}_i}{\mathbf{m}_i} \tag{7}$$

$$\dot{p}_{i} = -\nabla_{r_{i}} V \equiv -\frac{\partial V}{\partial r_{i}} = F_{i}$$
(8)

hence

$$\mathbf{m}_{\mathbf{i}}\ddot{\mathbf{r}}_{\mathbf{i}} \equiv \mathbf{m}_{\mathbf{i}}\dot{\mathbf{q}}_{\mathbf{i}} = \mathbf{F}_{\mathbf{i}} \tag{9}$$

where F_i is the force acting on atom *i*. Solving the equations of motion then involves the integration of the 3N second-order differential equations (Newton's equations).

The classical equations of motion possess some interesting properties, the most important one being the conservation law. If we assume that K and V do not depend explicitly on time, and then it is straightforward to verify that $\dot{H} = dH/dt$ is zero, i.e. the Hamiltonian is a constant of the motion. In actual calculations this conservation law is satisfied if there exist no explicitly time or velocity-dependent forces acting on the system. A second important property is that Hamilton's equations of motion are reversible in time. This means that, if we change the signs of all the velocities, we will cause the molecules to retrace their trajectories backwards. The computer-generated trajectories should also possess this property.

There are many different methods for solving ordinary differential equations of the form of equation (9). Criteria for the proper choice of an algorithm include the following:

- Algorithm must not require an expensively large number of force evaluations per integration time step. Many common techniques for the solution of ordinary differential equations (such as the 4th order Runge-Kutta method) become inappropriate, since they do not fulfill this criterion.
- Algorithm should satisfy the energy conservation law. It is also desirable that it be time reversible and conserve volume in phase space (be symplectic).
- Algorithm should permit the use of a large time step dt.
- Algorithm should be fast and require little memory.

Concerning the solution of equations of motion for very long times, it is clear that no algorithm provides an essentially exact solution. But this turns out to be not a serious problem, because the main objective of an MD simulation is not to trace the exact configuration of a system after long time, but rather to predict thermodynamic properties as time averages and calculate time correlation functions descriptive of the dynamics [107, 108].

2.3 Verlet Methods

Algorithms in this family are simple, accurate and, as we will see below, time reversible. Thus, the Verlet methods are the most widely used methods for integrating the classical equations of motion. The initial form of the Verlet equations is obtained by utilizing a Taylor expansion at times t - dt and t + dt

$$r(t + dt) = r(t) + dtv(t) + \frac{dt^2}{2}\ddot{r}(t) + \frac{dt^3}{6} + O(dt^4)$$
(10)

$$r(t - dt) = r(t) - dtv(t) + \frac{dt^2}{2}\ddot{r}(t) - \frac{dt^3}{6} + O(dt^4)$$
(11)

Summing the two equations gives

$$r(t + dt) = 2r(t) - r(t - dt) + dt^{2}\ddot{r}(t) + O(dt^{4})$$
(12)

with $\ddot{r}(t)$ calculated from the forces at the current positions.

Two modifications of the Verlet scheme are of wide use. The first is the "leap-frog" algorithm where positions and velocities are not calculated at the same time; velocities are evaluated at half-integer time steps:

$$r(t + dt) = r(t) + dtv(t + \frac{dt}{2})$$
 (13)

$$\mathbf{v}(t + \frac{\mathrm{dt}}{2}) = \mathbf{v}(t - \frac{\mathrm{dt}}{2}) + \mathrm{dt}\ddot{\mathbf{r}}(t) \tag{14}$$

In order to calculate the Hamiltonian *H* at time t, the velocities at time t are also calculated as averages of the values at t + dt = 2 and t - dt = 2:

$$v(t) = \frac{1}{2} \left(v(t + \frac{dt}{2}) + v(t - \frac{dt}{2}) \right)$$
(15)

The problem of defining the positions and velocities at the same time can be overcome by casting the Verlet algorithm in a different way. This is the velocity Verlet algorithm according to which positions are obtained through the usual Taylor expansion

$$r(t + dt) = r(t) + dtv(t) + \frac{dt^2}{2}\ddot{r}(t)$$
 (16)

whereas velocities are calculated through

$$v(t + dt) = v(t) + \frac{dt}{2} [\ddot{r}(t) + \ddot{r}(t + dt)]$$
(17)

with all accelerations computed from the forces at the configuration corresponding to the considered time. To see how the velocity-Verlet algorithm is connected to the original Verlet method we note that, by equation (17),

$$r(t + 2dt) = r(t + dt) + dtv(t + dt) + \frac{dt^2}{2}\ddot{r}(t + dt)$$
(18)

If equation (17) is written as

$$r(t) = r(t + dt) - dtv(t) - \frac{dt^2}{2}\ddot{r}(t)$$
(19)

then, by addition, we get

$$r(t + 2dt) + r(t) = 2r(t + dt) + dt[v(t + dt) - v(t)] + \frac{dt^2}{2}[\ddot{r}(t + dt) - \ddot{r}(t)]$$
(20)

Substitution of equation (18)) into equation (20) gives

$$r(t + 2dt) = r(t) = 2r(t + dt) + dt^{2}\ddot{r}(t + dt)$$
(21)

which is indeed the coordinate version of the Verlet algorithm (for more see [108]).

In general, higher-order methods are characterized by a much better accuracy than the Verlet algorithms, particularly at small times. Their biggest drawback is that they are not reversible in time, which results in other problems, such as insufficient energy conservation, especially in very long-time MD simulations. On the other hand, the Verlet methods are not essentially exact for small times but their inherent time reversibility guarantees that the energy conservation law is satisfied even for very long times. This feature renders the Verlet methods, and particularly the velocity-Verlet algorithm, the most appropriate one to use in long atomistic MD simulations.

2.4 MD in NVT and NPT Ensembles

The methods described before consider the solution of Newton's equations of motion in a microcanonical (*NVE*) ensemble. In practice there is usually a need to perform MD simulations under specified conditions of temperature or/and pressure.

The thermostatting and barostatting is achieved by adding some dynamic variables which are coupled to the particle velocities (thermostatting) and simulation domain dimensions (barostatting). In addition to basic thermostatting and barostatting, we can also create a chain of thermostats coupled to the particle thermostat, and another chain of thermostats coupled to the barostat variables. The barostat can be coupled to the overall box volume, or to individual dimensions, including the *xy*, *xz* and *yz* tilt dimensions. The external pressure of the barostat can be specified as either a scalar pressure (isobaric ensemble) or as components of a symmetric stress tensor (constant stress ensemble). The time-averaged temperature and stress tensor of the particles will match the specified target values [110].

To constrain temperature, Nosé [111] introduced an additional degree of freedom, s, in the Lagrangian. The parameter s plays the role of a heat bath, whose aim is to damp out temperature deviations from the desirable level. This necessitates adding to the total energy an additional potential term of the form

$$V_{\rm s} = {\rm gk}_{\rm B} {\rm Tlns} \tag{22}$$

and an additional kinetic energy term of the form

$$K_s = \frac{Q}{2} \left(\frac{\dot{s}}{s}\right)^2 = \frac{p_s^2}{2Q}$$
(23)

In the above equations, g is the total number of degrees of freedom ($g = 3 N_{atoms} - N_{bonds} - 3$ with N_{atoms} and N_{bonds} standing for the total numbers of atoms and bonds in the model system, respectively), while Q and p_s represent the "effective mass" and momentum, respectively, associated with the new degree of freedom s. Equations of motion are derived from the Lagrangian of the extended ensemble, including the degree of freedom s. Their final form, according to Hoover analysis [112] is

$$\dot{\mathbf{r}}_{\mathbf{i}} = \frac{\mathbf{P}_{\mathbf{i}}}{\mathbf{m}_{\mathbf{i}}} \tag{24}$$

$$\dot{P}_{i} = -\frac{\partial V}{\partial r_{i}} - \frac{\dot{s}}{s} P_{i}$$
(25)

$$\dot{P}_{s} = \frac{\left(\sum_{i=1}^{N} \frac{P_{i}^{2}}{m_{i}} - gk_{B}T\right)}{Q} , \quad P_{s} = Q\frac{\dot{s}}{s}$$
(26)

An important result in Hoover's analysis is that the set of equations of motion is unique, in the sense that no other equations of the same form can lead to a canonical distribution.

The total Hamiltonian of the system, which should be conserved during the MD simulations, now becomes

$$H_{\text{Nose-Hoover}} = \sum_{i=1}^{N} \frac{P_i^2}{m_i} + V(r^n) + gk_B T \ln s + \frac{P_s^2}{2Q}$$
(27)

To construct MD simulations under constant P an analogous reformulation of the Lagrangian was proposed by Andersen [113]. The constant-pressure method of Andersen allows for isotropic changes in the volume of the simulation box. Later Hoover [112] combined this method with the isothermal MD method described before to provide a set of equations that probe MD simulations in the NPT ensemble. Parrinello and Rahman [114] have extended the Andersen method to allow the simulation box to respond not only to changes in its size but also in its shape. This is particular important in the simulation of solids (e.g. glassy polymers) since it allows for phase changes in the simulation involving changes in the dimensions and angles of the unit cell [107, 108].

2.5 Molecular Models

For standard problems in physics and chemistry of condensed matter (such as simple fluids containing gas atoms or diatomic molecules) computer simulation considers a small region of matter in full atomistic detail [7]. For simple fluids these methods works because they are homogenous on a scale of about 1-2 nm already. Reliable model for the effective forces are usually available from quantum chemistry methods.

MD simulations in long flexible polymers encounter a different situation due to the wide spread of length scales characterizing their structure and time scale characterizing their motion as we show in the introduction. As we have already seen in the introduction one solution to the problem of long relaxation times is to follow hierarchical approaches that are using combination of simulation techniques and theories. A different solution to the above problems is to abandon the chemical detail and concentrate in the dynamics of long wavelengths. This is the case of coarse-graining simulations.

Consider a polyethylene chain in full atomistic representation as the one shown in Figure 3.



Figure 3: (a) Schematic model of a piece of the polyethylene chain in the united atom representation. (b) Qualitative sketch of the torsional potential for alkane chains [23].

There are two ways of treating the hydrogen atoms. The one is to treat them explicitly, i.e. explicit atom (EA) models. The second is to introduce spherical segments, as in Figure 3a, representing a CH_2 , i.e. united atom (UA) models. There are two types of interactions in this atomistic representation. The first is between atoms that are bonded or next near up to n bonds (bonded interactions). The second one is between atoms that are belonging to different polymeric chains or to the same chain but their distance is above n bonds (non-bonded interactions) [23].

The model (set of equations) that describes the molecular interactions (see Figure 4) between atoms is:

$$U(r) = V_{bonded} + V_{non-bonded} = V_{str} + V_{bend} + V_{tors} + V_{LJ} + V_q$$
(28)



Figure 4: Molecular interactions between atoms

The bonded interactions depend on the type of the polymeric systems. There are, however, three general types of bonded interactions:

a) Interactions between atoms that are connected through a bond. The interaction of the chemical bond can be incorporated through a harmonic potential (bond stretching interaction) of the form

$$V_{\rm str}(l) = \frac{1}{2} k_{\rm b} (l - l_0)^2$$
(29)

where l is the bond length and l_0 is its equilibrium value.

b) For atoms that are belonging to 2 successive bonds a bond-bending potential of the following form is used

$$V_{\text{bend}}(\theta) = \frac{1}{2} k_{\theta} (\theta - \theta_0)^2$$
(30)

where θ is the bond length and θ_0 is its equilibrium value.

c) For atoms that are belonging to 3 successive bonds (see Figure 3b) there is a torsional potential, associated with each dihedral angle φ . The type of the torsional potential is usually of the form

$$V_{tors}(\phi) = \sum_{i=0}^{n} c_i (\cos(\phi))^i$$
(31)

with n around 3-5 and c_i constants characterizing the potential.

For systems with special types of interactions (double bonds, hydrogen bonds, special dihedral angles, etc.) there are other much more detailed and complicated types of bonded interactions [23].

The non-bonded interactions are usually of two types:

 a) The first are short-range interactions. These interactions are between atoms belonging to different chains or atoms that are in the same chain but they are separated by more than n (usually 3) bonds apart and have the following Lennard-Jones (LJ) form

$$V_{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$
(32)

where ε and σ are parameters characteristic of the type of the atom. The parameters between different types of sites (atoms) are usually determined by the Lorentz-Berthelot rules:

$$\varepsilon_{\text{CH}_2-\text{CH}_3} = \sqrt{\varepsilon_{\text{CH}_2}\varepsilon_{\text{CH}_3}} , \qquad \sigma_{\text{CH}_2-\text{CH}_3} = \frac{\sigma_{\text{CH}_2} + \sigma_{\text{CH}_3}}{2}$$
(33)

b) The second type of non-bonded interactions is the well-known long-range Coulomb interactions [115]. Consider a number of atoms N in a cubic box of length L. If periodic boundary conditions are applied and we assume that the system as a whole is electrically neutral, then the Coulomb contribution to the potential energy of this system is

$$V_{q} = \frac{1}{2} \sum_{n \in \mathbb{Z}^{3}}^{\infty} \sum_{i,j=1}^{N} \frac{q_{i}q_{j}}{|r_{ij} + nL|}$$
(34)

where $r_{ij} = r_i - r_j$, q_i and q_j are the charges, the first sum is over all periodic images n and the prime denotes that the summand for i = j has to be omitted for n = 0. For simulating systems with long-range interactions special simulation techniques needed, such as the Ewald summation, the particleparticle-particle mesh (PPPM) method or the fast multipole method [8, 115].

2.5.1 Wulff Construction

Gold nanoparticles are often found in their equilibrium shape [116-118]. At the thermodynamic limit, this is a polyhedron enclosed by faces of various (*hkl*) crystal orientations such that the total surface energy is minimum

$$\sum_{hkl} A_{hkl} \gamma_{hkl} \tag{35}$$

 A_{hkl} is the total area of faces parallel to the (*hkl*) plane of the crystal and γ_{hkl} is the energy required to create a surface of unit area that is parallel to the (*hkl*) plane of the crystal and is the analog of the surface tension of liquids.

The Wulff construction has been used to predict equilibrium shapes in a variety of systems [119-121]. G. Wulff proposed that the shape that minimizes equation (35) is such that the distance of each face from the center is proportional to the surface tension of the respective (hkl) surface [121]:

$$d_{hkl} \sim \gamma_{hkl}$$
 (36)

The equilibrium shapes of gold nanoparticles were predicted by Remediakis and Barmparis [116] by linking extensive quantum-mechanical calculations, based on density functional theory (DFT), to Wulff constructions. They constructed atomistic models of nanoparticles with diameters up to several tenths of a nanometer, inaccessible by direct atomistic simulations. The Wulff construction [116] for Au NP is shown in Figure 5.



Figure 5: Typical calculated Au nanoparticles for various sizes, d: (a) d = 12.1 nm (b) d = 27.2 nm, (c) d = 5.02 nm and (d) d = 5.04 nm (for the grafted system). Step and kink atoms are shown in darker color.

3. Polymer/Nanofiller Nanocomposite Systems

3.1 Introduction

Graphene, an sp2-hybridized carbon layer of macroscopic dimensions but of atomic thickness, is a very important material with a wide range of novel applications due to its exceptional physical properties (*i.e.*, electron transport capacity, electrical conductivity, high intrinsic tensile strength and stiffness, high thermal conductivity) [122]. One of the most promising applications of this material is as a dispersed phase in polymer nanocomposities (PNCs), since even a very small concentration of graphene may dramatically affect the properties of the hybrid material [123-126]. Therefore, graphene based polymer nanocomposites have a very broad range of possible applications in many different areas [125, 126]. For example, such hybrid materials can be used in electronic devices, for energy storage [125], while an emerging research direction is focused on biomedical applications [126].

Graphene based polymer nanocomposites are based on the incorporation of graphene in polymer matrices; thus the properties of the overall hybrid composite material depend strongly on how well graphene sheets are dispersed in the polymer. Furthermore, the improvement in the properties of the hybrid systems is influenced by the exfoliation techniques for the graphene flake as well as the dispersion method. An extensive review on different ways of exfoliation of graphite was given by Kim *et al.* [125], where advantages and disadvantages of each method were presented. The dispersion of graphene layers in the polymer matrix and possible functionalization of graphene sheets (e.g., graphite oxide) has been further recognized as crucial factors for the overall behavior (e.g., rheological, electrical, mechanical, thermal, and barrier properties) of nanocomposites [123].

Many simulation and experimental studies [77, 122, 127-139] explore the influence of the chemical functionalization of graphene on the various properties of the nanocomposites. For example, Konatham et al. [134] presented results based on atomistic Molecular Dynamics simulations combined with coarse grained Monte Carlo simulations, focused on graphene sheets dispersed in *n*-octane. They suggest that the functionalization of graphene sheets with short-branched hydrocarbons along the edges prevents agglomeration and leads to well-dispersed systems. They also mention the effect of the size of the graphene sheets, though their

atomistic simulations are limited to rather small sheets. More recently Skoutzos *et al.* [77] presented results for syndiotactic poly(methyl methacrylate)/graphene nanocomposities, based on atomistic Molecular Dynamics simulations. They found that the introduction of oxygen-containing functional groups in graphene sheets leads to a great enhancement of the mechanical properties of the hybrid system, even at extremely low loading.

In addition to the previous discussion other factors, which can potentially influence the reinforcing capabilities on the various properties of the nanocomposites, are the loading of the graphene sheets (i.e., their wt% in the polymer matrix), the morphological characteristics of the sheets (i.e., wrinkles), as well as the size of the graphene sheets. Note, for example, that volume (or weight) fraction of the fillers in traditional polymer composites is much larger (e.g., ~60 vol%) compared to the typical one in graphene based polymer nanocomposites. For the latter, very low loadings (e.g., ~1-5 vol%) can cause dramatic changes on various properties of the hybrid system. Ramanathan et al. [137], in a recent experimental work, have showed that the wrinkled single layer graphene and the functionalized graphene afford better interaction with the host polymer matrix and result to bigger enhancement of mechanical and thermal properties at exceptionally low loadings, compared to singlewalled carbon nanotubes or expanded graphite. On the other hand, a multiscale simulation approach [133], based on a combination of molecular dynamics, molecular structural mechanics and finite element method, showed that the presence of ripples on the graphene flakes causes a decrease in the axial Young modulus of the nanocomposite, compared to the case of the flat graphene sheet. In this study a poly(methyl methacrylate) polymer matrix was used.

The work presented here is based on detailed atomistic Molecular Dynamics simulations of model PNCs systems and is focused on the effect of the size of the graphene sheets on various properties of the hybrid material. We are primarily interested in the way that *spatial heterogeneities*, due to the polymer/graphene interfaces, affect the *structural* and *dynamical behavior* of the entire system. Our goal is twofold. First, we study various properties of the graphene sheets of different sizes. Moreover, comparisons between these systems and a hybrid system with a periodic graphene sheet (a model of the "infinite" graphene sheet) are performed. Second,

results concerning the translational and orientational dynamical behavior of the graphene sheet, as a function of its size, in the polymer matrix are presented. Furthermore, a conformational analysis for the sheet is performed.

This work is part of a more general detailed simulation study of polymer/graphene interfaces and graphene based polymer nanocomposites along multiple length and time scales. In our previous works, we have extensively studied the properties of various polymer/graphene interfaces through atomistic simulations in which infinite (periodic) graphene sheets were assumed [128, 140, 141]. The current work is focused on the properties of polyethylene/graphene nanocomposites with graphene sheets of various sizes. Here we have studied various PNC systems with the same concentration-loading of graphene (\sim 3 wt%), where the host matrix is comprised of polyethylene (PE) chains. Note that, according to our knowledge, in all previous atomistic simulation studies of polymer/graphene systems rather small graphene sheets were modeled (e.g., up to 2 nm).

3.2 Model Systems and Simulations

Detailed atomistic molecular dynamics simulations for various polyethylene/graphene nanocomposites systems were performed. In more detail, we have investigated three PNCs systems with a single flexible graphene sheet of different size (S1, S2 and S3), as well as a periodic flexible graphene layer, which reflects a sheet of "infinite" size (SP). All systems were compared to a bulk polyethylene system (SB) and the deviations from the bulk behavior in the various properties were reported in [128, 138]. More details for all systems are presented in Table 1.

Finite graphene sheets are modeled through an all-atom model, described by Bellido *et al.* [136], where partial charges are placed at all edge atoms. The concentration of graphene in the three systems with the finite-size graphene sheets is 3 wt% (weight percent), while for the periodic graphene the concentration is almost 10 wt%. For the representation of polyethylene a united atom model was used, where each methylene CH_2 and methyl CH_3 group was considered as a single Van der Waals interacting site. Polyethylene chains consist of 22 monomers.

Name	System	Graphene Atoms	PE Atoms
S 1	$(19 \times 20) Å^2$	190	5,456
S2	$(49 \times 51) \text{ Å}^2$	1,032	29,392
S 3	$(84 \times 86) \text{ Å}^2$	2,546	72,688
SP	Infinite	2,432	18,480
SB	PE Bulk	-	9,240

Table 1: Details for the simulated systems: Name; Size of graphene sheet; Number of graphene atoms; Number of PE atoms.

Non-bonded interactions between polymer atoms, as well as between the carbons of graphene and the CH_2 (or CH_3) groups of PE chain, are described by a spherically truncated 6–12 Lennard–Jones potential of the form:

$$V_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right), \quad r \le R_c$$
(37)

where, the cutoff distance $R_c = 10$ Å. For intramolecular interactions 1–4 exclusions are made for PE and 1–3 for graphene. Tail corrections were applied to both energy and pressure. For the interactions between polyethylene and graphene atoms, the Lorentz–Berthelot rules were used (*i.e.*, typically arithmetic average for σ , $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$, and geometric average for, ε , $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$).

A detailed description of the force field for both PE [142] and graphene [143] is presented in Table 2 and Table 3; Table 2 contains the non-bonded parameters, while all bonded interactions are presented in Table 3.

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

Non-Bonded Interactions						
$V_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right], r \le R_{c}$						
Atom Types	mass (g/mol)	σ (nm)	ε (kJoule/mol)			
CH_2	14.027	0.395	0.3824			
CH ₃	15.035	0.395	0.3824			
C_{GR}	12.011	0.347	0.2750			

		Bonded 1	Interactions			
$V_{b}(r_{ij}) = \frac{1}{2} k_{ij}^{b} (r_{ij} - b_{ij})^{2}$						
Bond	Bond b (nm)					
CH ₂ –CH ₂			0.154		100	000.00
CH ₂ CH ₃			0.154		100,000.00	
CH ₃ CH ₂			0.154		100,000.00	
	$V_{morse}(r_{ij})$	$) = D_{ij} \left[1 - \right]$	$-\exp\left(-\beta_{ij}\right)$	$\left[r_{ij} - b_{ij}\right]^2$		
Bond		b (nm)	D (KJ∙mol ⁻¹)	β (nm ⁻¹)
C _{GR} -C _{GR}		0.14180	4′	78.90000	21.86700	
	Vo	$_{\alpha}(\theta_{ijk}) = \frac{1}{2}$	$k_{ijk}^{\theta}(\theta_{ijk} - \theta_{ijk})$	$_{ijk}^{0}$		
Angle			θ° (deg)		k ^θ (kJ/i	mol*rad ²)
CH ₂ -CH ₂ -CH ₂	2 114			519.611		
CH ₃ -CH ₂ -CH ₂	114			519.611		
CH ₂ –CH ₂ –CH ₃			114		519.611	
$V_{\alpha}(\theta_{ijk}) = \frac{1}{2} k_{ijk}^{\theta} \left(\cos(\theta_{ijk}) - \cos(\theta_{ijk}^{0}) \right)^{2}$						
Angle	Angle θ° (deg)		k ^θ (kJ/mol)			
C_{GR} – C_{GR} – C_{GR}	120		562.2			
$V_{rb}(\varphi_{ijkl}) = \sum_{n=0}^{5} C_n(\cos(\psi))^n$						
Dthadual	C ₀	C ₁	C ₂	C ₃	C_4	C ₅
Dinedral	(KJ/mol)	(KJ/mol)	(KJ/mol)	(KJ/mol)	(KJ/mol)	(KJ/mol)
CH_3 – CH_2 – CH_2 – CH_2	9.2759	12.1545	-13.1168	-3.0585	26.2378	-31.4929
CH_2 – CH_2 – CH_2 – CH_2	9.2759	12.1545	-13.1168	-3.0585	26.2378	-31.4929
CH ₂ -CH ₂ -CH ₂ -CH ₃	9.2759	12.1545	-13.1168	-3.0585	26.2378	-31.4929
C_{GR} – C_{GR} – C_{GR} – C_{GR}	25.1200	0.0000	-25.1200	0.0000	0.0000	0.0000

Table 3: Model parameters and functional forms of all bonded interactions of the atomistic force field used here.

Molecular Dynamics (MD) simulations were performed in the isothermal-isobaric (NPT) statistical ensemble, using the GROMACS package [144, 145]. The pressure was kept constant using Berendsen barostat at P = 1 atm. The stochastic velocity rescaling thermostat was used to maintain the temperature at T = 450 K. The integration time step was 0.5 fs and periodic boundary conditions have been used in all three dimensions.

In order to obtain initial PE/graphene configurations finite graphene layers were placed at a close distance (about 0.5 nm) to a well-equilibrated polymer sample, taken from previous bulk PE simulations [128]. Graphene sheets were initially placed in the *xy*-plane at z = 0. All graphene atoms in the initial configuration were in the same

plane (*i.e.*, there were no fluctuations in the sheet). During the simulation a complete decorrelation of a vector defined along the graphene layer is observed (for the finite graphene sheets), as it is discussed in more details in the Results section. In data analysis we exclude a certain number of configurations such as our results to be independent of the initial state. For the equilibration of the systems, first MD (Molecular Dynamics) simulations for 50 ns were performed, during which the motion of the overall hybrid system was monitored. This time period is much larger than the time required for the de-correlation of PE end-to-end vector (about ~100 ps) [128]. Then production runs for times up to 100 ns were performed and several PE/graphene configurations were saved.

3.3 Data Analysis

All configurations that were gathered during the simulation runs were analyzed in a post processing procedure. Of particular importance are the *heterogeneous* characteristics of the hybrid systems, due to distribution of polymer/graphene intermolecular (adhesive) interactions. Therefore, properties of the polymer chains were examined as a function of the distance from the graphene sheets. Such an analysis for graphene-based polymer PNCs is in general not a trivial issue, due to the mobile, non-symmetric, polymer/graphene interfaces. The analysis presented here has been performed along radial distances from the center of mass of the graphene sheet, by creating spherical shells of increasing radius (*i.e.*, increasing distances form the graphene center). A sketch of this analysis scheme is depicted in Figure 6a. Because of the motion of the graphene sheet this calculation has to be repeated at every time step.

The mass density profiles were calculated according to the above-discussed radial distance, using spherical shells of thickness equal to 1 Å. The same binning was used for the calculation of the second rank bond order parameter. Thicker spherical shells were used for the calculation of dynamical properties, equal to 10 Å for both orientational and translational dynamics in the segmental level in order to improve statistics, whereas a 5 Å binning was used for the distribution of atoms according to their mean squared displacements in each shell. The choice of binning size (thickness

of spherical shells) for the computation of each specific property is the result of an optimized balance between detailed information and improved statistics.



Figure 6: (a) A sketch of the analysis scheme in spherical shells; (b) A Snapshot of a model polyethylene/graphene system at 450 K. Graphene layer of size (49×51) Å². Additional videos from the simulaitons can be found in the supplementary material.

Furthermore, for the calculation of the density of PE as a function of the distance from the surface we applied the following procedure: The volume of each spherical shell is equal to:

$$V_{shell} = \frac{4}{3}\pi[(r+dr)^3 - r^3], \qquad (38)$$

where *r* is the radius of a sphere, centered at the center of the graphene sheet and *dr* is the thickness of the shell. This volume contains both polymer and graphene atoms. In order to measure the precise PE density, we have to subtract the graphene volume from each spherical shell. For this purpose we calculated the mean density of graphene atoms within a sphere, around the center of the graphene sheet, with a radius equal to a distance, σ_{CGR} , of 3.47 Å (σ value for the C_{GR} atoms). Then the polymer number density is given by:

$$\rho_{PE} = \frac{N_{PE}}{[V_{shell} - (N_{GR}/\rho_{GR})]},\tag{39}$$

where N_{PE} and N_{GR} are the number of PE and graphene atoms, respectively, in the shell and

$$\rho_{GR} = \frac{N_{GR}}{\left(\frac{4}{3}\pi\sigma_{C_{GR}}^3\right)} \tag{40}$$

from which the corresponding mass density is extracted.

We have also to underline here that this radial analysis has to be taken into account in the interpretation of the obtained results. In more detail, within a spherical shell, despite the fact that all atoms are equidistant from the center of graphene, there is a broad distribution of polymer atom/graphene atom distances, and a corresponding distribution of adhesive energies, which contribute differently to the calculated property. This effect is more pronounced for the intrinsic shells and attenuates as the radius becomes larger. However, the same would be the case if someone has used slabs (instead of spheres) as in the case of the analysis of polymer/solid interfaces with periodic-infinite solid surfaces. Only for the later system the parallel to the surface slabs is a natural way to calculate local properties due to the periodicity [128, 140, 141]. Below, for the infinite graphene sheet we compare polymer chain density profile through both ways of analysis. This issue is further discussed below.

3.4 Results

Three different graphene sheets have been modeled (systems S1, S2, S3, see Table 1) as well as a PE system with a periodic ("infinite") graphene layer (SP) and a bulk PE system in the same conditions (temperature and pressure) in order to compare the properties of the PNCs with the unperturbed bulk one. A representative snapshot of a model system (S2) is shown in Figure 6b.

3.4.1 Polymer Properties

3.4.1.1 Density Profile

We start the analysis of the model PNCs with the calculation of the mass monomer density profile of the polymer (PE) chains as a function of the distance from the graphene sheet. Average density profiles, which have been calculated for the center of mass of the monomers, $\rho(r)$, are presented in Figure 7a,d for all four systems. In
Figure 7a, the polymer mass at each spherical shell has been divided with the total volume of the shell, which for the inner shells contains a number of graphene atoms as well, whereas the outer shells contain only polymer atoms. For this reason in Figure 7a PE mass density values at short distances are smaller than the corresponding bulk density value, while for longer distances bulk density is attained from the three systems with the finite graphene sheets. For the system with the infinite size graphene, monomer density approaches, but do not reach, the corresponding bulk value since graphene mass exists in all spherical shells. In all four systems the density of PE close to the sheet is almost the same and unaffected by the size of the sheet. Away from the graphene layer, all curves reach/approach the bulk density value, though at different distances, as a result of the graphene sheet dimensions.

In the next stage PE monomer density profiles are calculated dividing the polymer mass with a portion of the spherical shell volume that corresponds to this mass. For this purpose we have performed a rough estimation for the volume that graphene atoms occupy in each spherical shell and subtracted it from the total volume of the shell. This has been performed as mentioned in the previous section, through the following procedure: First, a sphere with a radius equal to a distance of 3.47 Å, which corresponds to the excluded volume between an atom in the graphene sheet and the polymer, is defined and the number of graphene atoms in this sphere is counted. No polymer atoms are included in this volume. Through these values the average effective volume occupied by each graphene atom in the graphene sheet is calculated. Second, the number of graphene atoms in any spherical shell is computed. Then, we calculate their effective volume within each spherical shell and subtract it from the volume of the whole shell. Finally, polymer mass is divided with the remaining volume which corresponds to the polymer atoms. In Figure 7c the density of the amount of the graphene in each spherical shell is presented for all systems studied here. We observe that these curves attain the same values up to a specific distance, defined from the size of the sheet, beyond which no more graphene atoms are included in the spherical shell.

Chain density profiles, derived with the above procedure, for all model systems are shown in Figure 7b. All systems exhibit the same behavior: a peak of rather similar height (larger than the bulk value) is observed for all four systems at a distance/radius of about 0.5 nm, which denotes the attraction of the polymer from the graphene at short distances, while at longer distances the bulk density is attained.





Figure 7: (a) Mass monomer density profiles of polyethylene as a function of r (distance from the center of the graphene layer) for the five systems studied here; (b) Density profiles of polyethylene chains excluding the volume occupied by graphene; (c) Mass density profiles of graphene layer as a function of r; (d) Density profile of polyethylene chains for the periodic graphene layer analyzed via spherical shells and parallel slabs.

As mentioned in the previous section, one issue related to the analysis method using spherical cells, is that this might not be the natural choice for systems with the infinite-periodic graphene sheet. For the latter the analysis in parallel slabs seems to be a more appropriate choice [128]. In Figure 7d we compare the density profiles of the polymer chains for this system (SP) and the two different analysis methods; *i.e.*, using spherical shells and parallel slabs. As we can see there are slight differences for the $\rho(r)$ data between the two methods in the region of 1–2 nm from the graphene sheet. Note finally that for the case of the parallel slabs the zero is defined on the position of the center of the graphene sheet, therefore due to thermal undulations of graphene it is probable to have polymer mass at zero distance.

In the following we analyze the distribution of ends and inner parts of the polymer chains at the PE/graphene interface. The preference of the chain ends to stay close to the surface, compared to the rest of the monomers, has been reported in previous studies of polymer/surface interfaces and it is primary of entropic origin [138]. We have also observed this behavior in our previous studies at the polymer/graphene interface of polymer thin films confined between two "infinite" (periodic) graphene

sheets, as well as at polymer/vacuum interface [128, 140, 141]. A similar analysis has been performed in our current systems for both the end and the inner monomers. It is interesting to observe the effect of the motion of the sheet, the range of fluctuations and the different size on this tendency. In Figure 8a,b the density profiles based on the monomer center of mass for the end and the inner monomers are presented for all systems, respectively. The "end part" concerns only two monomers, the first and the last one, while the "inner part" is defined as the monomer of the chain in the interval $\left[\left(\frac{N}{2}-2\right), \left(\frac{N}{2}+2\right)\right]$, where *N* is the total number of monomers per chain. Following such a convention some monomers on the left and on the right side of the central part of the chain do not participate in the analysis; thus avoiding any contribution of the chain end effects in the analysis of the inner segments and vise-versa. For the infinite layer the preference of the ends for the interface is comparable to the one observed before for a PE/graphene system with a frozen graphene layer [138, 140]; *i.e.*, thermal fluctuations of a very large ("infinite") graphene interface.



Figure 8: Mass monomer density profiles as a function of R (distance from the center of the graphene layer) based on (a) chain ends and (b) inner monomers of the polymer chain for the polymer/graphene nanocomposite systems.

Qualitatively different is the case for the systems with the finite graphene sheets. Data presented in Figure 8a for the two smaller sheets show that although an amount of end monomers are concentrated close to the graphene flake they do not exceed the highest density. In more details, for the S1 system the accumulation of end monomers in the bulk region is higher than the one at the interface, while for the S2 system the density of the end monomers at the interface increases and is almost equal to that in the bulk region. For the largest sheet (S3 system) there is a small increase of the end monomers' density close to the graphene layer, compared to the two smaller systems (S1, S2), which roughly speaking indicates a tendency of the end monomers to be accumulated at the interface. The preference of the end monomers for the interface becomes clear only in the case of "infinite" graphene layer (SP). The density profiles for the inner monomers, shown in Figure 8b, have a complementary to the end monomers behavior, as expected. This is a combinatory effect of the size, the mobility and the fluctuations of the sheet and as it will be discussed in a following section, *i.e.*, the smaller the sheet the higher its mobility while the smaller its fluctuations. In addition, for the graphene sheets of finite size considerable system size effects exist, which are more pronounced for the smaller sizes.

3.4.1.2 Conformational Properties

We start the analysis of the chain conformations by calculating the average chain endto-end distance,

$$R_{ee} = \langle R_{ee}^2 \rangle^{1/2} \,, \tag{41}$$

and the radius of gyration,

$$R_g = \langle R_g^2 \rangle^{1/2} \,. \tag{42}$$

An important question concerns whether chain swelling occurs due to chain adsorption at the polymer/graphene interface. In Table 4 we report data concerning the end-to-end distance of the polymer chains as a function of distance from the graphene sheets. As we can see chain dimensions are rather similar at all distances (and same to the bulk values) but the very first layer where a slight increase of the R_{ee} and R_g are observed. However, the latter values are within the error bars.

In the following we examine the orientation of the polymer chains close to the graphene layer in the segmental level through the v^{1-3} vector which connects two non-consecutive carbon atoms. In more detail, the second rank bond order parameter defined as

$$P_2(\cos\theta) = \frac{3}{2} \langle \cos^2\theta \rangle - \frac{1}{2}$$
(43)

is calculated. $P_2(\cos\theta)$ limiting values of -0.5, 0.0, and 1.0 correspond to perfectly parallel, random, and perpendicular vector orientations relative to the graphene layer, respectively. In the above formula θ is the angle between the vector, which is defined along the molecule (here the v^{1-3} one) and the radial distance from the center of graphene. The bond order parameter of v^{1-3} for all four systems is depicted in Figure 9. In all cases there is an obvious tendency of the segments of the polymer chain for an almost parallel to the graphene layer orientation at short distances which is gradually randomized with the distance. However, there is a systematic increase of the order of the PE segments closest to the graphene layer with the increase of the size of the layers; the minimum values are about -0.17 for the two smaller sheets, whereas the value for the system with the largest sheet (S3) is about -0.25 very similar to that of the infinite sheet.

Table 4: Average chain end-to-end distance, $R_{ee} = \langle R_{ee}^2 \rangle^{1/2}$, and radius of gyration, $R_g = \langle R_g^2 \rangle^{1/2}$ for chains belonging in different adsorption layers, *R*. Corresponding bulk values: $R_{ee} = 17.20$ Å, $R_g = 6.15$ Å. Error bars are 3%–5% of the actual values based on block averaging techniques.

	R_{ee} (Å)				R_{g} (Å)			
<i>R</i> (Å)	S 1	S 2	S 3	SP	S 1	S2	S 3	SP
0–6	17.30	17.46	17.48	17.48	6.44	6.55	6.51	6.46
6–10	17.28	17.41	17.44	17.46	6.32	6.54	6.50	6.45
10-20	17.24	17.33	17.36	17.41	6.28	6.31	6.36	6.35
20-30	17.23	17.28	17.32	17.37	6.21	6.24	6.28	6.27
30–40	17.22	17.25	17.30	17.35	6.18	6.22	6.23	6.26
40–50	-	17.24	17.27	17.33	-	6.20	6.23	6.23
50-60	-	17.24	17.25	17.31	-	6.18	6.21	6.19
60–70	-	-	17.25	-	-	-	6.20	-
70–80	-	-	17.25	-	-	-	6.19	-



Figure 9: Second rank bond order parameter $P_2(\cos(\theta))$ of polyethylene for v^{1-3} vector as a function of *R* distance (distance from the center of the graphene layer) for all polymer/graphene nanocomposite systems studied here.

A further analysis of the PE chain conformations is based on the calculation of the distribution of the torsional (dihedral) angles, P_{dih} , in different distances from graphene. This is of particular importance since for PE the distribution of its (backbone) dihedral angle is critical for the determination of its overall chain conformation (e.g., radius of gyration and characteristic ratio). In the analysis performed here all torsional angles with values between -60° and $+60^{\circ}$, are defined as "trans", whereas outside this interval angles are considered as "gauche+" or "gauche-". Our results which are depicted in Figure 10a-c indicate clear spatial heterogeneous dihedral angle distribution, for all PNCs. Figure 10a contains a comparison of the distribution of the torsional angles in the (spherical) first adsorption layer (*i.e.*, from 0 to 6 Å) for the four systems together with the corresponding bulk system. A non-negligible enhancement of the trans states with a consequent reduction of the gauche ones is observed for all systems compared to the bulk case. This observation reflects the more ordered PE chains close to the graphene sheet, something which has been reported previously as well, for thin polymer films supported by graphene or graphite [128, 138]. Enhancement of "trans" population would be expected to affect the cystallinity of PE chains as well as the mechanical properties of the hybrid PNC system. This will be studied in a forthcoming work. Moreover no differentiation in the torsional angle distributions among the various sizes of graphene sheets is detected. The corresponding information for the most distant adsorption layer (*i.e.*, bulk region) is presented in Figure 10b, where the curves are completely identical to each other and to the corresponding bulk one.

Furthermore, if we compare P_{dih} as a function of radial distance from the center of the graphene sheet, the enhancement of "trans" states remains, presenting a small but gradual decrease compared to the first adsorption layer, up to a different distance depending on the system. Beyond a specific distance for each system the rest of the curves coincide with those of Figure 10b. The enhancement of "trans" states for dihedral angles of the S2 system, and for the various regimes studied here, is presented in Figure 10c, where it is clear that the curves are distance dependent, despite the rather noisy data due to the small size of each regime. Overall, the distance above which all P_{dih} 's become similar to the bulk P_{dih} defines the width of the interphase for the particular property and the way that it is affected by each graphene sheets (*i.e.*, size, mobility, fluctuations), which will be analyzed in detail in a following section.





Figure 10: Torsional angles distribution as a function of *R* distance (distance from the center of the graphene layer). (a) Data for the first adsorption layer (R = 0.6 nm) for all systems; (b) Data for the last adsorption layer (distant layer) ($R = L_{BOX}/2$) for all systems; (c) Magnification for all spherical shells of the (S2) system. In all cases the corresponding bulk curve is included.

Based on the above discussion of the spatial chain structural-conformational heterogeneities, a rough estimation of the distance beyond which the bulk behavior of the hybrid PNC system, is attained can be given as: ($\sim r \leq 10$ Å), for the smallest

grapheme sheet, (S1), extended to larger values ($\sim r \le 30$ Å) for the S2 system and even further ($\sim r \le 40$ Å) for the S3 system, while for the infinite graphene layer (SP) system size limitations do not allow the prediction of a specific value for the distance beyond which the bulk behavior is attained.

3.4.1.3 Dynamics

We continue the analysis of the model PNCs by presenting dynamical properties of PE as a function of the distance from the graphene layer. Using the time autocorrelation function (ACF) of the second Legendre polynomial:

$$P_2(t) = \frac{3}{2} \langle \cos^2 \theta(t) \rangle - \frac{1}{2} , \qquad (44)$$

we first study the *orientational* dynamics at the segmental level. The v^{1-3} vector, which has been defined previously, is used and $\theta(t)$ is the angle of this vector at time t relative to its position at t = 0. Results for the autocorrelation function, $P_2(t)$ are presented in Figure 11a–c for all hybrid PE/graphene nanocomposites studied here. Corresponding data for a bulk PE system are shown in these Figures as well. Note that for these calculations we monitor the position of each segment/vector only for the time period it belongs to the corresponding analysis regime.

First, in Figure 11a data concerning the $P_2(t)$ function of PE chains, averaged throughout the entire hybrid systems, are presented for the four nanocomposite systems as well as for the bulk PE system. There are only small differences between the different systems, *i.e.*, hybrid systems show a slightly slower average segmental dynamics compared to the bulk one. In more detail, at very short times $P_2(t)$ curve that corresponds to the system with the smallest graphene sheet (S1) coincides with the bulk one, while for the other three systems $P_2(t)$ curves attain higher values. This can be thought as a result of the fast motion of the very small sheet, which hinders the immediate effect on the polymer chains, so for a very short period they behave like being in bulk, but they diverge rapidly from this behavior.

Second, in Figure 11b $P_2(t)$ at different radial adsorption layers (*i.e.*, different distances from the graphene sheet's center) for the S1 system are shown. PE chains in

the first adsorption layer show much slower segmental dynamics compared to the bulk one. A faster decorrelation is then observed moving away from the surface up to a specific distance, while beyond this all curves coincide. This distance determines the width of the PE/graphene interphase for the orientational segmental dynamics. Qualitatively similar data were found also for the other two hybrid PE/graphene systems (S2, S3). An extended interphase is also detected here as a result of the different kinetic behavior among the graphene flakes of various sizes. The width of the interphase is found to be rather similar to the one reported previously, concerning the distribution of the dihedrals angles.

To further quantify differences, concerning the segmental dynamics of the PE chains in the vicinity of the PE/graphene interface, $P_2(t)$ for the first adsorption layer for all systems studied here are shown in Figure 11c. It is clear that the relaxation of PE chains is much slower in all systems compared to the bulk case. In addition, there are small differences between the different systems; the S1 system exhibits slightly faster relaxation (larger mobility) compared to the S2 and S3 systems. Overall, in agreement to the structural characteristics of the hybrid systems, it seems that the behavior of the PE chains for the two larger systems is closer to the infinite one, whereas for the smallest system the differences are more pronounced.





Figure 11: Time autocorrelation function (ACF) of bond order parameter $P_2(t)$ as a function of time for the characteristic vector v^{1-3} of polyethylene for all systems. (a) Average $P_2(t)$ values are over the entire system; (b) $P_2(t)$ values for the S1 system, for various spherical shells; (c) $P_2(t)$ values for all systems in the first adsorption layer. In all cases the corresponding bulk system is presented as well.

Another important aspect concerns the examination of the polymer chain dynamics at the polymer/graphene interface of the PNC, compared to previous studies of PE/graphene thin films [128, 140, 141]. Slight differences exist between the current study and our previous publications concerning PE/graphene systems (using a periodic and frozen graphene layer). In more detail data reported here show a slightly faster decorrelation of the $P_2(t)$ function of v^{1-3} vectors that are at the polymer/graphene interface (distances up to about 1 nm) compared to the frozen graphene sheets, whereas for longer distances relaxation times are identical for both cases. The analysis in the last studies was based on layers parallel to the graphene sheet and equidistant from the surface. For this reason we observed that at long distances the $P_2(t)$ curves overlap with the corresponding bulk curve. It is the periodicity of the sheet that favors this geometry in contrast to the present work where the finite size of the sheets demands a different geometric scheme for the analysis of the model configurations.

The effect of the PE/graphene interface on the PE segmental dynamics of each system can be further quantified by computing the corresponding segmental relaxation times, through proper fits of curves shown above (Figure 11a–c), with a Kohlrausch–Williams–Watts (KWW) stretch exponential function [146] of the form:

$$P_2(t) = A \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta}\right],\tag{45}$$

where, *A* is a pre-exponential factor which takes into account relaxation processes at very short times (e.g., bond vibrations and angle librations), τ_{KWW} is the KWW relaxation time and β the stretch exponent, which describes the broadness of the distribution of the relaxation times (*i.e.*, the deviation from the ideal Debye behavior— $\beta = 1$). Then, segmental relaxation time, τ_{seg} , is calculated as the integral of the KWW curves through:

$$\tau_{seg} = \frac{\tau_{KWW}}{\beta} \Gamma\left(\frac{1}{\beta}\right),\tag{46}$$

where Γ () is the gamma function.

The results of the above analysis for both the segmental relaxation time τ_{seg} and the β exponent for PE chains of the S2 system are presented in Figure 12a,b, respectively. Bulk values are also shown in this figure with dashed lines. It is clear the much slower orientational dynamics (larger segmental relaxation time τ_{seg}) of PE chains that are very close to the graphene layer (about 0.5 nm); τ_{seg} is about 10 times larger than the bulk one. As expected polymer segments become more mobile as their distance from the graphene layer increases, reaching a plateau, bulk-like regime, at distances of about 4.0–5.0 nm away from the graphene sheet. In addition, β -exponent values of PE chains at all distances are smaller than the bulk value (~0.62), shown in Figure 12b with dashed line.

Qualitatively similar to the above behavior is also the case for the other systems studied here. In order to compare the behavior of the PE chains closest to the graphene layer we present in Table 5 the τ_{seg} and the β exponent for the different systems in the first adsorption layer as well as for the bulk system. We observe that as the size of the graphene layer increases the relaxation time of the PE chains slightly increases, *i.e.*, their mobility becomes slower, for the cases of the finite graphene sheets. However, in periodic graphene a slightly smaller relaxation time, compared to the finite sheets, is observed, which can be attributed to the reduced motion of the periodic graphene's center-of-mass. Values for the β exponent are similar for all systems (around 0.4), smaller than the bulk value of 0.62. The latter indicates a broader distribution of the polymer segmental dynamics, compared to the bulk one, even for distances far away from the graphene sheets, where the *average* τ_{seg} is similar to its bulk value. Therefore, when the way that polymer/graphene interfaces affect the dynamical properties of a PNC system is considered, average properties do not provide the full information, but rather the whole distribution of segmental dynamics should be examined. This results shows that dynamical heterogeneities present in polymer nanocomposites systems is an even more complex phenomenon than those appeared in polymer/solid interfacial systems (e.g., PE confined between graphene sheets [128]), for which the behavior far away from the surface reaches the bulk one.



Figure 12: (a) Segmental relaxation time, τ_{seg} , of ν^{1-3} characteristic vector based on $P_2(t)$ time autocorrelation as a function of *R* (distance from the center of the graphene layer) for the S2 system; (b) The stretch exponent β , as extracted from the fit with KWW functions. Dashed lines represent τ_{seg} and β values of bulk PE under similar conditions (T = 450 K, P = 1 atm).

Table 5: Average segmental relaxation times τ_{seg} and stretch exponents β of PE chains for all systems studied here (columns 2 and 3). τ_{seg} values and stretch exponents β for all systems in the first adsorption layer are shown in columns 4 and 5. Error bars are obtained using block averaging techniques.

Systems	τ_{seg} -Average (ps)	β-Average	τ _{seg} -1st Layer (ps)	β-1st Layer
S1	4.6 ± 0.3	0.53 ± 0.05	44 ± 6	0.40 ± 0.05
S2	6.7 ± 0.4	0.46 ± 0.05	62 ± 6	0.40 ± 0.05
S3	6.1 ± 0.4	0.49 ± 0.05	63 ± 6	0.38 ± 0.05
SP	5.8 ± 0.4	0.52 ± 0.05	47 ± 5	0.41 ± 0.05
SB	3.9 ± 0.3	0.61 ± 0.05	-	-

In the next stage, we examine the *translational* segmental dynamics of PE chains. To distinguish translational dynamics for different layers we have calculated the average segmental mean-square displacement (msd) defined as:

$$g^{j}(\tau) = \langle [r_{i}(t+\tau) - r_{i}(t)]^{2} \rangle$$

$$\tag{47}$$

where *j* is a specific radial region, *i* is a particular segment (CH₂ or CH₃ group here) within region *j*, $\mathbf{r}_i(t)$ and $\mathbf{r}_i(t + \tau)$ are the coordinate vectors of segment *i* at time *t* and *t* + τ , respectively, whereas brackets < > denotes statistical average. Note, that in the analysis used here a segment *i* contributes to the above average msd for a given time interval τ and for a radial region *j*, if and only if it was constantly present in that region in the entire course of time τ . First, in Figure 13a data concerning $g^i(\tau)$ for all (radial) adsorption layers for the S2 system are shown. The segmental dynamics of the polymer atoms that are closer to the graphene sheet atoms (mainly in the first two adsorption layers) is slower compared to the one of the atoms in the other layers. On the contrast, segments belonging to the other regimes, (above second layer) exhibit rather similar dynamics, which is slightly slower to the bulk one, shown in Figure 13a with dash line.

In Figure 13b data concerning $g^{i}(\tau)$ for the first adsorption layer (j = 1) for all systems studied here are presented. It is clear that the segmental dynamics of the PE chains closest to the graphene layers is slower, compared to the bulk one, for all model PNCs systems. In addition, there is a slight dependence of the PE segments $g^{i}(\tau)$ msd on the size of the graphene sheet mainly in the ~5–20 ps time regime, *i.e.*, the segmental dynamics for the small-graphene system (S1) is faster than the two other systems, whereas $g^{i}(\tau)$ for the biggest graphene system (S3) is similar to the periodic-infinite case. In Figure 13c $g^{i}(\tau)$ msd data for PE chains belonging in a radial layer far away from the graphene sheet are shown for all systems. Segmental translational mobilities of different systems are very similar to each other, slightly slower than the unconstrained bulk one.





Figure 13: (a) Segmental mean squared displacement for polyethylene chains along *R* (distance from the center of the graphene layer); (a) Values for the S2 system, for various spherical shells; (b) Data for the first adsorption layer (distant layer) (R = 0.6 nm) for all systems; (c) Data for the last adsorption layer ($R = L_{BOX}/2$) for all systems. In all cases the corresponding bulk curves are included.

The *dynamical heterogeneity* of polymer atoms discussed above can be examined in greater detail if we consider the probability distribution of segmental $g^{i}(\tau)$ msds for a specific time period τ . An important aspect is related to the disturbance of such a distribution, compared to the bulk polymer system. Data for the distribution of $g^{i}(\tau)$ for the S2 system and a specific time period similar to the bulk segmental relaxation time ($\tau = 5$ ps) are shown as bars in Figure 14a–c for three different radial regimes: 0–6 Å, 20–25 Å and 45–50 Å. 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 (Figure 14b,c), for which msds have been found in the range 0–80 Å² 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 msds in a 0–40 Å² range. Second, the probability distribution of $g^{i}(\tau)$ msd's, of atoms belonging in the first adsorption regime (Figure 14a), is larger than the bulk one for small displacements (Δr^{2}), up to about 10 Å². On the contrary, the probability to find larger msds, above about 10 Å² is smaller than the bulk one. As we move far away

from the graphene sheet the probability distribution of the $g^{j}(\tau)$ msd's data approaches the bulk one, *i.e.*, probability of finding small msds decreases, whereas the probability to find larger msds increases. This is particular clear for the longer distances 45–50 Å, which exhibit very similar distribution to the bulk PE atoms.



Figure 14: Probability distribution of the mean squared displacements, $g^{i}(\tau)$, for the S2 system at a specific time period ($\tau = 5$ ps) for three different radial regimes: (**a**) 0–6 Å; (**b**) 20–25 Å and (**c**) 45–50 Å. In all cases the distribution of a bulk system is shown with a solid line.

Data concerning the probability distribution of $g^{i}(\tau)$, computed at three different regimes and for the specific time period discussed above ($\tau = 5$ ps), are shown in Figure 15a–c for all S1, S2 and S3 systems, respectively. All systems exhibit a similar behavior to the S2 system discussed above (see Figure 14); *i.e.*, for segments belonging to the radial regime closest to the graphene surface there is a larger probability for smaller msds, compared to the bulk one. This is in agreement with the average $g^{i}(\tau)$ data presented above in Figure 13a–c. On the contrary, segments belonging to the regime that is far away from the graphene sheet show similar distribution to the bulk system. In the same graph the distribution for the infiniteperiodic system (SP) is shown as well. The latter exhibit qualitatively similar behavior as expected. There is only a small difference in the far distant layer for the SP system that still exhibits larger (smaller) probabilities for small (large) distances, compared to the bulk one. The reason for this difference is that due to the "infinite" size of the periodic graphene layer there are always some atoms in the radial analysis used here that are in small distances from the graphene atoms. The msds of these atoms is on the average smaller; thus increasing the probability to find smaller msds in the graphs shown in Figure 15c.



Figure 15: Probability distribution of the mean squared displacements, $g^{i}(\tau)$, for all three systems at a specific time period ($\tau = 5$ ps) for three different regimes: (**a**) First layer: 0–6 Å; (**b**) intermediate layer: (10–15 Å for S1, 20–25 Å for S2, 30–35 Å for S3, 15–20 Å for SP) and (**c**) distant layer: (25–30 Å for S1, 45–50 Å for S2, 65–70 Å for S3, 35–40 Å for SP). In all cases the distribution of a bulk system is shown.

3.4.1.4 Desorption Kinetics

An important quantity related to the response of the nanocomposites to external stimuli (e.g., changes in temperature or imposed deformations) is the adsorption/desorption behavior of polymer atoms at the polymer/graphene interface. The latter is examined by calculating the rate with which atoms, which are initially close to the graphene sheet, are desorbed from this regime with time. In more detail, we label atoms that are initially (at time t_0) within the adsorption (radial) regime defined in the range 0–1.5 nm, and then we compute the number of atoms that are still in the same regime after time t, $n(t_0 + t)$. In Figure 16a the percentage of the adsorbed atoms, $n(t_0 + t)/n(t_0)$ is shown. To improve statistics model configurations were analyzed every few hundreds of ps (different t_0 values were considered using multiple time origin technique).

All systems shown in Figure 16a exhibit the same behavior: Atoms are desorbed from the graphene sheet with a stretched exponential-like behavior and all of them are desorbed from the graphene flakes in time periods of about 100 ps. To further quantify the kinetic behavior of **PNCs** all shown data in Figure 16 were fitted with a KWW equation. Then a characteristic relaxation time, τ_{des} , was calculated from the integral of the KWW curves. $\tau_{des} = 36.5 \pm 0.5$ ps has been computed for the three PNC systems (S1, S2 and S3) and a value of $\beta = 0.57 \pm 0.05$ for the β-exponent. The broad distribution of the PE atom desorption kinetics provides another indication of the strong dynamic heterogeneities appeared the PNCs due to the polymer/graphene interfaces.

The same calculation was made for the desorption kinetics of the whole chains based on their center of masses (cms) as depicted in Figure 16b. The decay of the percentage of the adsorbed cms in the range 0–1.5 nm as a function of time has a similar behavior to the one of atoms, though desorption kinetics is slower in this case, as expected. A fit with a KWW function provides the corresponding values for the desorption of the PE cms: $\tau_{des} = 52.07 \pm 1.0$ ps and $\beta = 0.66 \pm 0.05$.



Figure 16: Evolution of the percentage of (a) polymer atoms and (b) chain center-of-masses that are within the adsorption regime, as a function of time for all systems.

3.4.2 Graphene Properties

3.4.2.1 Translational Dynamics

In this section results concerning the properties of the graphene flakes, in the hybrid model polymer-graphene systems studied here, are presented. First, the dynamical behavior of the graphene sheet in each system is examined by computing its center-of-mass mean squared displacement:

$$\Delta \mathbf{R}_G^2 = \langle (\mathbf{R}_G(t) - \mathbf{R}_G(0))^2 \rangle, \tag{48}$$

where R_G (0) and R_G (*t*) are the positions of the center of mass of the sheet at time 0 and *t*, respectively. Data for ΔR_G^2 as a function of time for the three finite systems are presented in Figure 17. Note that the center-of-mass of the "infinite" graphene sheet does not exhibit any translational or orientational motion as expected. Several important observations are made in Figure 17. First, all graphene sheets exhibit a considerable translational motion; *i.e.*, they are moving along distances of about 20– 100 nm for the time period of the current simulations (50 ns), much larger than their size. Second, the smaller the graphene sheet the higher its mobility. More specifically in Figure 17a big difference in the mobility is found between the smallest sheet (S1) and the other two sheets (S2, S3). For the S2 and S3 systems, mean squared displacements attain comparable values though the smaller one (S2) is again a little faster. Third, all curves are rather noisy due to poor statistics. This is not surprising if we consider the small graphene percentage (~3 wt%) in all systems.

In order to check whether the diffusion of the graphene sheets in the polymer matrix is linear we present in the sub-plot of Figure 17 an effective time-dependent diffusion coefficient for graphene defined as:

$$D(t) = \Delta R_G^2 / (6t) \tag{49}$$

as a function of inverse time. For a system exhibiting linear (Fickian) diffusion a plateau-time independent value is expected for long time, that is the macroscopic diffusion coefficient. It is not possible to find such a time regime here, especially for the two larger graphene sheets, showing that the systems practically do not yet follow

linear diffusion. For the smaller system there is a short linear-like time period from 15 to 20 ns where *D* is about 0.07 Å²/ps.



Figure 17: Mean squared displacement as function of time for the center of mass of the graphene sheet for the S1, S3 and S3 systems. (Inset): Effective time dependent diffusion coefficient of graphene sheets as a function of inverse time for the three systems.

3.4.2.2 Orientational Dynamics

Next we study the dynamical behavior of the graphene sheets related to their orientational motion. This can be quantified through the de-correlation of a vector along the graphene sheet. In more detail, we have calculated the first bond order parameter

$$P_1(t) = \langle \cos\theta(t) \rangle, \tag{50}$$

where $\theta(t)$ is the angle of the vector under consideration at time *t* relative to its position at t = 0. The $P_1(t)$ time autocorellation function as a function of time is presented in Figure 18 for the three hybrid systems. The vector which has been chosen for this calculation is the one connecting the center of the graphene sheet with a corner atom (*i.e.*, half diagonal), denoted in Figure 19a with a dash line. A complete

decorrelation of $P_1(t)$ is observed for all systems during the simulation time but at different characteristic time scales; the smaller graphene layer (system S1) decorrelates within 1 ns, much faster than the other two, which decorrelate within 10–20 ns.



Figure 18: The time autocorrelation function of bond order parameter $P_1(t)$ as a function of time for a characteristic vector along the half diagonal of the graphene sheet for S1, S2 and S3 systems.

To further quantify the orientational dynamics of the graphene sheets we calculate corresponding relaxation times based on fittings of $P_1(t)$ data with KWW functions [146]. Results for the orientational relaxation time ($\tau_{graphene}$) and the β exponent are presented in Table 6. For the smallest sheet (S1) segmental relaxation time is about one order of magnitude smaller than the other two systems whereas the largest sheet (S3) has an almost double $\tau_{graphene}$ compared to the S2 system. Moreover β values indicate very narrow distribution of relaxation times in all cases (*i.e.*, $\beta \sim 0.9-1.0$). Note that as expected a similar behavior is observed for any other vector chosen along the graphene, mainly in long time regime, above 100 ps, which is dominated by the overall orientational motion of the whole graphene sheet.

Table 6: Orientational relaxation times $\tau_{graphene}$ defined for a characteristic vector along the half diagonal of the graphene sheet and stretch exponents β for S1, S2 and S3 systems. Error bars are obtained from the standard deviations, based on block averaging calculations throughout the simulation runs.

Systems	$\tau_{graphene} (ps)$	β	
S1	360 ± 20	0.90 ± 0.04	
S2	$8,\!300\pm450$	0.88 ± 0.04	
S 3	$15,300 \pm 800$	0.96 ± 0.04	

3.4.2.3 Wrinkling of Graphene

The final part of the analysis of the graphene sheets concerns their conformational characteristics in terms of fluctuations—wrinkling behavior. For this purpose we define one cross line on the sheet (denoted with red full line in Figure 19a), parallel to the *y*-direction, and observe its motion during the simulation starting from a completely straight line (*i.e.*, a planar conformation of the graphene sheet). The line passes from a series of graphene atoms, which are spaced one lattice constant apart in a sequential way. Initially, when the flake is planar, all these atoms are on a straight line and in the following their vertical shift is recorded with respect to the plane of the sheet at its instantaneous position. This requires an Eulerian transformation of the first atom of the straight line (zero point) and (b) three vectors, the first two of which are defined along the plane of the graphene sheet at its represented schematically in Figure 19b.

A "wavy" motion is observed with crests and troughs for all systems studied here. 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. However, this motion does not happen in a periodic way, even for the largest graphene sheet studied, but it seems more like random thermal fluctuations. Two representative snapshots are depicted in Figure 19c. The motion of the defined line at different times is presented for the S2 sheet in Figure 20, 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. For the latter cases a difference in the number of crests and troughs along the line among the four systems is expected due to the different size of the sheets. Wrinkling of graphene has been studied experimentally by transmission electron microscopy measurements on individual graphene sheets in vacuum or air [147]. These measurements detected out-of-plane deformations of the sheets of the order of 1 nm. On top of that atomistic Monte Carlo simulations which were performed on single-layer graphene [148] in vacuum, found ripples spontaneously appeared on graphene sheets with a size distribution peaked around 80 Å, are in agreement with the experimental findings.







(**c**)

Figure 19: (a) A schematic representation for the conformational analysis of graphene sheets. The characteristic vector along the half diagonal is shown; (b) A schematic representation for the Eulerian transformation of the coordinates from the original Cartesian system to a new one at the instantaneous position of the sheet; (c) A characteristic snapshot of graphene layers with fluctuations.



Figure 20: 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 S2 system.

A rough quantification of the above pictures in order to perform a comparison among the systems is based on the calculation of the square root of the second moment of the out-of-plane displacement, averaged over all the atoms of the line, $\sqrt{\langle \Delta z_i^2 \rangle}$, throughout the simulation. Results for all systems are presented in Table 7. Increasing amplitude of fluctuations is observed as the size of the graphene sheets become bigger. Nevertheless the statistics of these calculations is poor and as a consequence the error bars are very large. For the accurate estimation of such long-time fluctuations longer simulations are required. A further investigation of the wrinkling on graphene sheets, concerning a more detailed analysis of graphene conformations, as well as the frequency of the interchange among different conformations (*i.e.*, from one crest to one trough or to crests and troughs) will be the subject of a following study.

Table 7: The square root of the second moment of the out of plane graphene motion averaged over all the atoms of the cross line for S1, S2 and S3 systems.

Systems	S1	S2	S3
$(<\Delta z^2>)^{0.5}$ (Å)	0.035 ± 0.023	0.058 ± 0.060	0.085 ± 0.083

4. Polymer/Metal Nanocomposite Systems

4.1 Introduction

From the broad family of polymer nanocomposites (PNCs) here we focus on systems with (bare and core/shell) metal nanoparticles (NPs). Such systems have been used in the recent past in bio-nano-technology for biomedical utilization, including antibacterials [149], antimicrobials [150, 151], biosensors [152], cancer treatment [153] and biomedical tissue engineering [154, 155]. Their usage is also explored in other technological applications involving catalytic devices, in the textile industry and in food packaging [156-161]. In particular, polymer systems with dispersed gold (Au) NPs, or core/shell gold NPs, have been extensively studied due to their exceptional properties, such as biocompatibility, tunable conductivity and catalytic properties. Au nanoparticles of few nanometers (1 to 100 nm) have a great surface/volume ratio and that enables their surface to be coated with many molecules (including therapeutics and targeting agents). Applications most stable of metal nanoparticles and they also provide a stable immobilization platform of the molecules while their reactivity is conserved. Their properties include of polymer nanocomposites with Au NPs span many scientific fields, such as medicine [162] biotechnology [163], catalysis [164], and electronics [165]. In all these applications, the shape of Au nanoparticles has a key role in every aspect of their functionality, from sensing [166] and biolabeling applications [167] to plasmonics [168], photonics [169] and fuel cells [170]. Additional technological areas in which gold nanoparticles have been used include: the storage of energy [171], the delivery of molecules into cells [162, 172], use as a heat source [173], as sensors [174-176], labeling [177, 178], Light Emitting Diode (LED) applications [179], optical and electronic applications [168], drug delivery vehicles [180, 181] and in the field of catalysis [117, 118, 164, 182].

Besides experiments [183-191], molecular simulations have been used to study the properties of polymer-based complex materials [6, 7, 74, 192-195], including atomistic molecular dynamics (MD) [27, 35, 55, 99, 196, 197], dynamic Monte Carlo simulations (MCMD) [23, 198, 199], self-consistent field theory (SCFT) and density functional theory (DFT) [200], dissipative particle dynamics (DPD) [201], coarse-grained (CG) MD simulations [202-205] and stochastic dynamics simulations [29].

We should note that polymer/NP hybrid system have been already simulated in the past, mainly via qualitative CG bead spring models, but atomistic simulations as well. However, limited are the atomistic works including metals, and especially Au, NPs. Given the important role of the actual chemistry on the polymer/NP interaction and on the overall properties of the hybrid material, quantitative atomistic simulations of specific systems can be valuable tools, complementary to experiments, to provide a fundamental study of specific systems.

Here we study via atomistic simulations polymer nanocomposites with bare and grafted Au NPs; the latter were constructed in their minimum energy configuration, via the Wulff method, whereas the PE/Au interaction is derived via DFT calculations. We further examined and compared hybrid systems with bare and grafted Au NPs, focusing on the PE/Au interphase. Moreover, properties of polymer chains are studied as a function of: (a) size of the Au NP, (b) MWs of the polymer matrix and (c) lengths of the anchored polymeric chains.

It is now acknowledged that the behavior of polymer chains close to a polymer/solid interface is different from the behavior of the bulk [14, 15, 105, 138, 206, 207]. For such systems, an interphase between the substrate and the bulk phase of the polymer is postulated, and the width of this interphase layer has been the focus of many studies. For example, it has been observed that segmental packing and orientation return to bulk values within just a few segment lengths from the surface and chain properties reached the bulk values after a few 1–2 times the radius of gyration R_g using atomistic and systematic coarse-grained models [32, 206], or bead–spring models [30, 31]. In addition, concerning the segmental dynamics of the macromolecules, relaxation times of segments at the vicinity of a solid surface strongly depend on the strength of the polymer/surface interactions [3, 14]. For polymer chains supported by a solid substrate the size of the interface or interphase depends on the actual property under study [206].

Furthermore, coarse-grained MD, Monte Carlo MD and atomistic MD simulations have been used to examine the viscoelastic behavior and the dispersion–aggregation transition of NPs in polymer nanocomposites with polymer-grafted nanoparticles systems [208-212], to compute the mean square displacement and the mean relaxation time of various intramolecular vectors [75], the structural properties and the mass

density profiles of polymers brushes (grafted) [74, 198]. Moreover, several studies have investigated the polymer's structure, rheological properties and the shearing of the polymer between two gold surfaces, using MD simulations [213-215]. Finally, the mass density profiles, the mean square displacement, the end to end distance and the radius of gyration of polymer chains for PNCs with gold nanoparticle have been examined through MD simulations as well [196].

Despite the above works, the study of the polymer/metal NP interface, and interphase as well, by predicting quantitatively the properties of polymer chains of specific polymer nanocomposites, using realistic atomistic models for both polymer matrix and the Au NP is still a challenging problem. The main goal of this work is to provide a detailed investigation of polymer nanocomposites with dispersed gold nanoparticles and core/shell gold nanoparticles, at the molecular level through detailed MD simulations. As model polymer we consider polyethylene (PE). Bulk PE and PEbased nanocomposite materials are among the most widely used polymers in industry, and have been studied in depth during the recent years through experiments [216-218] and simulations [3, 26, 219]. The Au NPs and the functionalized Au NPs are made with Wulff construction derived directly from density functional theory (DFT) calculations [116, 220] in order to obtain model Au NPs with the minimum surface free energy, i.e., at thermodynamic equilibrium.

4.2 Model Systems and Simulations

We study PE nanocomposites with bare Au NPs and with functionalized, with short PE chains, (core/shell) NPs. The model gold nanoparticles, were generated using an atomistic Wulff construction algorithm [116, 220]. The grafting of the gold nanoparticles was accomplished by using anchored polyethylene chains. In all cases the temperature is 450 K, above the melting temperature of PE. Ten (10) different model systems are considered, involving two different monodisperse PE matrices (Table 8); one consists of chains with 22 monomers (MW = 310 gr/mol) and the other one with 100 monomers (MW = 1400 gr/mol) [25, 26, 219]. Two different gold NP sizes with Wulff construction were modeled [116, 220]: one with diameter of 25 Å and one with 50 Å. Systems with the same polymer matrix but a different nanoparticle are also studied. Both of the grafted Au nanoparticles have a diameter of 5 nm and 53

grafted polyethylene chains. The first one has 20 monomers per chain and the other one 62 monomers per chain. The grafting density is 0.67 chains per square nm. That value has been used in several experimental studies of different PNCs [221]. The equilibrium shape of nanoparticles is a polyhedron that is derived through the Wulff construction. Small nanoparticles often deviate from this thermodynamically stable equilibrium shape: for example, at small diameters, an edge length might be smaller than the atom diameter. For Au, the smallest nanoparticle that has same polyhedral shape as the Wulff construction has a diameter of about 2.5 nm for both bare- and thiol-covered nanoparticles [116, 220]. For comparison, we also considered larger nanoparticles with diameters around 5 nm.

More details for all systems are presented in Table 8. Typical snapshots of the PE/Au NP and the Core/Shell PE/Au NP systems are shown in Figure 21 and Figure 22 respectively.

Name	Au NP Diameter	Au Atoms	Free PE Chains	Au/PE w/w%	Au/PE v/v%	Grafted PE Chains	Grafted PE Mers/Chain
PE100/Au2	25.1 Å	459	1200	4.9	0.2	-	-
PE100/Au5	50.2 Å	3101	1200	37.6	1.7	-	-
PE100/Au5/g20	50.4 Å	2461	1200	29.7	1.7	53	20
PE100/Au5/g62	50.4 Å	2461	1200	29.7	1.7	53	62
PE100	-	-	240	-	-	-	-
PE22/Au2	25.1 Å	459	5040	5.8	0.4	-	-
PE22/Au5	50.2 Å	3101	5040	38.8	1.6	-	-
PE22/Au5/g20	50.4 Å	2461	5040	30.8	1.6	53	20
PE22/Au5/g62	50.4 Å	2461	5040	30.8	1.6	53	62
PE22	-	-	420	-	-	-	-

Table 8: Details for the simulated systems.

We used the LAMMPS package [110] to perform Molecular Dynamics (MD) simulations in the isothermal-isobaric (NPT) statistical ensemble. We kept the pressure constant at P = 1 atm by using Nosé Hoover barostat. To keep the temperature at T = 450 K we used the Nosé Hoover thermostat. Periodic boundary conditions in all three dimensions were used, whereas the integration time step was 1.0 fs. Furthermore, we used a united atom model to represent the polyethylene. In this case, each methylene CH₂ and methyl CH₃ group represented as a single Van der

Waals interacting site. Harmonic potential was used to describe the polyethylene bonds and angles whereas the OPLS force field (Table 9) was used to describe the polyethylene dihedrals. For the Van der Waals interactions between the PE-PE (Table 10) we used a spherically truncated 6–12 Lennard–Jones potential with cutoff distance $R_c = 10$ Å [26]. The first gold nanoparticle with Wulff construction has 459 atoms with 2.51 nm diameter and the second has 3101 atoms with 5.02 nm diameter [116, 220]. The interaction between the Au and PE is described via a Morse potential, which is taken from the literature and is based on detailed DFT calculations [32, 206, 222]. This potential is parametrized in order to describe with accuracy extensive DFT data regarding the adsorption energy of the ethylene on the Au surface as a function of distance for several different adsorption sites.



Figure 21: Snapshot from MD simulation of hybrid polyethylene/gold nanoparticle at 450K. Au nanoparticle (3101 atoms, diameter of 5.02 nm) and polyethylene (5040 chains, 22-mers per chain) are shown. With yellow is the Au and with grey are the edges of Au nanoparticle. With blue are the CH_2 and with green the CH_3 monomers.



Figure 22: (Left) Snapshot from MD simulation of hybrid polyethylene/grafted gold nanoparticle at 450K. Au nanoparticle (2461 atoms, diameter of 5.04 nm) and polyethylene (5040 chains, 22-mers per chain) are shown. With yellow is the Au and with grey are the edges of Au nanoparticle. With blue are the free CH_2 and with green the free CH_3 monomers. With red are the grafted CH_2 and with white the grafted CH_3 monomers. (**Right**) The grafted Au NP without the brushes and the initial configuration of the grafted NP with the short brushes and with the long brushes.

For the core/shell Au NP systems the S atoms were placed on the Au NPs in their minimum energy positions as computed from the DFT calculations [222]. Interactions between the S and CH_x groups of PE were modeled via a 6–12 Lennard–Jones potential with cutoff distance $R_c = 10$ Å (see Table 10). For the S–CH₂–CH₂–CH₂–CH₂ dihedral angle interactions the OPLS force field was used. The entire atomistic force field is given in Table 9 and Table 10. Tail corrections were applied to both energy and pressure. For the non-bonded interactions between PE-PE monomers, the Lorentz–Berthelot rules were used. The gold nanoparticles are frozen during the duration of the MD runs. This is not expected to be a crude assumption since the Au NPs are very stable under conditions (temperature and pressure) similar to those of the current simulations.

Table 9: Model parameters and functional forms of all non-bonded interactions of the atomistic force field.

Non-Bonded Interactions								
$V_{LJ}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$, $r \le R_c$ Lennard-Jones								
Atom Type	Atom Types mass (g/mol) σ (nm) ε (kJoule/mol)							
CH_2	14.0	27	0.395	0.3824				
CH ₃	15.0	35	0.395	0.3824				
S - CH ₂	32.066 -	14.027	0.372	0.7219				
S - CH ₃	32.066 -	15.035	0.372	0.8761				
$V_{Morse}(r_{ij}) = D_0 \left[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right], r \le R_c$ Morse								
Atom Types	mass (g/mol)	D ₀ (kJoule/mol)	α (nm ⁻¹)	r ₀ (nm)				
Au - CH ₂	196.967 - 14.027	1.6885	11.69	0.4085				
Au - CH ₃	196.967 - 15.035	1.6885	11.69	0.4085				

Table 10: Model parameters and functional forms of all bonded interactions of the atomistic force field.

Bonded Interactions								
$V_{b}(r_{ij}) = \frac{1}{2} k_{ij}^{b} (r_{ij} - b_{ij})^{2}$								
Bond	Bond b (nm) k ^b (kJ/mol·nm ²)							
$CH_2 - CH_2$		0.154	100),000.00				
$CH_2 - CH_3$		0.154	100,000.00					
$CH_3 - CH_2$		0.154	100),000.00				
$V_{lpha}ig(heta_{ijk}ig)= rac{1}{2} k^{ heta}_{ijk}ig(heta_{ijk}- heta^0_{ijk}ig)^2$								
Angle		θ° (deg)	$k^{\theta} (kJ/mol*rad^2)$					
$CH_2 - CH_2 - CH_2$		114	519.611					
$CH_3 - CH_2 - CH_2$		114	519.611					
$CH_2 - CH_2 - CH_3$		114	519.611					
$S - CH_2 - CH_2$		114	519.611					
$V_{opls}(\varphi_{ijkl}) = \frac{1}{2}K_1[1 + \cos(\varphi)] + \frac{1}{2}K_2[1 - \cos(2\varphi)] + \frac{1}{2}K_3[1 + \cos(3\varphi)] + \frac{1}{2}K_4[1 - \cos(4\varphi)]$								
Dihedral	K_1 (KJ/mol)	K ₂ (KJ/mol)	K ₃ (KJ/mol)	K_4 (KJ/mol)				
CH ₃ CH ₂ CH ₂ CH ₂	4.276	-1.12968	13.1545	0.00				
CH ₂ CH ₂ CH ₂ CH ₂	4.276	-1.12968	13.1545	0.00				
CH2-CH2-CH2-CH3	4.276	-1.12968	13.1545	0.00				
S- CH ₂ –CH ₂ –CH ₂	4.276	-1.12968	13.1545	0.00				

Generation and equilibration of model polymer nanocomposites is not a trivial issue. Below we describe shortly the procedure followed in order to obtain the model PE/Au nanocomposites:

- (a) First, in order to obtain initial PE/grafted Au configurations, we added the anchors to the Au surface randomly by using a Monte Carlo algorithm in suitable positions according to the shape of the Au and taking into account the absorption sites of sulfur in the DFT calculations of alkanethiols adsorbed on Au.
- (b) Second, we equilibrate the hybrid system through energy minimization and long simulation runs. Energy minimization of the core/shell system was performed followed by MD simulation runs up to 10 ns in the NVT ensemble. Then, the Au nanoparticle, grafted or not, was placed at a close distance (about 0.5 nm) to several well-equilibrated polymer samples [26].
- (c) The final step of our "equilibration protocol" involves the execution of long MD simulations, of the order of 30 ns. Throughout this time we monitored the motion of the whole hybrid system. Our simulations run times were much higher than the relaxation times of the chains [26].

We used various criteria to ensure equilibration of the model systems. We computed the time evolution of the radius of gyration, R_g , values and checked the de-correlation of the end to end vector (ACF) of polymer chains. Furthermore, we performed several (3–5) different simulations by following the exact same procedure but starting with different initial configurations and we end with the same results.

Starting from the well equilibrated atomistic PE/Au configurations, we executed production runs for times up to 100 ns. We saved many thousands of PE/Au NP configurations. We used these configurations to estimate the properties of the whole hybrid systems and for the detailed analysis of PE/NP interfaces. Note, that the above methodology can be expanded to provide well equilibrated atomistic configurations of other polymer/core shell NP nanocomposites as well.
4.3 Data Analysis

The structural, conformational, and dynamical properties of the chains were analyzed and compared to the behavior of the bulk polyethylene system. In more detail, we report data concerning polymer density profiles, bond order parameter, segmental and terminal dynamics. Our main goal is to study the spatial and dynamical heterogeneities of model hybrid polymer/nanoparticle systems in a detailed way at the molecular level. The reported data could be very useful for the prediction of the properties, as well as for the design, of such materials, in particular since typical experiments are not able to distinguish easily between the interface at the solid surface and the free surface and, therefore, the measured properties are an average value of the entire system.

The analysis presented here has been performed along radial distances from the center of mass of the gold NP, by creating spherical shells of increasing radius (*i.e.*, increasing distances form the Au NP). This calculation has to be repeated at every time step. A sketch of this analysis scheme is depicted in Figure 23.



Figure 23: a) A sketch of the analysis scheme in spherical shells. b) Inside view of the Figure(a).

The mass density profiles were calculated according to the above-discussed radial distance, using spherical shells of thickness equal to 1 Å. The same binning was used for the calculation of the second rank bond order parameter. Thicker spherical shells were used for the calculation of dynamical properties, of around 5 - 10 Å for both orientational and translational dynamics in the segmental level in order to improve

statistics, whereas a 15 - 20 Å binning was used for the distribution of atoms according to their mean squared displacements in each shell. The choice of binning size (thickness of spherical shells) for the computation of each specific property is the result of an optimized balance between detailed information and improved statistics. Furthermore, for the calculation of the density of PE as a function of the distance from the nanoparticle we applied the following procedure: The volume of each spherical

$$V_{shell} = \frac{4}{3}\pi [(r+dr)^3 - r^3]$$
(51)

where r is the radius of a sphere, centered at the center of the gold NP and dr is the thickness of the shell. Then the polymer number density is given by:

$$\rho_{\rm PE} = \frac{N_{\rm PE}}{V_{\rm shell}} \tag{52}$$

where N_{PE} is the number of PE atoms in the shell.

4.4 Results

shell is equal to:

We start the analysis of the simulation results by investigating the structural properties of the model atomistic PE/Au nanocomposites.

4.4.1 Structural Heterogeneities on Density Profile

The analysis of the PE/Au model nanocomposites was commenced by calculating the mass monomer density profile of the polymer (PE) chains as a function of the distance from the gold NP. All systems consisting of polyethylene matrices of 100 mers per chain whose average density profiles we calculated for the center of mass of the monomers, $\rho(r)$, are shown in Figure 24 and all systems consisting of PE matrices of 22 mers per chain are shown in Figure 25.

In Figure 24, the polymer mass at each spherical shell has been divided by the total volume of the shell. Far from the Au NP, all curves reach/approach the bulk density value ($\rho = 0.75 \text{ gr/cm}^3$), though at different distances due to the different Au NP sizes. PE100/Au2 and PE100/Au5 systems exhibit the same behavior: a peak of rather similar height (but larger than the bulk value) is observed at a distance/radius of about

1.3 nm and 1.8 nm respectively, which denotes the attraction of the polymer atoms from the gold NP at short distances, due to vdW forces, while at longer distances the bulk density is attained. In the core/shell Au NP systems (PE100/Au5/g20 and PE100/Au5/g62), only few polyethylene chains can penetrate the anchors and reach the gold surface.



Figure 24: Mass monomer density profiles of polyethylene as a function of r (distance from the center of the gold NP) for the systems: PE100, PE100/Au2, PE100/Au5, PE100/Au5/g20 and PE100/Au5/g62.



Figure 25: Mass monomer density profiles of PE chains as a function of distance from the center of the gold NP, *r*, for the systems: PE22, PE22/Au2, PE22/Au5, PE22/Au5/g20 and PE22/Au5/g62.

We observe a similar behavior for the systems consisting of PE matrices of 22 mers per chain although in this case the average density is lower than that of the systems consisting of PE matrices of 100 mers per chain. The above values are in very good agreement with experimental data for bulk PE chains [223].



Figure 26: Mass monomer density profiles of polyethylene as a function of r (distance from the center of the gold NP). Au5/g20 and PE100/Au5/g62 systems. The density profile was decomposed to free polyethylene chains and grafted polyethylene chains.

For the core/shell NP systems, the density profile can be decomposed to free polyethylene chains and grafted polyethylene chains. As free PE chains we consider the PE matrix and as grafted PE chains, the grafted chains that are anchored on the gold NP. In Figure 26, the total PE density profiles is shown as well as its decomposition in "free" and "grafted" chains. We observe that the density values for the free polyethylene chains are lower than the corresponding bulk value close to the surface due to the nanoparticle's anchors, which do not allow the interpenetration. However, the NP with short anchors allows more free PE chains to reach close to the surface compared to the case of long anchors NP. On the other hand for the grafted polyethylene chains (i.e., PE100/Au5/g20 and PE100/Au5/g62 systems) we observe a peak close to the Au NP due to the attraction from the surface. This peak is more pronounced for the case of PE100/Au5/g62 system due to the longer anchors. Moreover, the extension of anchors is up to 35 Å and up to 55 Å for the PE100/Au5/g20 and PE100/Au5/g20 systems respectively. Therefore, the

corresponding bulk values are attained at these distances, as is observed in the density profiles of the total density curves (sum of free and grafted polyethylene chains). A similar behavior is observed for the PE22/Au2, PE22/Au5, PE22/Au5/g20 and PE22/Au5/g62 systems however in this case the average density is lower than that of the systems consisting of PE matrices of 100 mers per chain.

4.4.2 Orientational Properties

Bellow we examine the orientation of the polymer chains close to the gold NP in the segmental level, through the v^{1-3} vector, which connects two non-consecutive carbon atoms (see Figure 27). The segmental orientation is quantified via the second rank bond order parameter [9, 224] defined as:

$$S_{1-3} = \frac{3}{2} \langle \cos^2 \theta \rangle - \frac{1}{2}$$
 (53)

where θ is the angle between a vector which is defined along the chain (here the v^{1-3} one) and one that connects the center of the gold NP with the midpoint of the above (v^{1-3}) vector (see Figure 28), and whereas brackets $\langle \rangle$ denote statistical average. S_{1-3} limiting values of -0.5, 0.0, and 1.0 correspond to perfectly parallel, random, and perpendicular vector orientations relative to the Au NP, respectively. For the limiting values we assume smooth plain surface.



Figure 27: Snapshot of oligomers of PE chain. Characteristic vectors along the backbone and from the backbone to the side groups are drawn.



Figure 28: The definition of the θ angle for the calculation of the second rank bond order parameter S_{1-3} of polyethylene chains for v^{1-3} vector. In blue is the PE and in yellow is the Au NP. The orange line connects two non-consecutive carbon atoms and the blue line connects the center of the gold NP with the midpoint of the orange line. In red is the θ angle.



Figure 29: Second rank bond order parameter S_{1-3} of polyethylene chains for v^{1-3} vector, as a function of distance from the center of the Au NP, *r*, for all PE/Au systems with PE matrices consisting of 100 mers per chain.

The bond order parameter of v^{1-3} for all systems with PE matrices consisting of 100 mers per chain is depicted in Figure 29. In all cases there is an obvious tendency of the segments of the polymer chain for an almost parallel orientation relative to the Au NP surface at short distances which is gradually randomized the further the distance. There is a decrease of the bond order parameter of the PE segments closest to the Au NP and the minimum values are about -0.4 for all hybrid systems. The same behavior is observed for the other model systems studied here as well.

4.4.3 Conformational Properties

To further analyze the PE chain conformations at the segmental level we probe the distribution of the torsional (dihedral) angles, P_{dih} , of polymer chains at different distances from the gold NP. Results about the dihedral angle distributions of the PE chains are shown in Figure 30a for the PE100/Au2 system ("trans" corresponds to 0°, "gauche-" and "gauche+" to -60° and $+60^{\circ}$ respectively and "cis" to 180° degrees). For the first adsorption layer, defined via the first minimum in the density profile (0– 30 Å, see Figure 24), a non-negligible enhancement of the trans states with a consequent reduction of the gauche ones is observed for PE22/Au2, PE22/Au5, PE100/Au2 and PE100/Au5 systems compared to the bulk case (Figure 30b). This observation reflects the more ordered PE chains close to the gold NP. Enhancement of "trans" population would be expected to affect the crystallinity of PE chains as well as the mechanical properties of the hybrid system. Such a behavior has been observed for PE adsorbed on planar carbon-based surfaces, such as graphite or graphene, where the structure of PE commensurate to the underlying crystal structure of the substrate [3, 35, 225, 226]. Here the enhancement of "trans" population is rather weak.

Concerning the system with the functionalized Au NPs (PE22/Au5/g20, PE22/Au5/g62, PE100/Au5/g20 and PE100/Au5/g62) no differentiation in the torsional angle distributions is detected. Short anchors as in PE100/Au5/g20 and PE22/Au5/g20 systems are enough to make the dihedral distribution peak to disappear. For the most distant adsorption layer (i.e., bulk region), the curves are completely identical to each other and to the corresponding bulk one.

In addition, the radius of gyration (R_g) for the PE was calculated and found approximately 6 Å in the systems consisting of 22 monomers per chain (Figure 31)

and approximately 16 Å in the systems consisting of 100 monomers per chain (Figure 32). These values are very close to the experimental data [227].



Figure 30: (a) Torsional angles distribution of PE chains for various distances from the center of the gold NP for the PE100/Au2 system and the corresponding PE bulk curve. (b) Torsional angles distributions of all model systems for PE chains belonging in the first adsorbed layer, i.e., being closer to the Au NP. The corresponding curves for bulk PE are also shown.



Figure 31: Radius of gyration of PE chains, scaled with its bulk value (R_g/R_g bulk) as a function of *r* distance from the center of the Au NP. Data for the PE22, PE22/Au2, PE22/Au5, PE22/Au5/g20 and PE22/Au5/g62 systems are shown.



Figure 32: Radius of gyration of PE chains, scaled with its bulk value ($R_g R_{g \text{ bulk}}$) as a function of distance, *r*, from the center of the gold NP. Data for the PE100, PE100/Au2, PE100/Au5, PE100/Au5/g20 and PE100/Au5/g62 systems are shown.

Moreover, we observed a small increment, about 5%, of the R_g close to the surface area, as we expected. Such perturbation of the R_g has been also observed in other polymer nanocomposite systems as for example PE with graphene [3].

4.4.4 Orientational Dynamics

In this section we present data concerning the dynamical properties of polymer chains in the model nanocomposites with bare, and functionalized core/shell Au NPs. We perform the analysis by calculating corresponding quantities of PE chains, both as averages for the entire nanocomposite and as a function of distance from the PE/Au interface.

4.4.4.1 Terminal Orientational Dynamics

First, we study the orientational dynamics at the terminal level, via the reorientation time autocorrelation function (ACF) of the end-to-end vector, defined as:

$$C_{\text{end-end}}(t) = \frac{\langle \mathbf{R}(t) \cdot \mathbf{R}(0) \rangle}{\langle \|\mathbf{R}\|^2 \rangle}$$
(54)

where $\mathbf{R}(t)$ and $\mathbf{R}(0)$ is the end-to-end vector at time t and 0 respectively, $|\mathbf{R}|$ is its magnitude, and $\langle \rangle$ denotes statistical average. Results for the autocorrelation function, $C_{\text{end-end}}(t)$ at different radial adsorption layers are presented in Figure 33 for the hybrid PE100/Au5 system and the comparison with PE22/Au5 system in Figure 34. In these figures corresponding data for a bulk PE system are also shown. It should be noted that we monitored the position of each vector only for the time period it belongs to the corresponding analysis regime in order to make these calculations. It is clear that in all systems slower PE chain dynamics at the vicinity of the Au nanoparticles is shown. In particular, PE chains in the first adsorption layers show much slower terminal dynamics compared to the bulk one. Then moving away from the Au NP surface up to a specific distance, we observed a more rapid decorrelation, whereas beyond this all curves coincide. We've also calculated the average value of the ACF for the entire system, which is almost identical with the bulk's one.



Figure 33: The reorientation time autocorrelation function (ACF) $C_{\text{end-end}}(t)$ as a function of time for the end-to-end vector of polyethylene for PE100/Au5 system. PE chains are analyzed across various shells from the Au NP.



Figure 34: Time ACF of the end-to-end vector of PE chains, $C_{\text{end-end}}(t)$, as a function of time for PE22/Au5 and PE100/Au5 systems. $C_{\text{end-end}}(t)$ values for the PE22/Au5 and PE100/Au5 systems, for various spherical shells are presented.

The effect of the PE/gold nanoparticle interface on the PE terminal dynamics of each system can be further quantified by computing the corresponding chain relaxation times, through proper fits of curves shown in Figure 33, with a Kohlrausch–Williams–Watts (KWW) stretch exponential function [228] of the form:

$$C_{end-end}(t) = \exp\left[-\left(\frac{t}{\tau_{KWW}}\right)^{\beta}\right]$$
(55)

where, τ_{KWW} is the KWW relaxation time and β the stretch exponent, which describes the broadness of the distribution of the relaxation times (*i.e.*, the deviation from the ideal Debye behavior $\beta = 1$). Then, the relaxation time, $\tau_{end-end}$, is calculated as the integral of the KWW curves through:

$$\tau_{\text{end-end}} = \frac{\tau_{\text{KWW}}}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$
(56)

where $\Gamma()$ is the gamma function.

The results of the above analysis for both the relaxation time $\tau_{end-end}$ and the β exponent for PE chains of all the simulated systems are presented in Figure 35 and Figure 36. Bulk values are also shown in these figures. It is clear that the PE chains which are very close to the Au NP, have much slower orientational dynamics (longer terminal relaxation time $\tau_{end-end}$ and $\tau_{end-end}$ is about 2–10 times longer than the bulk one. As expected polymer chains become more mobile as their distance from the gold nanoparticle increases, reaching a plateau, bulk-like regime, at distances of about 2.5-3.0 nm away from the Au NP. From the relaxation times reported in Figure 35 it is clear that the adsorbed polymer chains are (several times) slower than the ones in the bulk-like regime, however they are still mobile, as it is also shown below by probing the translational dynamics of polymer chains. In addition, β -exponent values of PE chains are smaller than the bulk value (~ 0.89), the black line shown in Figure 36, at the majority of all distances. The latter indicates a broader distribution of the polymer terminal dynamics, compared to the bulk one. Furthermore as was expected, the 100 mers PE systems have much slower relaxation times in comparison to those of the 22 mers PE systems (Figure 37 - Figure 42).



Figure 35: Relaxation time of the end-to-end vector of PE chains, scaled with the value of bulk chains, $\tau_{\text{end-end}}/\tau_{\text{end-end bulk}}$, as a function of distance from the center of the Au NP, *r*, minus the half diameter of the NP, for all systems with PE matrices consisting of 100 mers per chain.



Figure 36: The stretch exponent β , as extracted from the fit with KWW functions, of the endto-end vector ACF, $C_{\text{end-end}}(t)$, as a function of distance from the center of the Au NP, *r*, minus the half diameter of the NP for all systems with PE matrices consisting of 100 mers per chain. Black lines represent β values of bulk PE chains.

Below in Figure 37 - Figure 42 data about the segmental dynamics of the PE chains are shown. We follow a methodology similar to the one for the end-to-end vector. First, we compute the angle θ of a segmental 1–3 vector, v^{1-3} , at time *t* relative to its position at t = 0. Second, we calculate the second order Legendre polynomial (correlation function) for this vector, defined as:

$$C_{1-3}(t) = \frac{3}{2} \left(\left\langle \cos \theta(t) \cos \theta(0) \right\rangle - \frac{1}{2} \right)$$
(57)

Then, we fit $C_{1-3}(t)$ using a KWW function and derive the characteristic segmental relaxation time, τ_{seg} and the corresponding β -exponent, by computing the integral below the KWW curve, similar to the analysis followed for the end-to-end vector ACFs.



Figure 37: Segmental relaxation times of PE chains, scaled with the value of bulk chains, $\tau_{seg}/\tau_{seg bulk}$, as a function of distance from the center of the Au NP, *r*, minus the half diameter of the NP, for all systems with PE matrices consisting of 100 mers per chain.



Figure 38: The stretch exponent β , as extracted from the fit of $C_{1-3}(t)$ ACF with a KWW, as a function of distance from the center of the Au NP, *r*, minus the half diameter of the NP, for all systems with PE matrices consisting of 100 mers per chain. Black lines represent β values of bulk PE.



Figure 39: Segmental relaxation times of PE chains, scaled with the value of bulk chains, $\tau_{seg}/\tau_{seg bulk}$, as a function of distance from the center of the Au NP, *r*, minus the half diameter of the NP, for all systems with PE matrices consisting of 22 mers per chain.



Figure 40: The stretch exponent β , as extracted from the fit of $C_{1-3}(t)$ ACF with a KWW, as a function of distance from the center of the Au NP, *r*, minus the half diameter of the NP, for all systems with PE matrices consisting of 22 mers per chain. Black lines represent β values of bulk PE.



Figure 41: Terminal relaxation times of PE chains derived for the end-to-end vector ACF, $C_{\text{end-end}}(t)$, scaled with the value of bulk chains, $\tau_{\text{end-end}}/\tau_{\text{end-end}}$ as a function of distance from the center of the Au NP, *r*, minus the half diameter of the NP for all systems with PE matrices consisting of 22 mers per chain.



Figure 42: The stretch exponent β , as extracted from the fit with KWW functions, of $v^{\text{end-end}}$ characteristic vector based on $C_{\text{end-end}}(t)$ time autocorrelation as a function of r (distance from the center of the Au NP) minus the half diameter of the NP, for all systems with PE matrices consisting of 22 mers per chain. Black lines represent β values of bulk PE.

4.4.5 Translational Dynamics

4.4.5.1 Segmental Translational Dynamics

Next, the translational segmental dynamics of PE chains was examined. We have calculated the average segmental mean square displacement (MSD) in order to distinguish translational dynamics for different layers. The average segmental MSD is defined as:

$$\Delta R_{i}(\tau) = \langle [r(t+\tau) - r(t)]^{2} \rangle$$
(58)

where *j* is a specific radial region, r(t) and $r(t + \tau)$ are the coordinate vectors of a segment (CH₂ or CH₃ group here) within region *j*, at time *t* and $t + \tau$, respectively, and brackets $\langle \rangle$ denote statistical average for all segments within the region *j*. Note, that in the analysis used here a segment contributes to the above MSD for a given time interval τ and for a radial region *j*, if and only if it was constantly present in that region in the entire course of time τ . Data on $\Delta R_j(\tau)$ for all (radial) adsorption layers, scaled with $t^{0.5}$, for the PE100/Au5/g62 system is shown in Figure 43. We observed

slower terminal dynamics of the polymer atoms closer to the Au NP atoms (mainly in the first adsorption layer) in comparison to the one of the atoms in the other layers. In contrast, chains which belong to the other regimes, (above the second layer) show quite similar dynamics, almost equal to the bulk one, the black line and the total average value of the entire system, the magenta line shown in Figure 43. All the simulated hybrid systems have a similar behavior. However, the PEs in PE22/Au2, PE22/Au5, PE22/Au5/g20 and PE22/Au5/g62 (see Figure 44) are faster than the equivalent systems with PE matrices consisting of 100 mers per chain.



Figure 43: Segmental MSD of PE chains along *r* (distance from the center of the gold NP), ΔRj , scaled with $t^{0.5}$ Data for the PE100/Au5/g62 system, for various spherical shells, and the total MSD of the PE100 and PE100/Au5/g62 systems are shown.

According to the Rouse model predictions [6] $\Delta R_j(\tau) \propto \tau^{1/2}$. Our calculations using the data for bulk PE (PE100 system) showed that the Rouse regime was well-attained for the linear bulk chains, as it has been shown also in previous works [229-231]. Concerning the different adsorption spherical shells we extracted exponents less than 1/2. Those exponents indicate the variation from the Rouse behavior which is more pronounced close to the Au NP. This attributed to the fact that there is attraction of the PE monomers from the Au NP and from the grafted polymers.



Figure 44: Segmental MSD of PE chains for the first adsorption spherical shell, ΔR_1 , scaled with $t^{0.5}$. Data for the PE22/Au2, PE22/Au5, PE22/Au5/g20 and PE22/Au5/g62 systems are shown, together with data for the bulk PE22 system.



Figure 45: Segmental MSD of PE chains for the first adsorption spherical shell, ΔR_1 , scaled with $t^{0.5}$. Data for the PE100/Au2, PE100/Au5, PE100/Au5/g20 and PE100/Au5/g62 systems are shown, together with data about the MSD of the entire PE100 and PE100/Au5 systems.

Furthermore, according to our analysis method, we calculated the MSD for the hybrid systems as long as the segments were within the spherical shells. Therefore the time frame window is not enough to reach the Rouse regime for the PE monomers that are close to the surface of the Au NP.

The MSD at the 1st adsorption spherical shell, $\Delta R_1(\tau)$, scaled with $t^{0.5}$, is presented in Figure 45 for all simulated systems with PE matrices consisting of 100 mers per chain. We observe that the MSD, $\Delta R_j(\tau)$ in all systems for the 1st adsorption shell is smaller than the corresponding bulk one. Nevertheless, in qualitative agreement with the orientational segmental dynamics discussed above, chains in the first adsorption layer are still mobile.

5. Polymer/Amorphous Nanocomposite Systems

5.1 Introduction

A special case of nanohybrids is the one composed of amorphous silica nanoparticles (NPs), SiO₂, dispersed in a polymer matrix. Silica nanoparticles are of great interest due to their excellent properties and the range of their applications in many scientific fields. Their high chemical stability, [232] attributed to the Si-O bond, is important for applications as drug delivery systems.[233-236] Moreover their excellent biocompatibility, [237] heat resistance, [238, 239] low toxicity, [240, 241], simple synthetic approach, [242, 243] and massive synthetic supply [244, 245] render them attractive for biological applications, [232, 246-249] like cell tracing, [250, 251] biosensing [252] and as diagnostic tools, [253] Extensive applications of silica nanoparticles are also found in rubber technology, where they are used to improve the properties of tires and other rubber materials. [56, 254, 255]

Poly(ethylene oxide), PEO, is a widely used polymer in many technological applications. [256] It is hydrophilic, biocompatible and it possesses high ion transport properties; therefore, it is suitable for many fields of research including biomaterials, drug-delivery and solid state polymer electrolytes. [257-261] PEO is the most frequently studied polymer ionic conductor; however, its high crystallinity prevents its further utilization. Different additives can be used to suppress its crystallization and, thus, its nanohybrids can be utilized as promising materials for applications in solid-state lithium batteries.[262] Specific attractive interactions exist between PEO and silica nanoparticles, mainly attributed to the formation of hydrogen bonds, which force polymer chains to adsorb onto the surface of the nanoparticle[263, 264], resulting in the stabilization of the systems.[55, 59, 67, 68, 86, 265] Numerous pharmaceutical and industrial applications have been reported for such nanocomposite systems.[266-269]

The properties of PEO/SiO₂ nanocomposites have been investigated utilizing various simulation models [73, 86, 87, 270] and experimental techniques [88, 92, 96, 271-273]. In a previous work, we have investigated the structural and conformational properties of PEO chains of various molecular weights in PEO/SiO₂ nanocomposites

as a function of temperature and degree of confinement [55]. A combined experimental and theoretical approach revealed that spatial confinement affects significantly the conformational behavior of polymer chains causing an important increase of the *gauche* conformations in comparison to the neat PEO at the same temperatures. Moreover, the type of end group of the PEO (CH₃ or OH) did not affect the average conformational properties of the simulated polymer chains. The presence of the SiO₂ affects significantly the degree of crystallinity of PEO as well [59]. The degree of confinement that the chains suffer and the curvature of the nanoparticles, which affects the chain adsorption, has been shown to be the two determining factors that can act synergistically and lead to a significant decrease of the crystallinity for nanohybrids with high inorganic content.

Contrary to the conformational properties, which do not seem to depend on the PEO end groups, the dynamics was found to be affected by the type of end-groups with the chains with OH end-groups exhibiting slower translation dynamics within an interphase region of ~2-3 nm close to the nanoparticle surface [87]. Recently, Skountzos, et al. [86] studied nanocomposites of PEO with silica nanoparticles and investigated the effect of the different chain end-group (CH₃ and OH) on the train, loop, and tail conformations of the chains adsorbed on the silica nanoparticle. It was shown that PEO-CH₃ chains adsorb along their entire backbone whereas PEO-OH chains prefer to adsorb mostly by their end-groups (OH). Moreover, PEO-CH₃ chains have faster chain (Rouse) relaxation times near the nanoparticle surface in comparison with the PEO-OH ones, whereas no difference in the dynamics is observed for the free chains away from the nanoparticle. The diffusivity and the arrangement of silica nanoparticles have been also investigated in hybrid systems of silica nanoparticles with either grafted PEO chains or in a matrix of PEO oligomers [270]. Analysis of the dynamics revealed that, at short time scales, grafted chains relax faster than the free chains at low temperatures; however, this behavior is reversed with increasing temperature.

From the experimental point of view, Kim et al. [273] studied the effects of polymer molecular weight, temperature and solvent dilution on polymer dynamics in PEO-silica nanocomposites. They found that the adsorption of PEO segments onto the silica surface produces a polymer layer of reduced-mobility over a temperature range 343 - 373 K, which is not observed at higher temperatures. Strongly anisotropic

segmental mobility was found within this layer compared to a rotation of the backbone. Glomann, et al. [88, 272] performed neutron spin echo (NSE) and high resolution time-of-flight (TOF) spectroscopy experiments on PEO/silica nanocomposites with PEO chains with different end groups (OH or CH₃); in the system with OH end-groups, suppressed translation diffusion was observed, whereas the segmental dynamics was found unaffected, while, in the one with CH₃ end-groups, an adsorbed but not glassy layer was reported possessing fast local dynamics.

Senses, et al. [92, 96] studied the nanoparticle dispersion, the polymer conformation as well as the macroscopic and microscopic chain dynamics by applying NSE and neutron backscattering spectroscopy. They found that the Rouse dynamics of the chains slows down with nanoparticle addition and no glassy effect appeared on the adsorbed layer.

From the above short discussion, it is clear that the dynamics of PEO under confinement and/or in the vicinity of inorganic nanoparticles has provided many contradictory results in different studies. Moreover, when PEO formed an intercalated structure between laponite sheets, a significant number of PEO monomer units were found to display a strong slowing down as compared to neat amorphous PEO. This decrease in the segmental mobility was mainly assigned to the complexation of PEO oxygens by the Na⁺ counterions located in the laponite interlayer galleries [274]. On the other hand, when PEO was confined between the layers of Na⁺-Montmorillonite, the segmental dynamics was found many orders of magnitude faster than the bulk exhibiting an Arrhenius temperature dependence. In that case, the different behavior was attributed to the severe confinement of the chains [68]. Moreover, no significant effect on the dynamics was detected when PEO was placed within 18 nm diameter Anodic Aluminum Oxide (AAO) pores [275]. When PEO is confined between graphene oxide (GO) layers, the intercalation of polymer chains does not only lead to the suppression of polymer crystallization but also to the suppression of the dielectric α -relaxation together with a slowing down of the β -relaxation modes [64]. It is, thus, evident that deep understanding of the dynamics of even such an investigated polymer like PEO in its nanocomposites is still missing.

In the current work a computational study of the dynamics in PEO/SiO_2 nanocomposites was made. A systematic exploration of the dynamical properties of

PEO in the segmental level through atomistic molecular dynamics (MD) simulations. All-atom MD simulations focuses on a detailed analysis in the atomic level, which can capture changes very close to the surface of the nanoparticle, the so-called "bound or dead layer". The effect of the interfacial area is highlighted through a detailed analysis of various measures as a function of the distance from the nanoparticle surface. Different concentrations and molecular weights were investigated by the simulation findings. The degree of confinement together with the adsorption capacity are found to be the critical parameters for the arrangement of polymer chains at the vicinity of the polymer/silica interface, and, consequently, their mobility.

5.2 Model Systems and Simulations

Detailed atomistic molecular dynamics simulations of poly(ethylene oxide) / silica, PEO/SiO₂, nanocomposites were performed for nanohybrids of different concentrations of silica nanoparticles and at different temperatures. As reference, simulations of a bulk PEO with molecular weight MW=2,200 g/mol and methyl terminal groups at the same temperatures have been performed. Following the notation of the material utilized experimentally, from here on, the simulated polymer is denoted as PEO₄₉ utilizing as subscript the number of its monomeric units. As nanoadditives, silica nanoparticles with almost spherical shape and radius of ~2.1 nm were utilized. All calculations were performed for three different concentrations of silica nanoparticles (i.e., 2% vol, 19% vol and 39% vol) and four different temperatures ranging from 330 up to 400 K. Details for all simulated systems are presented in Table 11 as well.

Table 11: Details of the synthesized PEO_{2270} / NP_7 and simulated PEO_{49} / NP_2 nanocomposites

Hybrids	w _{SiO2} ^a (wt)	ϕ_{SiO2} ^b (vol)	<i>d</i> ^c (nm)	d/\mathbf{R}_{g}^{d}
PEO ₄₉ /NP ₂	0.05	0.02	11.58	6.81
PEO ₄₉ /NP ₂	0.33	0.19	5.82	3.42
PEO ₄₉ /NP ₂	0.57	0.39	4.59	2.70

 a w_{SiO2}: weight fraction of the SiO_2 nanoparticles

^b ϕ_{SiO2} : volume fraction of the SiO₂ nanoparticles

^c *d*: the nearest inter-particle distance

 $^{^{}d}$ *d*/R_g: the degree of chain confinement (R_g is the radius of gyration of the bulk polymer chains)

Typical snapshots of the model PEO₄₉/ NP₂ systems are shown in Figure 46.



Figure 46: Snapshots of the model PEO/SiO₂ nanocomposite systems: (a) The PEO₄₉/NP₂ hybrid system with a concentration of $\phi_{NP} = 2\%$ at 400 K. (b) The PEO₄₉/NP₂ hybrid system with the periodic images that shows the simple cubic like structure of nanoparticles. The concentration is $\phi_{NP} = 39\%$ and the temperature is 400 K. In both, the PEO₄₉ chains are shown green and the SiO₂ NP₂ red.

For the simulations, PEO_{49} was represented by a united atom model and interactions were described by a modified united atom (UA) TraPPE based force field [270, 276]. A full atom representation was used for the SiO₂ nanoparticle [277]. The particlemesh Ewald (PME) method [278] was applied for the calculation of the electrostatic interactions. MD simulations were performed in the NPT statistical ensemble, where the pressure was kept constant with the use of Parrinello–Rahman barostat [279] and the temperature using the Nosé–Hoover thermostat [112]. The simulations were performed using the GROMACS simulation package [145]. The entire atomistic force field is given in Table 12 and Table 13.

 Table 12: Model parameters and functional forms of all non-bonded interactions of the atomistic force field.

$V_{LJ}(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right], r \le R_c$ Lennard-Jones					
Atom Types	mass (g/mol)	σ (nm)	ε (kJoule/mol)	charge	
CH_2	14.027	0.395	0.3824	0.250	
CH_3	15.035	0.375	0.3824	0.250	
O (PEO)	15.9994	0.280	0.457296	-0.500	
Si	28.086	0.392	2.5104	1.020	

Non-Bonded Interactions

O (Silica)	15.9994	0.3154	0.636	-0.51
Н	1.008	0.2352	0.092	0.255
CH ₃ - CH ₂		0.385	0.558247	
O - CH ₂		0.3375	0.418210	
O - CH ₃		0.3275	0.610424	

Table 13: Model parameters and functional forms of all bonded interactions of the atomistic force field.

Bonded Interactions

$V_big(r_{ij}ig)=rac{1}{2}k^b_{ij}ig(r_{ij}-b_{ij}ig)^2$						
Bond			 b (nm)		k ^b (kJ/mol·nm ²)	
CH ₂ - CH ₂			0.154		217700	
CH ₂ -	0		0.141		26	7900
CH ₃ -		0.141 2679		7900		
Si - O			0.163		323984	
H - C)		0.095		533549	
$V_lpha \Big(heta_{ijk} \Big) = rac{1}{2} k^ heta_{ijk} \Big(heta_{ijk} - heta_{0ijk}^0 \Big)^2$						
Ang		θ° (deg)			$k^{\theta} (kJ/mol*rad^2)$	
CH ₂ - CH		112		418.218		
CH ₂ - O -		112		502.194		
CH ₃ -O-CH ₂			112		502.194	
Si - O - Si			144		209.6	
O - Si - O			109.47		469.72	
Si - O - H			119.52		228.84	
$V_{rb}\left(\varphi_{ijkl}\right) = \sum_{n=0}^{5} C_n \left(\cos(\psi)\right)^n$						
Dihedral	<i>C</i> ₀	C_1	<i>C</i> ₂	<i>C</i> ₃	<i>C</i> ₄	C_5
	(KJ/mol)	(KJ/mol)	(KJ/mol)	(KJ/mol)	(KJ/mol)	(KJ/mol)
O-CH ₂ -CH ₂ -O	2.22267	17.03651	8.29835	-31.2451	5.13025	-1.91522
CH ₂ -CH ₂ -O-CH ₂	1.60941	19.79231	-7.82474	-15.72474	6.43215	-4.5435
CH ₂ -CH ₂ -O-CH ₃	1.60941	19.79231	-7.82474	-15.72474	6.43215	-4.5435

In general, the simulation protocol involves: (a) generation and equilibration of the PEO/SiO_2 model nanocomposites and (b) performing long atomistic MD simulations. Initial PEO/SiO_2 configurations were obtained from our previous work [55]. After generating the systems, equilibration MD runs for times up to 500 ns, depending on the system and the actual temperature, were performed, followed by long production runs, for times up to 1.0 μ s. During the simulations, a full relaxation, i.e., a complete decorrelation of the end-to-end vector, of the polymer chains is observed. For the calculated properties, analysis is performed over the last 0.8 μ s of the trajectory. It should be also noted that the simulation model systems consider a scenario of welldispersed nanoparticles in a simple cubic arrangement induced by the periodic boundary conditions, whereas experimental systems refer to rather random packing in the dispersion of the SiO₂ nanoparticles within the PEO matrix.

5.3 Data Analysis

The main goal is to study the spatial and dynamical heterogeneities of model hybrid polymer/nanoparticle systems in a detailed way at the molecular level. Consequently, the properties of the polymer chains are examined as a function of the distance from the SiO_2 nanoparticle center, by creating spherical shells of increasing radii (i.e., increasing distances form the SiO_2 center).

The mass density profiles were calculated in two ways. The first (radial type) is by using spherical shells of thickness equal to 1 Å, defined from the center-of-mass of the nanoparticles. Then, the polymer mass density is calculated within each shell. The second way of analysis involves a 3D reconstruction of the PEO mass density using a decomposition of the simulation box in rectangular parallelepipeds (cuboids) with dimensions of $3.2 \times 3.2 \times 4.46$ Å. The choice of the cuboids dimension was a result of balance between the detail of the analysis and the statistical accuracy. The average mass of PEO atoms within each cuboid is calculated and divided with its volume.

The investigation of the dynamical properties of PEO chains involves the calculation of time correlation functions; for this reason, thicker, compared to the density, spherical shells are used. The choice of binning size (thickness of spherical shells) for the computation of each specific property is usually defined from the first minimum of density profile data, which defines the first adsorption layer [2, 3, 55]. In this work, for the calculation of the orientation autocorrelation function, three different analysis regimes were defined: (a) the whole simulation box, denoted as "Total", (b) the

adsorption region, i.e., 0-25 Å from the center of the nanoparticle (4-5 Å from the outer surface of the nanoparticle), denoted as "Ads", defined based on the first minimum in the density profile, shown below, and (c) the whole simulation box except the adsorption region, denoted as "Matrix". Note that for these calculations, the position of each segment/vector was monitored depending on the corresponding analysis regime, where it was initially located.

For the calculation of the desorption kinetics, the atoms that belong to the adsorption region at a given time t_0 were first labelled. Then, for each time step t, these atoms were monitored and a function $S(t + t_0)$ was defined that equals 1 when the atom is still within the adsorbed region and 0 when it is outside, i.e., when it is desorbed. Finally, the autocorrelation function of the adsorption state S was calculated as [280]: $C_{ads} = \langle S(t + t_0) \cdot S(t_0) \rangle$. It is noted, that a buffer of 3Å (about the size of an atom) around the adsorption region shell was used, in order to take into account the fluctuations of the atoms that are located on the borders of the adsorption region. Therefore, an initially adsorbed atom is considered "desorbed" if it moves further that 28 Å from the center of the nanoparticle. Last, during the analysis of all dynamical properties, and in order to improve statistics, the multiple time origin technique was used.

5.4 Results

5.4.1 Density Profile

The analysis of the model nanocomposite systems begins by probing directly the density heterogeneities at the PEO/silica interface. For this, the mass monomer density profile of the PEO₄₉ chains is calculated as a function of the distance from the center of mass of the SiO₂ nanoparticle, r, as described in the previous section. Average density profiles, based on the center of mass of the monomers, $\rho(r)$, are presented in Figure 47a for all systems with concentration 2%, 19% and 39% vol at 400 K. The bulk density of PEO₄₉ at 400 K is also included (dashed horizontal line). A rather similar peak at a radial distance ~2.3 nm (about 3-4 Å from the outer surface of the silica nanoparticles) is observed for all three systems denoting the attraction of the PEO₄₉ chains onto the NP₂. As the distance from the surface of the nanoparticle

increases, peaks of lower intensity follow up at 2.8 nm for 2% and 19% vol and at 3.2 nm for the 2% vol in NP₂ systems. It is noted that at longer distances, the bulk region is attained only for the 2% vol. In the systems with higher concentration in nanoparticles (more confined systems), the radial density profile of PEO₄₉ does not attain the bulk density. Moreover, in the case of the PEO₄₉ / NP₂ with 39% vol nanoparticle concentration, even the first peak of the density profile is roughly reached.



Figure 47: Mass monomer density profiles of PEO chains as a function of the distance from the SiO₂ nanoparticle center, *r*, for nanohybrids with: (a) $\varphi_{NP} = 2\%$, $\varphi_{NP} = 19\%$ and $\varphi_{NP} = 39\%$ in NP₂ at 400 K and (b) $\varphi_{NP} = 19\%$ NP₂ concentration at 330, 350, 370 and 400 K. The dashed lines correspond to the bulk PEO₄₉ values at each temperature.

The monomer density profiles are presented in Figure 47b for various temperatures for the system with 19% vol concentration. A gradual decrease of the density is observed with increasing temperature, whereas the density curves retain the same characteristics. Similar temperature dependence is observed for the other two concentrations as well.

The above analysis, using spherical shells, neglects parts of the (cubic) simulation domain, mainly the parts that are situated at its corners. Therefore, a more complete picture of the polymer density is provided through the calculation of the density profile in three dimensions, using a "3D polymer density tomography" as described in the Data Analysis section. Based on the analysis described there, the 3D density profile is calculated throughout the simulation box, scanning its volume and exploring various cross sections from the bottom to the top, as presented schematically in Figure 48f. Slices of increasing distance from the center of the SiO₂ nanoparticle, parallel to the *xy* plane, are presented in Figure 48a-4e accordingly. Slices have thickness of 3.2Å and correspond to distances of 1.5 Å (slice A), 8.4 Å (slice B), 15.3 Å (slice C), 22.2 Å (slice D) and 29.1 Å (slice E) from the central plane.

In Figure 48, the density of PEO₄₉ is shown with different colors. Blue is the region of the nanoparticle (zero density of PEO), whereas yellow corresponds to regions with density very similar to the (average) bulk value whereas red denotes regions with density higher than that of the bulk polymer. It is clear from all the data referring to regions (slices) around the nanoparticle that shell-like areas ("rings") of different PEO density are observed. For the closest spherical shell to the nanoparticle (cyan region) the roughness of its surface, allows some polymer amount to be attached on it, but PEO density is smaller than the bulk PEO value. The next (red) ring corresponds to the first adsorption shell (i.e., the first peak of the radial density profile shown in Figure 47), whereas consequent rings indicate a gradual decrease of PEO density towards its bulk value, with moving away from the NP. However, it is interesting to observe that for all slices the polymer density attains values similar to the bulk one on the face diagonal of the simulation box. Therefore, it is clear that even for the most confined system investigated computationally, a considerable amount of polymeric material exists at the corners of the simulation domain, where the effect of the nanoparticle on its properties is attenuated. This is not obvious in the radial density

profiles, since the analysis in radial distances from the center of the NP (spherical shells) does not allow to cover these (corner) regions.



Figure 48: 3D representation of the PEO₄₉ density profiles in the PEO/SiO₂ system with φ_{NP} = 19% at 400 K. Different slices, of 3.2 Å thickness, parallel to the *xy* plane are used at various distances form the center-of-mass of the NP₂: 1.5 Å (slice A), 8.4 Å (slice B), 15.3 Å (slice C), 22.2 Å (slice D) and 29.1 Å (slice E). At the bottom right, a sketch of the polymer nanocmposite system illustrates the five slices. The distances scaled with the radius of the silica NP₂ are: 0.07 (slice A), 0.40 (slice B), 0.73 (slice C), 1.06 (slice D) and 1.38 (slice E).

5.4.2 Orientational Dynamics

Autocorrelation functions of $P_2(t)$ are presented in Figure 49 and Figure 50 for all hybrid PEO/SiO₂ nanocomposites studied in the current work together with the corresponding data for the respective bulk PEO system. Figure 49 presents $P_2(t)$ as a function of time for all three volume fractions of 2%, 19% and 39% vol at 400 K. Calculations have been performed in two shells with respect to the surface of the nanoparticle 0-25 Å (i.e., the adsorption region "Ads") and 25-end Å (i.e., the rest area "Matrix") as well as on the entire box, probing the average value ("Total"). In all cases, slower decorrelation is observed in the first adsorption shell, whereas the average curve lies between the "Ads" and "Matrix" area. The effect of confinement (i.e., of different concentrations) becomes clear comparing the three figures: starting from the nanocomposite with the smaller concentration of 2% vol in nanoparticles (less confined polymer chains), the three curves corresponding to the bulk PEO, the "Matrix" and the "Total" almost coincide, indicating the predominance of the bulk behavior in this concentration. As the amount of the nanoparticles increases, the ratio of the chains in the "Matrix" vs the "Ads" chains decreases.



Figure 49: Time autocorrelation function of the vector connecting two non-consecutive atoms along a monomer, $P_2(t)$, as a function of time for the characteristic vector v_{1-3} of poly(ethylene oxide) for all systems at 400 K. (a) $\phi_{NP} = 2\%$; (b) $\phi_{NP} = 19\%$; (c) $\phi_{NP} = 39\%$. In all cases, the corresponding curve for the bulk polymer is shown as well.

In a moderate confinement (19% vol), the "Matrix" still prevails (like for the low concentration) defining the total dynamics in this case as well, however with slower relaxation times; differences between the curves of the hybrid system and the corresponding bulk curve can be observed. On the contrary, for the most confined

system (39% vol), there is an obvious difference in the autocorrelation curves between the "Ads" and the "Matrix" as well as between all curves of the hybrid system and the corresponding bulk curve with the latter being much faster.

Differences among the systems of different concentrations become clearer in Figure 50a and Figure 50b, where a direct comparison of the relaxation of the autocorrelation function in each shell distinctly is provided at 400 K. It is clear, that for the first adsorbed layer, there is a significant deviation from the bulk dynamics, which becomes more and more significant with increasing the nanoparticle content, with the bulk dynamics being the fastest. The dynamics of the "Matrix" slows down with respect to the bulk with increasing the nanoparticle content as well, however less strongly than the respective one in the adsorbed layer.



Figure 50: Autocorrelation function of bond order parameter $P_2(t)$ as a function of time for the characteristic vector v_{1-3} of poly(ethylene oxide) for (a) all concentrations in the "Ads" shell at T=400 K; (b) all concentrations in the "Matrix" at T=400 K; (c) all simulated temperatures in the "Ads" shell of the $\phi_{NP} = 19\%$ nanocomposite; (d) $P_2(t)$ all simulated temperatures in the "Matrix" of the $\phi_{NP} = 19\%$ nanocomposite. In (a) and (b) the corresponding curves for the bulk polymer is shown as well.

In Figure 50c and Figure 50d the temperature dependence of the autocorrelation relaxation function P₂(t) is depicted. The curves are presented at four different temperatures for the segments in the "Ads" and "Matrix" areas. As expected, the decorrelation is faster at higher temperatures with a gradual retardation from 400 K to 330 K; however, it is clear that all dynamics is slower in the "Ads" than in the "Matrix" area for all temperatures. The above observations can be quantified by analyzing the autocorrelation functions and the determination of the corresponding segmental relaxation times. The autocorrelation functions were analyzed using a pair of Kohlrausch-Williams-Watts (KWW) stretch exponential functions to effectively fit the curves and the segmental times were derived by integrating the fit curve as the most probable relaxation time. This procedure was followed since utilization of a single KWW failed to fit the data successfully. Segmental relaxation times of PEO chains for all systems are presented as a function of inverse temperature in Figure 51. The values for the polymer in the bulk are also included for comparison.

As expected, the segment relaxation time τ_{seg} increases as temperature decreases, for all model PEO₄₉/NP₂ systems. Starting from the nanocomposite with the smallest volume fraction of nanoparticles (2% vol, Figure 51a), it is clear that the dynamics of polymer segments at the vicinity of the PEO/SiO₂ interface ("Ads" region) is slower than the ones in the "Matrix" region; for all temperatures τ_{seg} of "Ads" segments is about 10 times larger than the "Matrix" ones. On the contrary, the dynamics of the segments in the "Matrix" region is very similar to the bulk one (black squares). The average dynamics in the nanocomposite ("Total" data) is also very similar to the bulk, since the percentage of "Ads" segments over their total number is calculated to be only about 2%; therefore, it is very small to affect the overall dynamic behavior.

As the concentration of the nanoparticles increases, the effect of the confinement on the segmental dynamics of PEO becomes more important. The data for the system with 19% volume fraction of nanoparticles, shown in Figure 51b, indicate that the "Ads" segments exhibit relaxation times about ~10 times larger than the "Matrix", which are ~10 times slower than the corresponding values in the bulk as well. The percentage of "Ads" segments is about 18%, so the average dynamics ("Total" data) are again very close to the ones for the "Matrix" region.



Figure 51: Segmental relaxation time, τ_{seg} , of v_{1-3} characteristic vector determined by analyzing the P₂(t) time autocorrelation functions for all simulated systems: (a) $\phi_{NP} = 2\%$; (b) $\phi_{NP} = 19\%$; (c) $\phi_{NP} = 39\%$. τ_{seg} for "Ads" and "Matrix" chains are shown, as well as the average values for the entire systems ("Total") and the values for PEO₄₉ in the bulk.

Even stronger is the effect of confinement on the segmental dynamics of the PEO chains for the model PEO_{49}/NP_2 systems with the highest concentration of nanoparticles studied computationally (39% vol, Figure 51c). Similarly to the systems with concentration 19% vol, the "Ads" segments exhibit relaxation times about ~10 times larger than the "Matrix"; however, now the latter are about 100 times larger than the ones in the bulk. In addition, the values for the average dynamics ("Total") is in between the values for the "Ads" and "Matrix" regions; this is not surprising if one

considers the large fraction of "Ads" segments for these systems (about 44%) compared to the ones with lower nanoparticle concentrations. Finally, for the strongly confined PEO chains, the corresponding differences in τ_{seg} are more pronounced for systems at low temperatures; for example, at T=330 K the ratio between the "Ads" and the "Matrix" segments is ~25 times whereas the ratio between the "Matrix" and the bulk is ~60 times.

5.4.3 Desorption kinetics

In order to better understand and interpret the findings on the computationally derived PEO segmental dynamics in the PEO₄₉ / NP₂ nanocomposites, the desorption times of the polymer segments from the surface of the nanoparticle were calculated. Figure 53 shows the autocorrelation functions C_{ads} of the adsorption state S (see Model Systems and Simulations section) of the polymer atoms for all examined temperatures and concentrations. Polymer atoms desorb from the vicinity of the PEO/SiO₂ interface (adsorption shell) faster at higher temperatures, as expected, for all concentrations.



Figure 52: Desorption times of the polymer chains, τ_{des} , being in the first adsorption shell 0-25 Å from the center of the nanoparticle for all simulated nanohybrids. The error bars are about 5-15% of the actual values.

The desorption times of all systems are presented in Figure 52, calculated as the integral of the curves presented in Figure 53. As a result of the strong confinement, there is an obvious retardation of PEO atoms to desorb from the surface of the
nanoparticle at all temperatures in the system with 39% vol NP₂. It is noted that differences in the desorption times are larger between the nanohybrids with 39% vol and 19% vol nanoparticles when compared to those between the 19% vol and 2% vol NP₂. Analogous trends were observed to the corresponding decorrelations of the P₂(t) for the v_{1-3} characteristic vector (Figure 49-Figure 51).



Figure 53: The autocorrelation functions C_{ads} of the adsorption state S of the PEO atoms for all temperatures and for the systems with concentration of: (a) $\phi_{NP} = 2\%$; (b) $\phi_{NP} = 19\%$; (c) $\phi_{NP} = 39\%$.

6. Conclusions - Future Work

Overall, nanofillers and nanoparticles affect the properties of the polymeric material and in some cases of the entire system. The role of the interface is highlighted and an interphase region is defined for the various properties under investigation. The polymer architecture, the molecular weight, the energetic interactions, the concentration of the nanofiller in the polymeric matrix, which define the degree of confinement of polymer chains, the temperature, the size and the shape of the nanoparticles, have a critical role in the degree of the effect on the properties of the nanocomposite.

The behavior of graphene based PNCs is strongly affected by the spatial heterogeneities induced by the presence of polymer/graphene interfaces. In the present work we have presented results from a detailed atomistic simulation study of various graphene based polymer (polyethylene) nanocomposites. The simulation method was carried out by following a hierarchical modeling strategy consisting of: (a) generation of initial structure; (b) equilibration of the hybrid system for long time; (c) execution of long MD simulations (production runs) for times up to 100 ns; and (d) a detailed analysis of the atomistic configurations gathered in part (c). Here such a detailed analysis was proposed based on averaging over atoms (or chains) within radial layers equidistant from the center of the graphene sheet. PNCs with graphene sheets of different sizes but with the same concentration of graphene (~3 wt%) were modeled in order to study the *effect of the graphene size* on the properties of the hybrid material.

The above-discussed detailed analysis allows us to examine the way *spatial heterogeneities* are related to structural and dynamical features of the hybrid PNC system as a function of distance from the polymer/graphene interface. The main findings of the present work can be summarized as following:

• Local *structural* and *conformational* features were analyzed at the level of both individual segments (atoms or bonds) and entire chains. The local monomer PE mass density near the graphene plane exhibits a maximum due to the intermolecular PE/graphene (adhesive) interaction, which is similar for all systems. Chain segments show a tendency for an almost parallel to the

graphene layer orientation at short distances which is gradually randomized as one moves away from the interface, over a distance roughly equal to (\sim 3–5 nm). However, there is a systematic increase of the order of the PE segments closest to the graphene layer with the increase of the size of the layers. In addition, increase of "trans" population in the dihedral angle distribution at the PE/graphene interface compared to the bulk one has been observed, which reflects the more ordered polymer chain structures.

- Orientational relaxation of PE chains in the hybrid PNC systems at the segmental level was quantified through the time autocorrelation function of the second Legendre polynomial. Qualitatively similar behavior was found for all systems: PE chains closest to the graphene sheet show much slower segmental dynamics (segmental relaxation time τ_{seg} is about 10 times larger) compared to the bulk one. Faster $P_2(t)$ decorrelation is observed moving away from the interface up to specific distance (about а 4–5 nm), while beyond this, all curves coincide. A slight dependence of chains mobility on the size of the graphene layers was also found; the larger the sheet, the slower the segmental dynamics of the PE chains. In addition, broader distribution of the polymer segmental dynamics, compared to the bulk one was found (smaller β -exponent values), even for distances far away from the graphene sheets where the average τ_{seg} is similar to its bulk value.
- Translational segmental dynamics of PE chains was examined through the calculation of the average segmental mean-square displacement. PE chains closest to the graphene layers are slower, compared to the bulk one, for all model PNC systems. In addition, there is a slight dependence of the PE segmental msd on the size of the graphene sheet mainly in the short time (~5–20 ps) regime, *i.e.*, the smaller the sheet the larger the PE atoms msds. Equilibrium desorption kinetics of polymer atoms and chains' center of masses that are initial close to the graphene sheet, was also found to follow a rather broad distribution of characteristic times, which is an additional indication of the strong dynamic heterogeneities induced in the PNCs due to the polymer/graphene interfaces.
- Moreover, a detailed investigation of the *properties of graphene* sheets in the PNC has been performed. All graphene sheets exhibit a considerable

translational motion for the time period of the current simulations (50–100 ns); center-of-mass msds are much larger than their size. As expected the smaller the graphene sheet the higher its mobility. However, a rather long anomalous diffusion regime has been observed for all systems; *i.e.*, a clear linear regime cannot be found in the time window of the present simulations. Orientational dynamics was also observed for all graphene sheets by following the time evolution of a vector connecting the center of the graphene sheet with a corner atom. For the smallest sheet (S1) orientational relaxation time is about one order of magnitude smaller than the other two systems, whereas the largest sheet (S3) has almost double the relaxation time compared to the S2 system. Finally, fluctuations (wrinkling) of graphene sheets were analyzed. A "wavy" motion is observed with crests and troughs for all systems studied here. In addition, increasing amplitude of fluctuations is observed as the size of the graphene sheets become bigger.

Furthermore, we studied, through detailed atomistic MD simulations, the effect of the Au NP and the Core/Shell Au NP on the structural and dynamical properties of polyethylene systems.

The behavior of polyethylene is affected by the spatial heterogeneities induced by the presence of PE/Au NP interfaces. Overall properties of the hybrid systems are almost like the bulk ones, due to the rather low concentration of gold NP. A detailed analysis was proposed based on averaging over atoms (or chains) within radial spherical shells equidistant from the center of the gold NP which allows us to examine the way that spatial heterogeneities are related to structural and dynamical features of the hybrid system as a function of distance from the polymer/gold nanoparticle interface.

From our analysis we found that Au NP attracts polymers at distances close to it. Moreover, for the case of the Core/Shell NPs the brushes change gold NP's behavior/properties and especially the density profile. Furthermore, all systems attain bulk value in all properties away from the Au NP's surface. Results can be summarized as follows:

• Local *structural* and *conformational* features were analyzed at the level of both individual segments (atoms or bonds) and entire chains. The local monomer PE mass density near the gold surface exhibits a maximum due to

the intermolecular PE/Au NP (adhesive) interaction. Chain segments show a tendency for an almost parallel to the Au NP orientation at short distances which is gradually randomized as one moves away from the interface. In addition, increase of "trans" population in the dihedral angle distribution at the PE/gold NP interface compared to the bulk one has been observed, which reflects the more ordered polymer chain structures.

- Orientational relaxation of PE chains in the hybrid systems at the segmental and terminal level was quantified through the time autocorrelation function of the second Legendre polynomial. Qualitatively similar behavior was found for all systems: PE chains closest to the Au NP show much slower orientational dynamics (segmental relaxation time τ_{seg} is about 10 times larger) compared to the bulk one. Faster $P_2(t)$ decorrelation is observed moving away from the interface up to a specific distance, while beyond this, all curves coincide. In addition, broader distribution of the polymer orientational dynamics, compared to the bulk one was found (smaller β -exponent values).
- *Translational* segmental and center of masses dynamics of PE chains were examined through the calculation of the average mean-square displacement. PE chains closest to the Au NP are slower, compared to the bulk one, for all model hybrid systems, due to the polymer/gold nanoparticle interfaces.

In Table 14 we summarize the effect of interface on various properties.

Property	Bare Au NPs	Grafted Au NPs
Density	0.5–1.0 nm	1.7–3.0 nm
Structural	0.5–1.0 nm	0.5–1.3 nm
Local (segmental) dynamics	1.0–2.0 nm	0.5–1.5 nm
Global dynamics	3.0–4.0 nm	1.0–2.0 nm

Table 14: The effect of interface on various properties for the PE/Au NP systems.

Moreover, PEO/SiO_2 nanocomposites have been studied via detailed atomistic MD simulations. Atomistic simulations reveal clear density heterogeneities in the model nanocomposites in the vicinity of the PEO/SiO_2 interface. A rather similar peak at a

radial distance about 3-4 Å from the outer surface of the silica nanoparticles is observed for all three simulated systems denoting the attraction between the PEO_{49} chains and the NP₂. From the 3D density analysis, it is clear that, even for the most confined system investigated computationally, a considerable amount of polymeric material exists at the corners of the simulation domain, where the effect of the nanoparticle on its properties is attenuated.

A strong slowing down of the segmental dynamics is observed computationally in the adsorption layer that extends up to ~0.5nm from the outer surface of the nanoparticle, at the high-temperature regime. As the volume fraction of nanoparticles increases, a clear retardation of the segmental dynamics for all PEO chains is also observed.

Overall, due to the importance of heterogeneities discussed above computation of the full distribution of dynamical properties of polymer/graphene PNCs is required. This has been recently recognized also in other hybrid polymeric systems, such as miscible polymer blends [281]. This will be the subject of a future work. In addition, the dependence of the properties of the PNC on the exact interaction between the polymer matrix and the graphene sheet is a very important issue. Current work concerns the study of functionalized graphene (reduced graphene and graphene oxide) into polar and non-polar polymer matrices and the calculation of the properties, of the studied here, hybrid systems as a function of temperature. Finally, in a future work we want to develop a Coarse Grain (CG) model for those hybrid systems.

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