Hierarchical Multi-Scale Computational Methodologies for the Study of Complex Molecular Systems

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***Abstract*—Here, we give a short overview of hierarchical multi-scale simulation methodologies for predicting structure-property relations of macromolecular systems. In the first stage, detailed microscopic (atomistic) Molecular Dynamics (MD) simulations are performed. Various properties related to thermodynamics, structure and dynamics of polymeric systems are being examined at the atomistic level. In the second stage, our work involves an extension to a mesoscopic, Coarse Grained (CG) description of the simulated systems. Finally, CG simulations of larger systems and for longer times are performed. The proposed approach allows us to extend the simulated spatio-temporal scales of macromolecular systems.**

Keywords-Hierarchical modeling; Multi-scale; Molecular dynamics simulation; Coarse-graining.

I. INTRODUCTION

Design and innovation in materials science requires nowadays the use of computer simulations. As the computational power continuously improves, it is possible to study, using molecular simulations, multiphase and nanocomposites systems with various applications in energy storage, biomaterials, elastomers, electronics, etc. [1]–[3]. By employing Molecular Dynamics (MD) simulations and having an accurate force field that is parameterized on quantum calculations, someone can reproduce the dynamics at bulk or interphases and extract information about interfacial properties. Nevertheless, the representation at the atomistic level does not always permit us to model realistic systems, due to the enormous range of length and time scales associated with complex macromolecular-based materials [1][4]. Therefore, the investigation of the structural and dynamical properties in complex molecular systems requires dimensionality reduction techniques. Such a technique is the Coarse Graining (CG), in which a group of atoms is represented as a CG super-atom. The CG level of representation allows the description of the involved structure and dynamics, and the temperature dependence of various properties, such as the density, the heat capacity, the viscosity, the modulus, etc., with fewer parameters [5][6]. Thus, hierarchical multi-scale computational methods can provide low cost tools for the industrial design of materials, but also for answering fundamental questions in soft matter science.

Coarse graining can be realized as a procedure of mapping the microscopic (atomistic) space, determined by N particles, $q = (q_1, ..., q_N) \in R^{3N}$, to a CG, mesoscopic space of fewer M particles [7], i.e., $q \mapsto Q$ where $Q \in R^{3M}$ and $M<N$. The probability of a certain macromolecular configuration in the microscopic space should be the same with the probability of the same configuration in the CG representation, in the mesoscopic space, thus the corresponding CG potential of the super-atom should incorporate the free energy of the building atoms.

The n-body Potential of Mean Force (PMF) can be defined as [7]:

$$\bar{U}^{(n),PMF}(Q^{(n)}) = -k_B T \ln g^{(n)}(Q^{(n)}), \quad n<M, \qquad (1)$$

through the n-body distribution function, $g^{(n)}(Q^{(n)})$, where $Q^{(n)}$ are the coordinates of the n particles [7]. In practice, usually the pair (n=2) distribution function is used. Then, the CG force field is based on the mean force:

$$\bar{F}_i^{PMF}(Q) = -\nabla_{Q_i}\bar{U}^{PMF}(Q), \quad i = 1,\ldots,M. \qquad (2)$$

The first step towards the mesoscopic representation is the definition of the CG sites/super-atoms. Usually, in a low degree of CG, 5-10 atoms or 1-2 monomers constitute a super-atom [5][7]. The advantage of such a mapping scheme is that it retains the ability to predict properties at the atomistic level, while at the same time it is possible for the equilibrated CG system to re-insert atomistic detail following a back-mapping procedure [5]. An example of PolyStyrene (PS) mapping onto CG representation has been presented in [5][8] and is depicted in Figure 1.

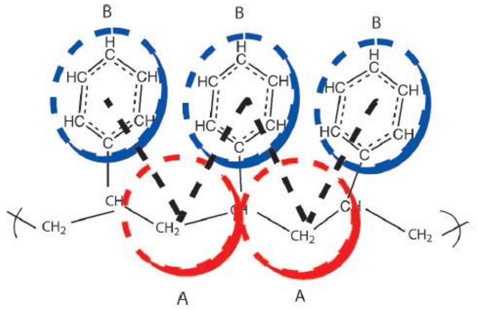

Figure 1. Representation of PS in atomistic and CG scale [5].

In the next step, we are interested in the development of a force field that governs the CG simulation. There exist several methods that allow the derivation of the CG potentials, based on (mainly structural) data derived from detailed atomistic simulations. All of them are characterized by an observable Φ and a minimization over a set of parameters Θ (cost functions) [7]. In structural or correlation methods the observable is the pair radial distribution function, *g(r)*. In the Force Matching (FM) or Multi Scale (MS) CG methods we focus on the description of the forces acting on a CG bead in order to reproduce the atomistic dynamics. Also, in the Relative Entropy (RE) approach the observable is related to the microscopic probability distribution [7].

For the intramolecular potentials that determine the internal structure of the macromolecule, in most cases we assume that they are described by the product of the probability distribution of each of the potentials [9]:

$$\mathrm{P}(l,\theta,\varphi) = \mathrm{P}(l)\mathrm{P}(\theta)\mathrm{P}(\varphi)\,, \tag{3}$$

where P(l), P(θ) and P(φ) refer to the distribution of the CG bond lengths, the angle between three consequent CG super-atoms and the dihedral angle formed by four consequent CG super-atoms respectively. The probability is defined based on the Boltzmann factor:

$$\mathrm{P}_i = \exp\left(-\frac{U_i}{k_B T}\right),\ i = l,\theta,\varphi. \tag{4}$$

Concerning the effective PMF ($\bar{U}_{eff}$) that defines the non-bonded interaction in the CG level, several numerical methods have been presented in the literature [1][2][4][7]. The structure-based methods are the Direct or Iterative Boltzmann Inversion (DBI or IBI respectively) and the Inverse Monte Carlo (IMC) method [4]. The force matching techniques solve a typical least squares problem [10], while the relative entropy methods use stochastic optimization and Newton-Raphson approaches. In case of the interaction between a super-atom and a surface, the effective potential can be calculated at a fixed distance *via* the constraint force required to keep the bead at this specific distance [8]. The latter can be determined based on oligomeric chains and then used for the description of longer polymeric chains, i.e., higher molecular weights.

In order to produce CG dynamics consistent with the atomistic simulation, one typical way is the use of the stochastic Langevin method [11] based on the equation of motion [9]:

$$m\frac{d^2\vec{r}_a}{dt^2} = -\vec{\nabla}\bar{U}^a_{eff} - m\Gamma\frac{d\vec{r}_a}{dt} + \vec{W}_a(t)\,, \tag{5}$$

where m is the mass of the particle a, Γ is the background friction and $\vec{W}$ is the statistical force of the heat bath. The use of a friction coefficient can allow us to correct the acceleration in the CG dynamics that is usually present due to the reduction in the degrees of freedoms compared to the atomistic representation [1].

The main goal of this work is to present the CG methodology focusing on polymer-based nanocomposites, i.e. a polymer matrix with nanoparticles or graphene as an additive phase. We intend to investigate the structural and dynamical properties at the polymer/nanofiller interface. The long relaxations times involved in such systems, even at temperatures well above the glass transition temperature (T_g), highlight the need for a mesoscopic approach. For this reason, the two stages of the hierarchical multi-scale methodology are elucidated. The first part includes atomistic simulations and the second part refers to the derivation of the needed CG force field for simulations at the mesoscopic level. As an example, a polyethylene (PE)/graphene nanocomposite is studied.

In the Section 2a, we present the parameters that describe the simulation at the atomistic level of PE in confined conditions formed by the presence of a modified (carboxylated) graphene sheet. In Section 2b, we give details of the CG procedure concerning the derivation of the force field for the simulation of the PE chain. Moreover, in Section 3, we present some preliminary results. The CG methodology is analyzed for the derivation of the non-bonded interactions, in the case of bulk PE. We close with Section 4, where the conclusions of our study and future plans are mentioned.

II. METHODOLOGY

A. Atomistic Simulation Details

The parameters of the force-field for PE were taken from the TraPPE (Transferable Potentials for Phase Equilibria) all-atom model [12] and in the case of the functionalized graphene we used the combination of all-atom OPLS (Optimized Potentials for Liquid Simulations) and a force field previously used for carbon structures (for more details see [13]). The bonds were constrained by LINCS (LINear Constraint Solver) algorithm [14] and the Coulomb cut-off [15] scheme with a cut-off distance of 1 nm was applied to account for the Coulomb interactions.

The nanocomposite system consists of one edge-functionalized graphene embedded in an oligomeric PolyEthylene (PE) matrix. Each polyethylene chain contains 11 monomeric units (11-mer, i.e., 22 carbons) and the number of chains in the systems has been adjusted to achieve 3.6 % weight percentage of the graphene nanofiller in polymer. The size of the graphene sheet is 5x5 nm^2 and its hexagonal lattice made of carbon atoms has been modified on the edges by attaching functional groups, namely either hydrogen or carboxyl groups.

We use the GROMACS [15] simulation package to perform the simulations. The temperature 450 K was kept constant by the stochastic velocity-rescaling algorithm and the Berendsen barostat was applied to maintain the pressure of 1 atm. The time step was 1 fs and a typical production run was about 100 ns long.

B. Coarse Graining Details

In the case of the bulk PE system used for the CG simulation, a first level of CG representation was performed by the use of the united atom approach. Each methyl (CH_3) and methylene (CH_2) group along the chain backbone is treated as one interaction site [12][16]. Nonbonded interactions were described again by the TraPPE force field [12]. The atomistic bulk system consists of 420 chains of 11-mer PE, at 450 K.

In order to produce the CG force field that is consistent with the structure of the atomistic MD simulations, we have used the IBI method. The methodology is based on an iterative numerical minimization procedure having as target the extraction of an effective mean potential that agrees with the atomistic pair distribution function ($\bar{g}^{(ref)}$). The CG potential is refined at each iteration according to following recursive relation [7]:

$$\bar{U}_{eff}^{(i+1)}(r) = \bar{U}_{eff}^{(i)}(r) + ck_B T \ln \frac{\bar{g}^{(i)}(r)}{\bar{g}^{(ref)}(r)}, \qquad (6)$$

where c is a constant to ensure the stability of the iteration procedure. The criterion for convergence is whether in each iteration (i) the CG non-bonded distribution function $\bar{g}^{(i)}$ matches the one derived from the atomistic run, within the numerical accuracy. Thus, the two-body potential of mean force, also converges to the (two-body) reference effective potential. The same procedure is also applied for the bonded part of the potential, based on bonded distribution functions.

III. RESULTS ANS DISCUSSION

In Figure 2, we present a snapshot of the simulated PE/graphene system in atomistic detail. At the edges of the graphene sheet we may identify the hydrogen and the carboxyl groups. The normalized density as a function of the radial distance from the center of the graphene (data shown in [17]) indicates that at short distances close to 0.5 nm, a peak in the density of PE is present. This is accompanied by an orientation of the polymer chains parallel to the graphene, similar to the behavior observed in different systems [18][19]. At longer distances, as we approach the edges of the nanosheet the density reaches bulk values. The results verify structural heterogeneities.

Concerning the dynamical properties in the nanocomposite system, results based on the AutoCorrelation Functions (ACF) for the case of segmental (1-3 atoms vector) relaxation and the relaxation of the end-to-end vector (at T=450 K), are presented in Figure 3. The ACFs concern the whole nanocomposite system and confirm the different time scales that govern the relaxation at different length scales. The dynamical heterogeneities are expected to become more pronounced as the temperature decreases reaching values closer to the T_g (220 K [20]), where the diffusion is characterized by increased cooperativity [6].

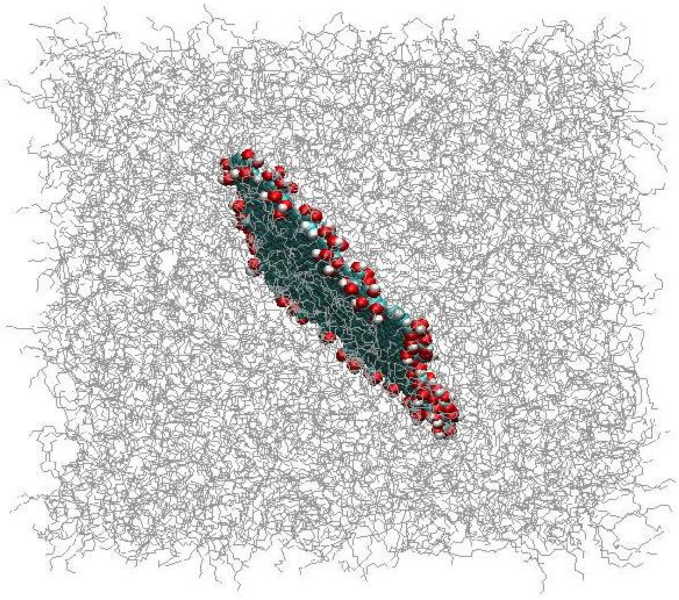

Figure 2. PE/graphene system visualized with VMD [19].

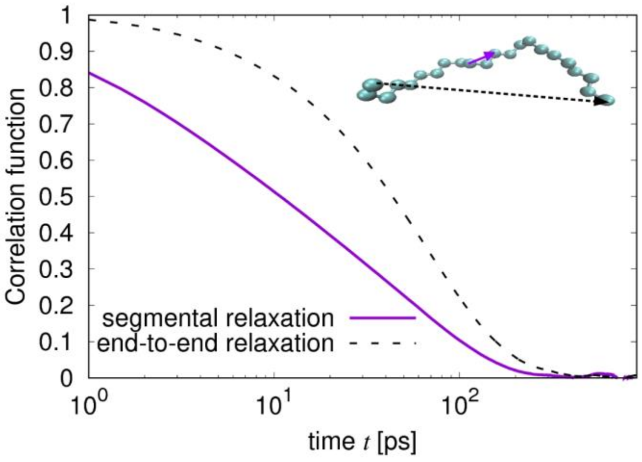

Figure 3. Autocorrelation function of the relaxation of the end to end vector and the segmental bond vectors, at 450K.

By defining the coordination systems of the nanosheet, based on the eigen vectors of the gyration tensor, we can also study the dynamics in different layers from the surface [21]. The layers' definition was based on the minimums in the density profile fluctuations. It is observed that the nanofiller also imposes a distribution in the relaxation times in layers parallel to to the nanosheet, that covers a wide range in the time scale (data shown in [8][21]). The adsorbed layer is characterized by adsorption/desorption times of the order of ms, while the bulk depicts decorrelation times close to ns. Because of this wide spread of time scales CG models could be of great importance.

In order to give a general idea of the CG methodology, here we present new results on a 11-mer bulk PE, focusing on the derivation of the effective PMF for the non-bonded interaction. In Figure 4, we show the chosen CG mapping. Four united atom carbons build a super-atom. The non-bonded pair distribution fuction of the CG beads, g(r), using the atomistic simulation data, is shown in Figure 5 as "target".

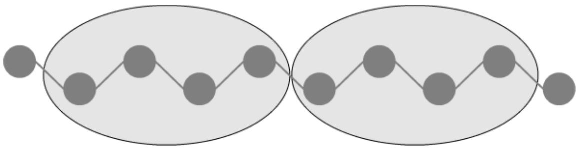

Figure 4. Representation of PE in CG methodology.

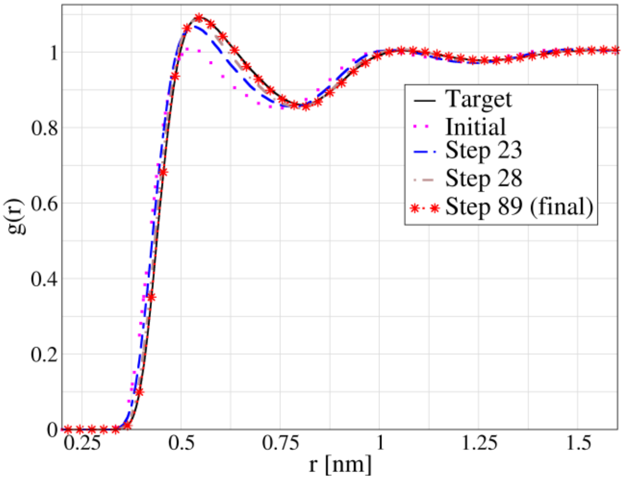

Figure 5. Radial distribution function evolution in the IBI iteration procedure.

Using the IBI method (5), we may determine the non-bonded potential for the CG simulation. In Figure 6, we show the first estimation based on the DBI approach (first iteration), while the evolution of the CG effective potential and respective evolution of the g(r) are depicted by the same kind of lines in Figures 5 and 6. We may conclude that a convergence is succeeded at the 89th step of the iteration. The final CG effective potential is depicted with asterisks in Figure 6. It consists of a repulsive part at distances lower than 0.6 nm and an attractive part at further distances. A similar procedure is followed for the bonded potentials (not shown).

Structure based CG models using a pair potential usually do not determine adequately the (long-range) atractive part of the effective potential and the virial pressure of the system, as the structure is more affected by the repulsive part of the effective pair potential [3][7]. Incorporation of ideas [6] concerning the temperature depedence of the cohesion energy at the super-Arrhenius region may lead to different approaches in the calculation of the effective potential that could allow the transferability in different temperatures and molecular weights.

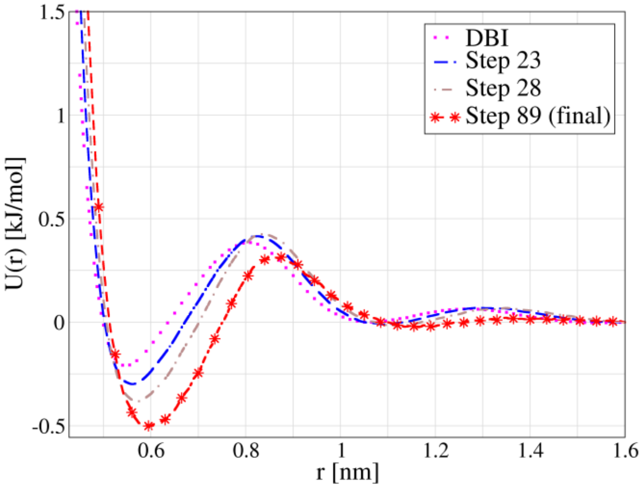

Figure 6. CG effective non-bonded potential evolution. The respective g(r) in each iteration is depicted in Figure 5.

IV. CONCLUSIONS AND FUTURE WORK

In this work we have provided an overview of atomistic and coarse-grained simulations of macromolecular systems. A hierarchical description of such systems requires at the first stage an atomistic description, which was presented for the case of PE/graphene system. We have computed results concerning the structure and the dynamics of polymeric chains at the polymer/graphene interface. The results depict increased structural and dynamics heterogeneities in the nanocomposite system and underline the significance of CG modelling. Derivation of CG potentials that describe the non-bonded interaction were illustrated for the case of bulk PE chains. Moreover, we have presented ideas for the extension of the transferability and predictivity of such methods based on universal characteristics at the super-Arrhenius region.

Current and future work concerns the development of CG models for heterogeneous polymer/particle nanocomposites.

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