

MULTISCALE MOLECULAR SIMULATIONS OF NANOMATERIALS

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Abstract

Two different multiscale simulation approaches suitable for polymer composites are compared, coarse-grained models based on effective beads (superatoms) parametrized using reference atomistic simulations and particle-field models based on a hybrid particle continuum description. Applications of these approaches to nanoparticles and carbon nanotubes polymer composites are discussed.

1 Introduction

The understanding of material performances, in particular the connection between chemical structure and properties, needs a description at atomic level of both structure and dynamics. Atomistic models provide accurate descriptions and using suitable force fields are potentially able to give good reproduction of several macroscopic properties. A computational approach to nanomaterials should involve the study of large size systems on large timescales. This prevents the use of detailed atomistic models. Coarse-grained models can be used in order to save computational time. Two different strategies to obtain models suitable for polymer composites are compared, coarse-grained models based on effective beads (superatoms) parametrized using reference atomistic simulations and particle-field models based on a hybrid particle continuum description. The two strategies are schematized in the figure 1 below.

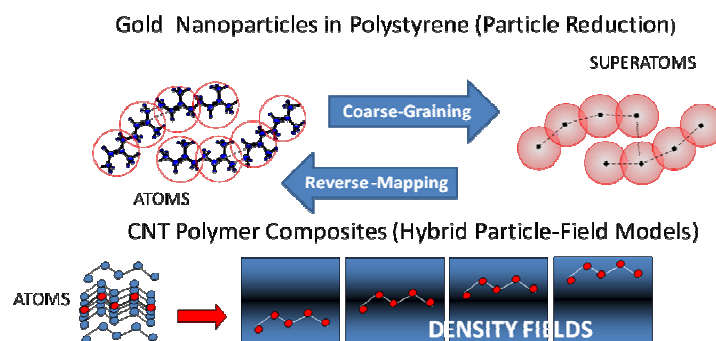


Figure 1. Two possible multiscale strategies are schematized. In the first case (upper part) the number of particle can be reduced (Coarse-Graining) and after equilibration restored (Reverse Mapping). In the second case (bottom) non-bonded interactions are modeled using a continuum approach.

In the first case a larger computational efficiency can be achieved developing models having a smaller number of particles. Atoms are grouped in effective beads interacting with potentials developed by suitable procedures.[1] In the second case, the number of particle does not change, but interactions are not calculated by particle pairs but between single particles and density fields.[2] For simplicity, along the paper, first strategy will be named particle-particle coarse-graining (PPCG) the second strategy particle-field coarse-graining (PFCG).

Polymer nanocomposites based on nanometer-size metal particles are experiencing an explosive growth during the last years due to their technological applications.[3] A vast array of applications of this class of materials are emerging in the field of nanoelectronics. Yang Yang and co-workers developed several devices based on nanoparticles included into organic or polymeric materials.[4] Organic non volatile memory devices made from a polystyrene (PS) film containing gold nanoparticles and 8-hydroxyquinoline (8-HQ) sandwiched between two metal electrodes shows electrical bistability.[4] The first example of PPCG strategy will be focused on these systems. In particular this approach helped the understanding the structure of the interfaces, in this new class of materials. This basic knowledge is fundamental to improve device function and efficiency.[5]

On the other hand, composite materials based on carbon nanotubes(CNTs) and polymers have received tremendous attention since the first CNTs were observed by Iijima.[6] Recently, a considerable research effort has been devoted to get CNT/polymer nanocomposites with improved properties by efficiently dispersing the CNTs into the polymer matrix. A typical problem is a mechanical such as storage module and electrical percolation threshold that are clearly affected by the difference in the processing approach.[7]

Despite the existence of a wide literature, there is still a great challenge to understand and to rationalize and possible address the manipulation, the fabrication in order to control the structures of the CNTs/polymer nanocomposites at a microscopic scales. For such purposes, computer modeling and simulation can play an important role. The large time and lengthscales involved in the processing of these materials prevent an efficient use of molecular simulation methods. A standard coarse-graining approach like PPCG is still too expensive to reach large time (at least μs) and length (at least 100 nm) scales. In this case a combination of both PP and PF Coarse Graining approaches can be useful. In particular, simple models obtained reducing the number of particles can be treated in a particle-field fashion.

2 Materials and methods

2.1 PPCG Strategy and Initial Configurations Set Up

The basic idea of PPCG models is to group several atoms in one effective bead. This allows to reach simulation times suitable for the relaxation of polymeric systems reducing the number of degrees of freedom and the computational cost of simulations. The adopted coarse-graining scheme considers a configurational base unit, in particular a diad, as superatom at the mesoscale level. According to this choice, as depicted in Figure 2, the center of a superatom is the methylene carbon.

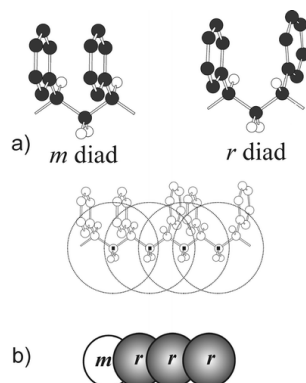


Figure 2. The mapping scheme of the PS adopted coarse-grain model. The atoms belonging to a *m* or *r* diad are grouped in one coarse-grained particle. (a) Atomic structures of *m* and *r* diads. (b) Example of atomistic structure of PS and the corresponding CG model.

In order to have specific CG models, the mesoscale potentials are optimized in a way to reproduce target distributions obtained from reference atomistic simulations. In particular, for intramolecular interaction terms between bonded superatoms (bond and angle potentials) mesoscale potentials obtained by Boltzmann inversion based on a sum of several Gaussian functions have been employed.[8] For the nonbonded part of the potential, pressure-corrected CG numerical potential optimized by iterative Boltzmann inversion have been used.[1] The effective nonbonded potential $V(r)$ is derived from a given tabulated starting potential $V_0(r)$, targeting to match the radial distribution function $g(r)$.

The potential is iteratively improved by successive corrections,

$$V_{j+1}(r) = V_j(r) + kT \ln \frac{g_j(r)}{g_{target}(r)} \quad (1)$$

Further details of the parametrization procedure, including a complete set of distribution plots can be found in reference [8]. These coarse-grain models have been successfully tested using MD [8]. Chain dimensions were found in very good agreement with experiments. Well relaxed all-atom melts successfully tested against experimental data have been obtained by using a reverse-mapping procedure based on quaternion algebra that, starting from equilibrated mesoscale melt structures, allows a very fast and efficient reconstruction of the atomistic detail. This procedure gives atomistic structures able to reproduce structural experimental data of large molecular weight stereo regular and stereoirregular PS samples.[9] A similar approach using coarse-grain simulations and successive reverse-mapping can be employed to obtain initial configuration for systems modeling a polymer melt including a nanoparticle.[5]

In particular as first stage, starting from one configuration obtained by MD equilibration of coarse-grain polymer chains, with periodic boundary conditions, an equilibrated atomistic configuration has been obtained applying the procedure described and validated in reference [9]. The initial configurations of a nanoparticle embedded into a polymer melt can be obtained inserting the gold nanoparticle into a cavity placed in the center of the cubic box. The cavity has been obtained discarding from the back mapping procedure the polymer chains overlapping with the nanoparticle.

2.2 PFCG Strategy

The main feature of the hybrid PFCG approach, is that the evaluation of the non bonded force and its potential between atoms of different molecules, *i.e* the most computationally

expensive part of MD simulations, can be replaced by the evaluation of an external potential dependent on the local density at position \mathbf{r} in PF simulations. According to the spirit of SCF theory, a many body problem like molecular motion in many molecule systems is reduced into the problem of deriving the partition function of a single molecule in an external potential $V(\mathbf{r})$. Then non bonded force between atoms of different molecules can be obtained from a suitable expression of the $V(\mathbf{r})$ and its derivatives.

In the frame of SCF theory, a molecule is regarded to be interacting with the surrounding molecules not directly but through a mean field. Assuming that the density dependent interaction potential W , where each component species is specified by the index K , takes the following form:

$$W[\{\phi_K(\mathbf{r})\}] = \int d\mathbf{r} \left(\frac{k_B T}{2} \sum_{KK'} \chi_{KK'} \phi_K(\mathbf{r}) \phi_{K'}(\mathbf{r}) + \frac{1}{2\kappa} \left(\sum_K \phi_K(\mathbf{r}) - \phi_0 \right)^2 \right), \quad (2)$$

Where $\phi_K(\mathbf{r})$ is the coarse-grained density of the species K at position \mathbf{r} and $\chi_{KK'}$ are the mean field parameters for the interaction of a particle of type K with the density fields due to particles of type K' , it can be shown that, using the so called saddle point approximation, the external potential is given by:

$$V_K(\mathbf{r}) = \frac{\delta W[\{\phi_K(\mathbf{r})\}]}{\delta \phi_K(\mathbf{r})} = k_B T \sum_{K'} \chi_{KK'} \phi_{K'}(\mathbf{r}) + \frac{1}{\kappa} \left(\sum_K \phi_K(\mathbf{r}) - \phi_0 \right). \quad (3)$$

The main advantage of hybrid MD-SCF scheme is that the most computationally expensive part of the MD simulations, i.e. the evaluation of the non-bonded force between atoms of different molecules, is replaced by the evaluation of forces between single molecules with an external potential. In order to connect particle and field models, for the proposed hybrid MD-SCF scheme, it is necessary to obtain a smooth coarse-grained density function directly from the particle positions. This function is obtained implementing a mesh based approach suitable to obtain also the density derivatives needed to calculate forces. The details of the implementation of this approach and a complete derivation of eq. 2 is reported elsewhere.⁵ The MD-SCF simulations reported here have been performed using the parallelized version of the OCCAM code. [10]

Coarse-Grained (CG) model for SWCNT with aspect ratio 10.6 are composed of 13 particles and the corresponding length of SWCNT is 14.84nm. In this model, bonds between two successive particles are described by a harmonic potential $V_{bond}(R)$ type, $V_{bond}(R) = \frac{1}{2} K_{bond} (R - R_{bond})^2$, where R_{bond} is the equilibrium distance, corresponding to $0.8 \times \sigma = 1.12\text{nm}$. The stiffness of the SWCNT is taken into account by a harmonic potential $V_{angle}(\theta)$ depending on the cosine of angle between atoms, where θ is the angle between two successive bonds. $V_{angle}(\theta) = \frac{1}{2} K_{angle} \{\cos(\theta) - \cos(\theta_0)\}^2$, where K_{angle} is the force constant and θ_0 is the equilibrium bond angle 180° for SWCNT. Furthermore, the CG model of homopolymer is a bead a spring model having the same parameters of CNT obviously excluding the angle potential

3 Results and Discussion

Molecular Dynamics simulations have been performed to obtain detailed all-atom models of the interface between polystyrene (PS) and gold nanoparticles. Considering their relevance in the memory technology, systems containing gold nanoparticles included in PS polymer melts also in presence of 8-hydroxyquinoline (8-HQ) molecules have been studied. Four different systems have been compared. In figure 4 the calculated radial density profiles are reported for the four considered systems. Density profiles show that the presence of non-coated nanoparticles in a polymer melt causes an ordering of polymer chains. A similar ordering behavior is found for the 8-HQ molecule. In presence of a coated gold nanoparticle, calculated radial density profiles, show much less order. When 8-HQ is present, this molecule is closer to the nanoparticle surface and when in contact with a coated nanoparticle shows penetration into the thiols layer. The orientation of 8-HQ results short ranged and parallel with respect to the surface of non-coated gold nanoparticles. In the case of a coated gold nanoparticle the 8-HQ orientation results perpendicular to the nanoparticle surface.

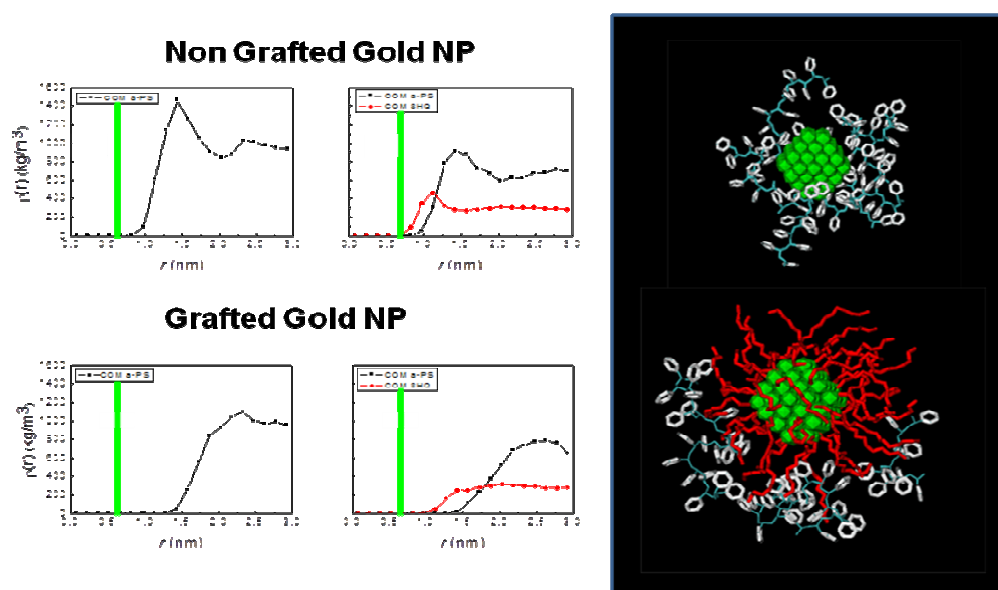


Figure 3. Radial density profiles of the centre of mass of PS chains, for systems containing a non-grafted (upper part) and grafted (lower part) gold nanoparticle as function of the distance from NP centre of mass. On the right side the curves corresponding to systems including 8-HQ molecules are also reported. Snapshot of simulations are also reported. Some of the polymer chains closer to the NP surface are depicted the remaining chains are omitted for clarity.

The results reported above show that the use of coarse-grained models combined with atomic simulation by reverse mapping techniques can provide the first opportunity to have useful insights to reach the minimal model size, essentially as small domain size (few nanometers) with a single nanoparticle inside. Nanoparticle aggregation is currently out of reach for MD at atomic resolution.

A very relevant example of this problem is the aggregation of CNT in a polymer melt as function of concentration.

In order to prevent severe finite size effect of the periodic boundary conditions. The box size needs to be at least several CNTs lengths in each dimension. In particular, the length of each side of a three dimensional cubic box can be set as a fixed multiple of the CNT length. This choice allows to have, independently from the length of the CNT the similar finite size effects. Four times of the length of SWCNT is a suitable choice to investigate the properties of percolation threshold reasonably.

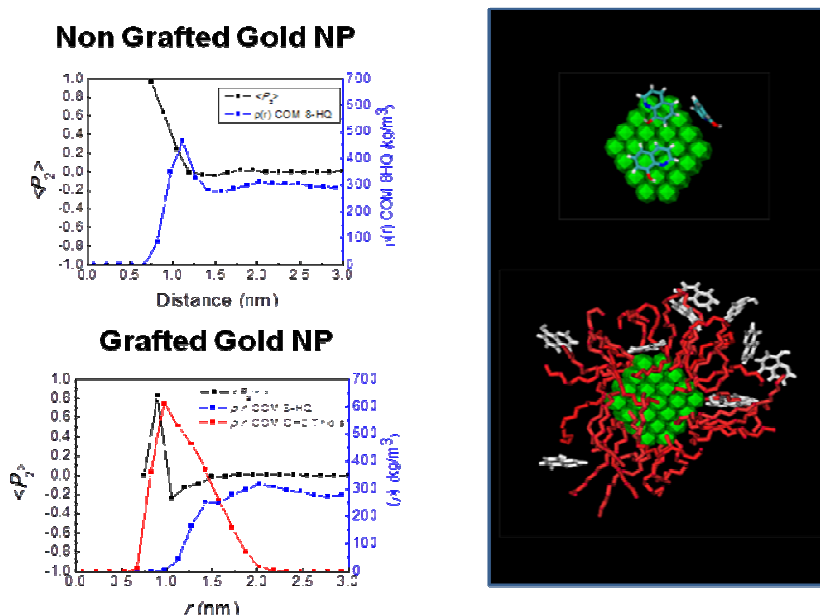


Figure 4. Order parameter of the angle between the 8-HQ molecular plane as function of the distance between NP and 8-HQ centers of mass for the system containing a non grafted and grafted NP. The blue curve shows the behavior of 8-HQ centre of mass radial density. Snapshot of simulations are also reported. Some 8-HQ molecules closer to the NP surface are depicted polymer chains are omitted for clarity.

This choice implies that already for moderate aspect ratios (around 30) the size of the system to be simulated, for the models under investigation, goes beyond one million of particles. In particular for a system having CNT of aspect ratio 30 the size of simulation box is about 170 nm with a total number of particles of 1,529,994. Simulations of this size are extremely expensive using PP methods. The particle-field approach allows to treat these kind problems more efficiently. Furthermore, Because of the peculiar formulation of the hybrid method, considering single particles interacting with density fields, the most computationally expensive part of the hybrid particle-field MD simulation can be efficiently parallelized using a straightforward particle decomposition algorithm. To have an idea about the parallel performances of this approach in figure 5 the number of steps performed every second for a system of 1,000,000 of Lennard-Jones particles by the efficient program GROMACS [11] are compared with the ones obtained using a particle-field approach with the program OCCAM. [10] The two blue curves indicate two different sets of results obtained with a different frequency of density field update (every 300 and 100 steps). In both cases the performances of the particle-field model, especially for large number of processors are much higher than the corresponding particle-particle one. It is worth noting that for the large systems under investigation the number of processors employed is much higher (around 200) than for tests simulations of figure 5.

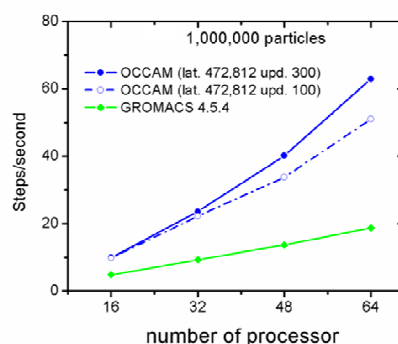


Figure 5. Performances of particle-field model in parallel MD simulations as steps/s in comparison with GROMACS 4.5.4 (green curve). Results of OCCAM using 472,812 lattice points (blue curves) are shown.

Particle-field MD simulations have been done using update frequency of 100 time steps (empty symbols and dash dot lines) and 300 time steps (filled symbols and solid lines), respectively.

Simulations aimed to understand the aggregation behavior need to be long enough to allow large CNT diffuse enough to reach equilibrium structures. The simulations reported here have been run for several μ s (i.e. several 10 million of steps). In figure 6, the percolation behavior of CNT polymer composites having CNT of three different aspect ratios has been studied.

As shown in eq. 3. in the hybrid particle-field MD-SCF simulations, the interactions between different species are evaluated using the mean field parameters $\chi_{KK'}$ describing the interactions between particles of type K and the density field due to the particles of type K'. These interactions parameters can be related to the Flory-Huggins theory. A repulsive interaction parameter χ parameter of 4.8 has been chosen. Using the square of the difference of the Hildebrand solubility parameters of pure-components it can be shown that this value is in the typical range of interaction of single walled nanotubes with synthetic polymers. Interaction parameters between polymer beads and polymer density field and between CNT beads and CNT density field are set to zero.

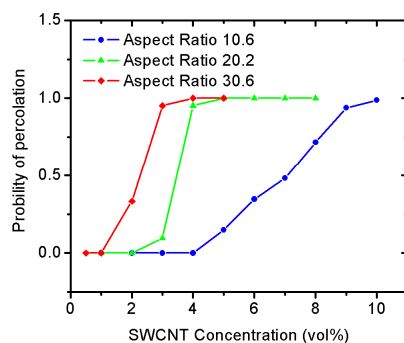


Figure 6. Percolation behavior of CNT/Polymer composites having CNT of different aspect ratios.

In figure 6 the percolation behavior of CNT aggregates is reported as function of concentration. A CNT cluster is considered as percolating one if in at least one direction (x , y or z) goes through the system. A CNT is considered member of a cluster if its the minimum distance between any other cluster member is less than a given value (in the present case 1.0 nm). The probability of percolation (reported in figure 6) is the fraction of configurations having at least one percolating cluster recorded along the simulation. In all considered cases a percolation transition is obtained. For the shortest CNT the transition is smooth more abrupt for the systems with aspect ratio 20.2 and 30.6. The minimum amount of CNT able to give percolation is also function of the aspect ratio. Longer is the CNT and earlier the percolation is obtained. In figure 7 the morphology corresponding to 1, 2 and 4 and 7 % vol. of CNT for the system with aspect ratio 30.8 are depicted. The CNT are reported in green and polymer chains are not shown for clarity. For the systems at higher concentration where the percolation already took place, the percolating clusters are reported in red.

The preliminary results reported above show that the proposed models lead to a reasonable behavior and that the particle-field approach, allowing the simulations of system of reliable size, can open the way to a better understanding of the assembly phenomena in composites. Further improvements of these models, involving the mapping of results of more detailed atomistic models, are in progress.

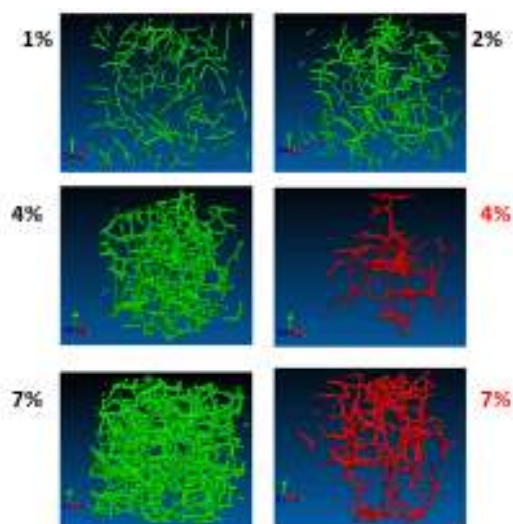


Figure 7. Morphologies of Polymer/CNT composite (aspect ratio 30.6, corresponding to red curve of figure 6) at different volume fractions. CNT are depicted in green, polymer chains are not shown for clarity. In red are depicted CNT belonging to percolating clusters for systems at concentration of 4 and 7%.

Acknowledgments

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