Multiscale molecular modelling of dispersion of nanoparticles in polymer systems of industrial interest.

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Abstract

Atomistic –based simulations such as molecular mechanics (MM), molecular dynamics (MD), and Monte Carlo-based methods (MC) have come into wide use for material design. Using these atomistic simulation tools, we can analyze molecular structure on the scale of 0.1-10 nm. However, difficulty arises concerning limitations of the time- and length-scale involved in the simulation, particularly when nanoparticles are involved in the system. Although a possible molecular structure can be simulated by the atom-based simulations, it is less realistic to predict the mesoscopic structure with nanoparticles defined on the scale of 100-1000 nm. For the morphology on these scales, mesoscopic simulations are available as alternatives to atomistic simulations allowing to bridge the gap between atomistic and macroscopic simulations for an effective material design. In this contribution, a hierarchical procedure for bridging the gap between atomistic and macroscopic (FEM) modeling passing through mesoscopic simulations will be presented and applications of systems with nanoparticles will be discussed.

Introduction

The main goal of computational materials science is the rapid and accurate prediction of properties of new materials before their development and production. In order to develop new materials and compositions with designed new properties, it is essential that these properties can be predicted before preparation, processing, and characterization.
Polymers are complex macromolecules whose structure varies from the atomistic level of the individual backbone bond of a single chain to the scale of the radius of gyration, which can reach tens of nanometres. Polymeric structures in melts, blends and solutions can range from nanometre scales to microns, millimetres and larger. The corresponding time scales of the dynamic processes relevant for different materials properties span an even wider range, from femtoseconds to millisec-

onds, seconds or even hours in glassy materials, or for large scale ordering processes such as phase separation in blends. No single model or simulation algorithm currently available can encompass this range of length and time scales. In order to simulate a polymeric system one must consider models that range from those including quantum effects and electronic degrees of freedom to chemically realistic, classical models.

One of the most important issue in computational materials research is the multiscale simulation, namely the bridging of length and time scales, and the linking of computational methods to predict macroscopic properties and behaviour from fundamental molecular processes [1,2]. Despite the advances made in the modelling of the structural, thermal, mechanical, and transport properties of materials at the macroscopic level (finite element analysis of complicated structures), there remains tremendous uncertainty about how to predict many properties of industrial interest containing nanoparticles dispersed at nanoscale level.

In this paper, we will show hierarchical procedures for bridging the gap between atomistic and macroscopic (FEM) modelling passing through mesoscopic simulations. In particular, we will present and apply to some cases of industrial interest the concept of "message passing multiscale modelling". Examples considered will be (i) mesoscale simulation for diblock copolymers with dispersion of nanoparticles and (ii) polymer - carbon nanotubes system.

The strategy described in this paper is based on an overlapping array of successively coarser modelling techniques. At each plateau (a range of length and time scales), the parameters of the coarse description are based on representative results of the immediately finer description, as it will be explained in the following paragraphs.

Multiscale Molecular Modeling

Molecular modelling and simulation combines methods that cover a range of size scales in order to study material systems. These range from the sub-atomic scales of quantum mechanics (QM), to the atomistic level of molecular mechanics (MM), molecular dynamics (MD) and Monte Carlo (MC) methods, to the micrometer focus of mesoscale modelling.

Quantum mechanical methods have undergone enormous advances in the past ten years, enabling simulation of systems containing several hundred atoms. Molecular mechanics is a faster and more approximate method for computing the structure and behaviour of molecules or materials. It is based on a series of assumptions that greatly simplify chemistry, e.g., atoms and the bonds that connect them behave like balls and springs. The approximations make the study of larger molecular systems feasible, or the study of smaller systems, still not possible with QM methods, very fast. Using MM force fields to describe molecular-level interactions, MD and MC methods afford the prediction of thermodynamic and dynamic properties based on the principles of equilibrium and non equilibrium statistical mechanics [3]. Mesoscale modelling uses a basic unit just above the

molecular scale, and is particularly useful for studying the behaviour of polymers and soft materials. It can model even larger molecular systems, but with the commensurate trade-off in accuracy [4,5]. Furthermore, it is possible to transfer the simulated mesoscopic structure to finite elements modelling tools for calculating macroscopic properties for the systems of interest [6].

Figure 1 shows the class of models that are available at each single scale. There are many levels at which modelling can be useful, ranging from the highly detailed ab-initio quantum mechanics, through classical molecular modelling to process engineering modelling. These computations significantly reduce wasted experiments, allow products and processes to be optimized, and permit large numbers of candidate materials to be screened prior to production.

QM, MM and mesoscale techniques cover many decades of both length and time scale, and can be applied to arbitrary materials: solids, liquids, interfaces, self-assembling fluids, gas phase molecules and liquid crystals, to name but a few. There are a number of factors, however, which need to be taken care of to ensure that these methods can be applied routinely and successfully.
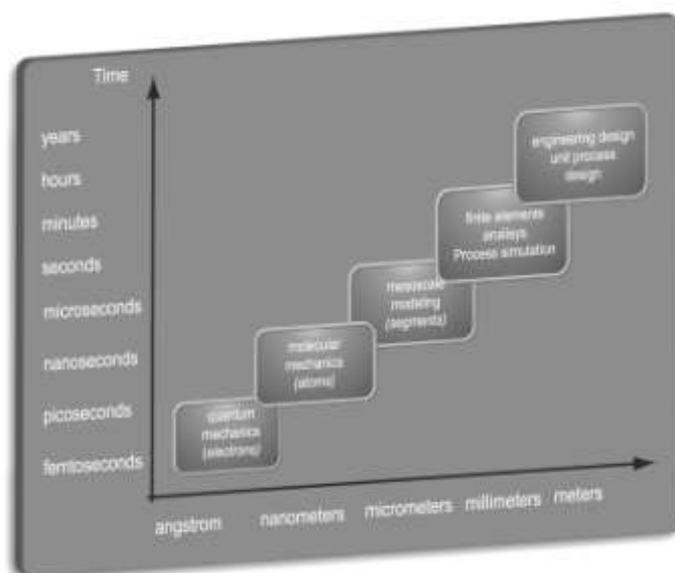

Fig. 1: Multiscale molecular modeling: characteristic times and distances.

First and foremost of course are the validity and usability of each method on its own, followed by their interoperability in a common and efficient user environment. Of equal importance is the integration of the simulation methods with experiment.

Multiscale simulation can be defined as the enabling technology of science and engineering that links phenomena, models, and information between various scales of complex systems. The idea of multiscale modelling is straightforward:

one computes information at a smaller (finer) scale and passes it to a model at a larger (coarser) scale by leaving out, i.e., coarse-graining, degrees of freedom. The ultimate goal of multiscale modelling is then to predict the macroscopic behaviour of an engineering process from first principles, i.e., starting from the quantum scale and passing information into molecular scales and eventually to process scales.

Thus, based on accurate QM calculations, a force field (FF) is determined, which includes charges, force constants, polarization, van der Waals interactions and other quantities that accurately reproduce the QM calculations. With the FF, the dynamics is described with Newton's equations (MD), instead of the Schrödinger Equation. The MD level allows predicting the structures and properties for systems much larger in terms of number of atoms than for QM, allowing direct simulations for the properties of many interesting systems. This leads to many relevant and useful results in materials design; however, many critical problems in this filed still require time and length scales far too large for practical MD. Hence, the need to model the system at the mesoscale (a scale between the atomistic and the macroscopic) and to pass messages from the atomistic scale to the mesoscale and to the macro scale. This linking through the mesoscale in which the microstructure can be described is probably the greatest challenge to developing reliable first principles methods for practical materials' design applications. Only by establishing this connection from micro scale to mesoscale it is possible to build first principles methods for describing the properties of new materials and (nano) composites.

The problem here is that the methods of coarsening the description from atomistic to mesoscale or mesoscale to continuum is not as obvious as it is in going from electrons to atoms [2]. For example, the strategy for polymers seems quite different than for metals, which seem different from ceramics or semiconductors. In other words, the coarsening form QM to MD relies on basic principles and can be easily generalized in a method and in a procedure, while the coarsening at higher scales is system specific.

This paper focuses the attention to the prediction of macroscopic properties of polymer systems and polymer nano-structured materials with particular attention to interface phenomena. Finite element analysis software is used to this aim, but the physical properties input to such programs are consequence of the microstructure at few nanometre scale. Multiscale simulation poses great challenges for polymer materials than for metallic and ceramic systems due to the larger range of length and time scales that characterize macromolecules. Although each tool performs calculations using only one technique, the output from one level can be used directly as input for another, allowing an off-line bridging of length and time scales. To achieve what he and others refer to as "seamless zooming", namely the ability to spawn higher resolution simulations using more detailed methods where needed, will require additional theoretical and computational advances.

Along similar lines, off-line multiscale simulations of nanofilled polymers using coarse-grained molecular dynamics, mesoscopic time dependent Ginsburg-Landau theory (TDGL), and macroscopic continuum finite element techniques have been carried out. Significant advances in uniquely mapping atomistic models of polymers onto coarse-grained models [7,8], have been made in recent years, in some

cases providing nearly exact quantitative agreement between the two models for certain quantities, but these mappings, too, are performed off-line, and the various methods are not linked within a single simulation.

Scale integration in specific contexts in the field of polymer modelling can be done in different ways. Any 'recipe' for passing information from one scale to another (upper) scale is based on the definition of multiscale modeling which consider 'objects' that are relevant at that particular scale, disregard all degrees of freedom of smaller scales and summarize those degrees of freedom by some representative parameters.

All approaches are initially based on the application of a Force field that transfers information from quantum chemistry to atomistic simulation.

From atomistic simulation to mesoscale one can use a traditional approach based on the estimation of the characteristic ratio, the Kuhn length, and the Flory Huggins interaction parameter [8]. This approach for determining the input parameters for mesoscale simulation is based on the following information: (i) the bead size and Gaussian chain architecture, (ii) the bead mobility M, and (iii) the effective Flory-Huggins χ interaction parameters. With this approach, the Flory-Huggins χ parameters between two components of the coarse-grained molecular models in the mesoscopic simulation are estimated through the atomistic simulation, and a mesoscopic structure is predicted using these parameters. Mesoscopic simulations are performed using a coarse-grained molecular model as shown in Figure 2: the particle in mesoscopic simulation is related to a group of several atoms in the atomistic simulation. Mesodyn and DPD mesoscale theory and simulation protocols are fully described in the literature [4,5].
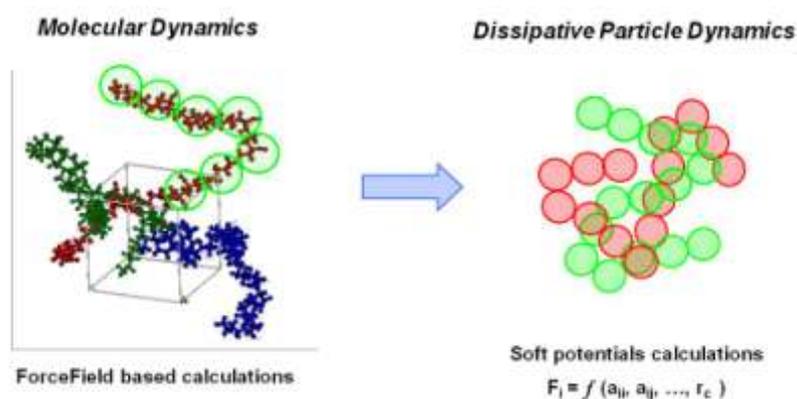

Fig. 2: Coarse grained modeling from atomistic model.

The traditional approach can be enhanced and improved by considering the detailed structure at the interface polymer – nanofiller [7]. If one resorts to a particle based method for describing the system at mesoscale, atomistic MD simulation gives the necessary details of the interface with a particular attention to the binding energies among components. Mapping of the binding energies on mesoscale beads by means of a combinatorial approach to repulsive parameter for particles is

then carried out and the system is simulated at mesoscale. If both particle based and field based methods are to be used at mesoscale, then an hybrid method can be adopted [9] in which particles are treated as described above and field interaction is calculated from pair–pair distribution function.

Mesoscale simulation typical result is the morphology and the structure of the matter at nanoscale level at the desired conditions of temperature, composition and shear.

For the representation of flow of polymeric materials on a processing scale, one must employ a hydrodynamic description and incorporate phenomena occurring on mesoscopic to macroscopic length and time scales. For example, to capture the non-Newtonian properties of polymer flow behaviour one can either use special models for the materials stress tensor, or obtain it from a molecular simulation using the instantaneous flow properties of the hydrodynamic fields as input. In the area of high-performance materials and devices, polymer composites are finding a widespread application, and the modelling of these materials was until recently done primarily through finite element methods (FEM), and are beyond the realm of application of molecular modelling approaches. Nonetheless, a real problem in using FEM is the definition of the physical property of a complex material such as a polymer blend with phase segregation and/or a polymer with micro inclusion of nanosized platelets [5,6]. Mesoprop technique is a method based on finite elements for estimating properties of a complex material starting from the density distribution at mesoscale. The method uses the results of a mesoscale simulation under the form of three dimensional density maps, and transforms such information into a fixed grid that is used for the integration of the equations to determine macroscopic properties. Palmyra is a different method that allows the simulation at FEM level with a variable grid methodology that allows to extend the size of the system studied.
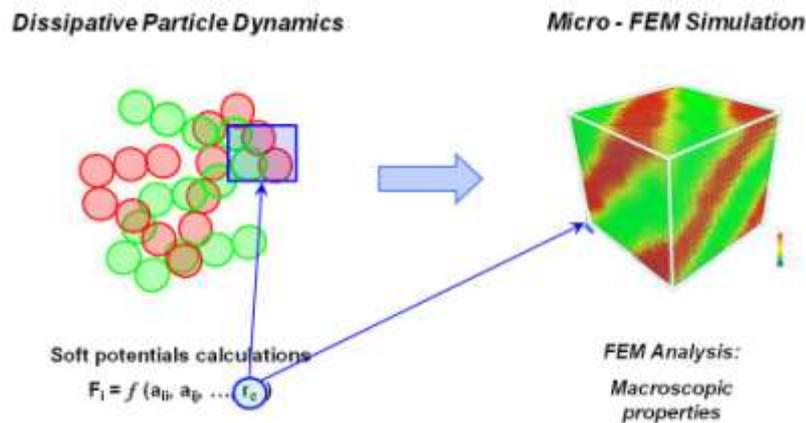

Dissipative Particle Dynamics

Micro - FEM Simulation

Soft potentials calculations

$F_i = f(a_{ii}, a_{ij} \dots r_c)$

FEM Analysis:

Macroscopic properties

Fig. 3. : From mesoscale morphology to FEM analysis..

Figure 3 shows how the mapping from mesoscale to macroscale is done. At FEM level each finite element corresponds to one phase, with property tensor P_i, at me-

soscale (MesoDyn or DPD) each element contains mixture of phases, with concentration C_i. It is necessary to perform a geometry mapping by converting MesoDyn cubic elements to Palmyra tetrahedrons. Once this is done, Laplace equation is solved directly for obtaining direct properties such as electric conductance, diffusion, permeability,.. Local deformation allows the calculation of mechanical properties.

Integration between these methods (from mesoscale to macroscale) is of paramount importance for the estimation of the properties of the materials, as it will be described in the following paragraphs with some illustrative examples of application.

Applications of multiscale modeling

In the following paragraphs, some applications of the message passing multiscale modelling described in the previous sections will be presented and discussed.

Mesoscale simulation for diblock copolymers with dispersion of nanoparticels

Mixing microphase-separating diblock copolymers and nanoparticles can lead to the self-assembly of organic/inorganic hybrid materials that are spatially organized on the nanometer scale. Controlling particle location and patterns within the polymeric matrix domains remains, however, an unmet need. Computer simulation of such systems constitutes an interesting challenge since an appropriate technique would require the capturing of both the formation of the diblock mesophases and the copolymer-particle and particle-particle interactions, which can affect the ultimate structure of the material. In this example [10] we discuss the application of dissipative particle dynamics (DPD) to the study of the distribution of nanoparticles in lamellar and hexagonal A-B diblock copolymer matrices. The DPD parameters of the systems were calculated according to a multiscale modeling approach, i.e., from lower scale (atomistic) simulations.

In agreement with some experimental evidence, we found that, depending on the nature and type of nanoparticle covering (e.g., only A- or B-type covering), the particles can segregate into the centers of the corresponding compatible domains (these being lamellae or cylinders), forming nanowire-like structures that extend throughout the material (Figure 4). In effect, the interplay between micro phase separation and favorable interactions do result in the self-assembly of spatially ordered nanocomposites.

Should these particles be, for instance, metals or semiconductors, these systems could constitute a sort of nanoelectrode array, which could be utilized to fabricate organized nanodevices. On the other hand, for a different covering type (e.g.,

A6B6), the particles segregate at the interfaces (figure 5) instead of the centers of the lamellae (or cylinders).
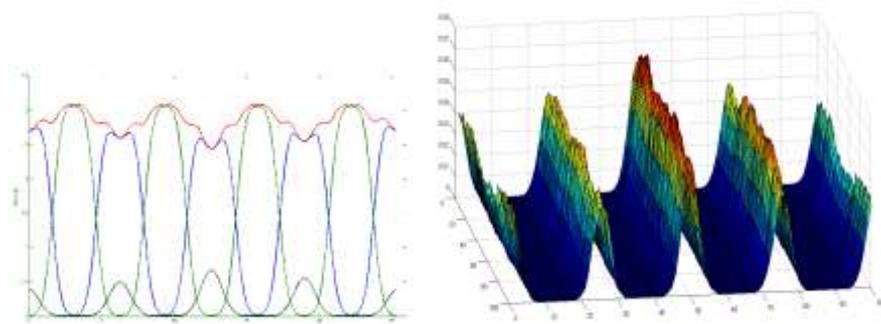

Fig. 4. distribution of a (or B) covered nanoparticles in diblock copolymers: nanoparticles are located in the center of each domain; left: distribution of the nanoparticles with respect to the copolymer domains; right: position of the center of mass of the nanoparticles.
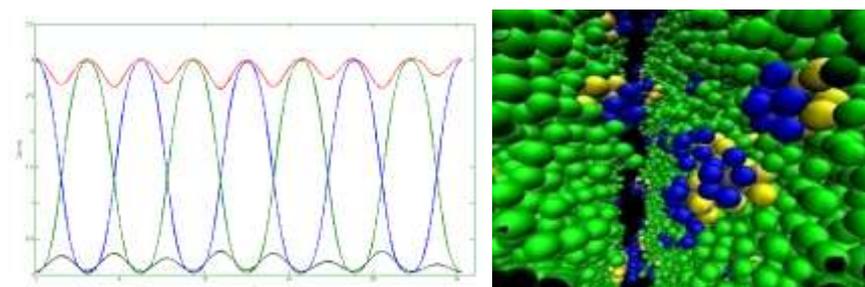

Fig. 5: distribution of A and B equal coverage nanoparticles in diblock copolymers: nanoparticles are located at the interface of the domains; left: distribution of the nanoparticles with respect to the copolymer domains; right: 3D representation of the nanoparticles at the interface.

In these cases, for instance, if the copolymer matrix was to be dissolved from the system, the remaining inorganic phase could give origin to a nonporous material, with a regular arrangement of uniform pores, which could find applications, for instance, in separation or catalytic processes.

The results also indicate that the morphologies of the organic/ inorganic hybrid materials can be tailored by adding particles of specific size and chemistry. The findings highlight the fact that, in such complex mixtures, it is not simply the ordering of the copolymers that templates the spatial organization of the particles: the particles do not play a passive role and can affect the self-assembly of the polymeric chains. In fact, we detected a phase transition from the hexagonal to lamellar morphology induced by a nonselective (i.e., A6B6(h)) block-particle interaction, indication that the particles actively contribute to the determination of the system structure.

In conclusion, the proposed multiscale computational approach, which combines atomistic and mesoscale simulations, can yield important information for the design of systems with desired morphology for novel applications.

Polymer - carbon nanotubes system.

Carbon Nanotubes (CNT) are interesting for several applications in different fields: structural, electromagnetic, chemical and mechanical. They have already been used as composite fibres in polymers and concrete to improve the mechanical, thermal and electrical properties of the bulk product. In this example we show one application of computer simulations involving CNT, namely the simulation at mesoscale level of the structure of a polymer CNT system. For simulating the mesoscale morphology of the system, information at atomistic level is necessary. This information is obtained in a 'multiscale' fashion. Firstly the same model of CNT developed for the atomistic simulation of the gas adsorption is used to determine the Flory – Huggins interaction parameters of the CNT for different diameters. This is obtained directly from the definition of cohesive energy by running two different simulation, one of the CNT in the bundle and another one with a single CNT isolated. The difference in the energy is the so-called 'bundling-debundling energy'. For the polymer the traditional approach to calculate the Flory – Huggins interaction parameter in MD and MC is followed [11].
A comparison of the interaction parameters obtained shows that only CNT of a given diameter are soluble in a given polymer. The calculations enable to predict the CNT diameter to be used for obtaining a homogeneous mixture.
The Flory Huggins interaction calculated by molecular modelling are then used at mesoscale level with a particle based method (DPD) for determining the mesoscopic structure of a CNT – polymer system. Recently these approaches has been used [12] for simulating the morphology of a polymer CNT system and simulate with FEM code the electric conductance as a function of copolymer morphology.

Conclusions

In this paper we have introduced the concept of multiscale molecular modelling and discussed the general guidelines for its implementation. The multiscale molecular modelling is applied in many fields of the material science, but it is particularly important in the polymer science, due to the wide range of phenomena accruing at different scales (from quantum chemistry to the mesoscale) influencing the final property of the materials. In this context, multiscale molecular modelling can play a crucial role in the design of new materials whose properties are influenced by the structure at nanoscale.

Multiscale molecular modelling can also be successfully used in process system engineering for the estimation of properties for pure components and mixtures in all cases in which the component data banks properties and interaction parameters of constitutive equations are missing.

Examples have been reported in this paper showing the methodology and describing the simulation protocols. A general good agreement in the comparison with experimental literature data of mechanical properties and morphologies is obtained, thus showing that the multiscale molecular modelling is a mature tool that may be used in the design and development of new coatings. Advances in computational materials science in general will continue to facilitate the understanding of materials and materials processing, the prediction of properties and behaviour, and the design of new materials and new materials phases, thus facilitating the application of process system engineering to more sophisticated and innovative processes.

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