

## Abstract

Most material simulation studies have been previously investigated individually by atomistic /molecular level microscopic calculations and by characteristics-predictable macroscopic simulations. Recently, the necessity for relating the characteristics of materials as chemicals with the behavior of materials as macroscopic objects is observed. Progresses in multi-scale simulation for cooperating spatially-temporally different calculation methods and in meso-scale simulation for the intermediate region between micro- and macroscopic scales are expected to satisfy this necessity. The present paper gives a conspectus of the background of such a necessity and of the related calculation techniques and presents a brief introduction to the methods appearing in the present special issue.

Keywords

Multiscale simulation, Mesoscopic simulation, Atomistic simulation, Molecular simulations, Fluid dynamics, Electronic state, Finite element method, Polyelectrolyte membrane, Porous media, Polycristalline

## 1. Introduction

Many concepts of new types of advanced materials have been recently proposed, e.g., nano-materials, porous/meso-porous materials, multilayered membranes, self-assembled materials, biomimetic materials, and structure/morphology controlled materials. Most of these concepts are based on a characteristic structure describable within the scale of the assembly of molecules. This scale is typically 10-100 nm and possibly includes 100 or more numbers in terms of small molecules. Because the characteristics of these materials strongly depend on the structure in such scales, the medium should not be considered as a homogeneous one. When the lifetime or the degradation of real materials is considered, inhomogeneity is an indispensable term. Considering destruction by metal fatigue as a typical example, it is easy to find the importance of inhomogeneity in usually available materials. In addition, biological cells are very important examples of inhomogeneous structures within the scale noted here. We call such a scale the "mesoscale" and we need to investigate meso-scale inhomogeneity as an important factor for studying the characteristic structures of both advanced and conventional materials.

Recently, trends in research on theoretical computation at a molecular level seem to be changing. Molecular computation has thus far pursued the expansion of the scale by developing the theory and method and improving performance of computer architecture. There are now signs that effective computational forecasting can be performed by developing models with an awareness of the hierarchy in nature. Substances that can be treated homogeneously in the macroscopic scale should be considered as groups of atoms or molecules at the resolutions definable using highperformance electron microscopes. The atoms and/or molecules construct the characteristic structure by themselves in the scale of the molecular assembly. Such a characteristic structure is smeared out to become homogeneous in the macroscopic scale of space. The problem is the composition of materials that appear to differ depending on the scale of space under observation. In other words, the new research trends are aimed at creating an effective method for forecasting the physical properties of a material by combining systematic characteristic methods in several scales of space. Computation methods with hierarchical levels can be called "multi-scale" material simulations. Standard computation methods have been proposed for



Fig. 1 Typical material simulation techniques arranged on the spatial natural hierarchy level.<sup>a)</sup>
a) This figure was drawn based on an idea introduced by Yamamoto, S. of Toyota Central R&D Labs. Inc.

several systems of materials.<sup>1-3)</sup>

In this conspectus of this special issue, several techniques for mesoscopic simulations and advanced theoretical models for electronic state calculation in extended systems are briefly explained with the relations among parts of them. The electronic structure is the most fundamental property of materials for the purposes of material design based on the knowledge at a molecular level. Although the variety of the techniques and the models, introduced here, might be incomplete, most of them are well noticeable methods both in the present and in the near future computational material investigations. Figure 1 shows typical material simulation techniques arranged on a spatial natural hierarchy level for reference. Lastly, the methods described in the papers in this special issue are introduced in the relation among those explained in this paper.

## 2. Methods of mesoscopic simulation

In the fluid mechanical analysis of many component systems for example, the calculation process becomes more complicated as realizing the model for analysis. We need the calculation process that is premised on the analysis of many component systems. One opinion for developing such a process is to employ the time-dependent Ginzburg-Landau theory or the dynamic density functional theory,<sup>4-7</sup> in which the Smoluchowski equation for the density distribution is solved on a lattice as a function of time, by relating the evolution of the local order parameter or densities to variations in the free energy via the proper Onsager kinetic coefficients.<sup>8</sup>

The theoretical foundations of the density functional methods (DFM) are based on the concept that the intrinsic Helmholtz free energy of a fluid that exhibits a spatially varying equilibrium density  $\rho(r)$ , is a unique functional  $F[\rho]$  and is independent of the applied external fields for a given intermolecular potential.<sup>9)</sup> An exact knowledge of  $F[\rho]$  allows obtaining in a self-consistent fashion the profile  $\rho(r)$  and all the spatial correlation via functional differentiation. The phase ordering dynamics of liquids has been based in schematic model Hamiltonians of the Ginzburg-Landau type, which neglect the microscopic structure or on heuristic approximations for the free energy.<sup>10)</sup> For solving nonlinear equations of the time-development of a density profile  $\rho(r)$ , real space grid methods such as finite difference methods are usually used,<sup>11)</sup> due to the time-consuming computations of Fourier transform calculations. The DFM can usually be classified into a category of real space grid methods. Extended versions of the DFM have been already developed for explicitly counting the timedevelopment of dynamical systems and are denoted the time dependent density functional method (TDDFM). Most TDDFM's have been based on stochastic equations like the Langevin equation, the Fokker-Planck equation, and so on.

As an alternative, to simulate fluid systems in an off-lattice representation, a method known as dissipative particle dynamics (DPD)<sup>12, 13)</sup> can be taken account. In this technique, the fluid system is described by particles that act as centers of mass, where each particle represents several numbers of atoms. They repel each particle other with a soft repulsive interaction force and extra noise and friction are added. If this is performed in a wellspecified manner, the time evolution yields the correct equilibrium statistical mechanics in the NVT ensemble and all hydrodynamic interactions.<sup>14-16)</sup> DPD can be naturally applicable to the analysis of many component systems based on its foundation. The simulation of vesicle formation was applied as a problem, which has not been simulated explicitly with the technique of molecular dynamics level calculations,<sup>17)</sup> for example. The interaction parameters of each DPD particle can be constructed by interatomic interaction parameters based on explicit molecular structures.

There has been a lot of investigations on the timedevelopment of nonlinear systems based on simple models of the inter-lattice interaction between neighboring lattice points. These models can be classified into a category of cellular automata type one. Of the various automata type models of nonlinear systems, the lattice Boltzmann method (LBM) offers important benefits in that it can fully recover the Navier-Stokes equations at the macroscopic scale, it deals with the fluid properties at the microkinetic level, it is capable of handling complex boundary conditions, and it is capable of various thermodynamic properties of a fluid system, such as multiphase flows.<sup>18)</sup> The characteristics of the LBM render it applicable to the simulations of mesoscopic structural formations. The recovering condition of the LBM for the diffusion equation has also been found recently.<sup>19)</sup>

The phase-field method (PFM)<sup>20)</sup> can be also taken account for the simulation of mesoscopic structural formations. The PFM is one of the numerical methods for solving the time-dependent Ginzburg-Landau equations. This method calculates the dynamics of many degrees of order parameters. For example, the structure of a polycrystal and the domain structure of liquid crystals can be analyzed by this method.

Within coarse graining methods such as the DPD, the internal degree of freedom for each coarse grained particle is not usually considered. This situation means that the coarse graining methods are difficult to calculate a system having a multicomponent order parameter, such as the orientation of a micro-crystal, etc., although they are based on simple and useful process for calculating the timedevelopment of multi-component density distribution. Conversely, multi-components of order parameters can be considered under PFM by assigning them to each lattice point on a numerical spatial grid. We should therefore select a suitable technique for the simulation of mesoscopic structure formations for each objective system.

For suitable selection among the variety of mesoscopic simulation methods, a wide choice of the methods is convenient for practical usage. A system of mesoscopic simulation for polymer technology was recently released by the national project "Research and Development of the Platform for Designing High Functional Materials" in Japan.<sup>2, 21)</sup> The system, named "OCTA", has a wide choice of mesoscopic simulation methods with wide range of spatial hierarchy on a cooperatively usable platform. The OCTA system is constructed from a simple and coarse-graining molecular dynamics code, a rheology simulator code based on the dual slip-link model for entangled polymer systems, a dynamical mean field calculation (one of the family of the DFM) code for phase separation of polymer blends, and a finite element calculation code for dispersive structural simulations for various problems of

polymer blends, with a cooperatively usable platform. We can choose a suitable mesoscopic method in the OCTA system. An example for a hierarchical simulation within the mesoscopic level was reported using the OCTA system.<sup>22)</sup> The effects of miscibility and polydispersity in chain length on the interfacial strength of polymer blend were analyzed for polypropylene/elastomer systems based on molecular dynamics simulation in which the initial configuration of polymer molecules derived by the distribution of volume fraction using the dynamical mean field calculation with density biased Monte Carlo method. While the yield phenomenon was dominated by a void formation in the bulk phase for the monodisperse system, that of the polydisperse system was found to be dominated by the failure of the interface where the long chains are depleted.<sup>23)</sup> This is a good example for a multiscale simulation within the mesoscopic level of polymer systems.

# 3. Multiscale simulation for lower level of natural hierarchy

Many simulation techniques have been advanced for macroscopic problems. The dynamics of materials, structural analysis, fluid dynamics, and so on are growing to supply indispensable tools for both academic and industrial fields. System designs based on information from those numerical calculations are commonly realized now. Introducing the parameterized material constants into a numerical equation, the characteristics of such a system are possibly understood and then the system design can be realized. However, information, what should be exactly synthesized, cannot be directly introduced from material constants. They can determine only the requested condition of the material under consideration. Synthesis chemists can not choose what kinds of materials should be synthesized within only such information. Syntheses based on trial and error processes are frequently challenged, and their sufficiency for given conditions are checked in realistic systems in a step-by-step manner. The names of the elements or molecules should be explicitly proposed in this design process. For this purpose, the electronic structure is likely understood

to be the most fundamental property of noticed materials. The reactivity of the states under investigation is also defined from the electronic state. If the interatomic potential parameters are well established for a noticed material, the thermochemical properties can be deduced by molecular dynamics or molecular mechanics simulations. Such a situation, however, cannot usually be expected. Especially for unknown materials, the parameter-reproducing process should inevitably be analyzed. Information on the electronic state is strongly needed for completeness, general applicability, and the requirements for fundamental knowledge on a realistic material design. As commonly acceptable understandings, the lowest level of the natural hierarchy can be decided as the levels of electronic states within the field of material sciences and technologies. Lower levels of the general hierarchy of nature, such as the quark, can be omitted here.

There are many types of theoretical models for calculating the electronic state in an arbitrary extended medium with large degree of freedom. Notable typical examples are the recently developed self-consistent reaction field  $(SCRF)^{24}$  approach, the quantum-mechanics/molecular-mechanics  $(QM/MM)^{25}$  hybrid method, the reference-interaction-site-model self-consistent field (RISM-SCF)<sup>26</sup> approach, the dipped adcluster model (DAM),<sup>27)</sup> etc.

The electronic state calculation of an adsorbed molecule on a material surface usually uses the cluster model and/or the slab model for the structure of the molecular-adsorbed surface. The cluster model assumes that an isolated assembled system can describe a part of the adsorbed surface structures. The slab model, on the other hand, adopts the two-dimensional periodic boundary condition for the adsorbed surface structures. The amount of surface atoms accounted for in both models is not large because of the limitation of computational resources. Equilibration between the electrons in the bulk metal material and that in the adsorbed molecule cannot be considered correctly in The electrostatic boundary those models. conditions, which are macroscopically definable, also cannot be taken in those models. Nakatsuji

successfully defined a scheme to satisfy the electron equilibration and the electrostatic boundary conditions.<sup>27)</sup> Nakatsuji and coworkers applied the model based on this definition, which they called the dipped adcluster model (DAM), to many kinds of surface adsorption and successfully described interesting surface phenomena.<sup>28)</sup>

The electrostatic potential, which satisfies the boundary conditions determined by the macro- or mesoscopic structure in a noticed system, is added to the corresponding Hamiltonian as an external potential term in those calculations. A similar treatment of electrostatic potential was also proposed in the electronic state calculation of a molecule in solution with dielectric continuum media (SCRF).<sup>24)</sup> In this theoretical model, the dipole moment in a cavity, which is apparently defined in the dielectric continuum medium, is calculated by the conventional molecular orbital method, and the induced electrostatic field in dielectrics and the reactively induced field in the cavity are accounted for. This reaction field is added into the Hamiltonian for the conventional molecular orbital calculation as an external potential, and the molecular structure and the dipole moment are then calculated iteratively to find the energy minimum. Electrostatic potential models of the environmental structure have been successfully applied to express characteristic experimental data for many corresponding systems. The environmental structure in these cases, however, is not as complicated as the meso-scale structural environment. The structure has a simple boundary, and most of the region to be considered can be treated as a homogeneous medium. For general purposes, the process to explicitly define more complicated mesoscopic structures is needed to be introduced.

There has been reported a lot of works using an explicit molecular configuration around the region for calculating electronic states. In contrary with the continuum models such as the SCRF, the structural constraint within the molecular assemble level can be introduced into electronic state calculations under calculation technique of classical mechanical methods. These methods can be called as "extended cluster models". The so-called QM/MM methods<sup>25)</sup> consider the explicit configurations of molecules,

divide the entire region into two subsystems for quantum mechanical calculation and classical mechanical calculation, respectively, and calculate the total energy classically using the results of the quantum mechanical electronic state calculation. The atomic configurations in the region for quantum mechanical calculation are restricted with the surrounding atomic configurations in the extended region for classical mechanical calculations. The ONIOM method<sup>29)</sup> is slightly different from the QM/MM methods. Energy calculations are performed for the total system, without distinguishing between the character of each region, and for each subsystem based on the theories suitable for each calculated region. The boundary following outermost contours of each subsystem should be terminated by some suitable techniques, such as hydrogen termination and capped atom termination, etc. The focusing region should be treated by the most accurate method in this model calculation. The correct energy in the focusing region can be estimated by correct counting energy differences between the resulted energies in each region with different levels of calculations. The process for estimating the correct energy in the focusing region is similar to the method of the Born-Haber cycle<sup>30)</sup> for thermo-dynamics calculation.

The readers of the present paper will understand that there are two types of calculation methods for multiscale calculation at the electronic structure level and these are illustrated in **Fig. 2**. One is based on the continuum models, which can treat the effects



Fig. 2 Two types of typical methods in multiscale calculation with an electronic level.a) an extended cluster model method.b) a continuum medium method.

of the surrounding medium in relatively large scales. The explicit configurations of surrounding atoms/molecules, of course, cannot be accounted for with this type of the model without any extensions. The other type is the extended cluster model and this can treat the configurations of surrounding atoms/molecules explicitly. In contrary to this merit, the extended cluster model method does not mention the constrained condition described by large scale configurations. Both methods seem to be suitable for the electronic states surrounded by homogeneous environments, because the details in the configurations will be smeared out under homogeneous conditions. When we treat mesoscopic structural information explicitly, however, the details in the configuration will be indispensable terms in counting the effects of the surrounding environment for electronic state calculations. The situation has not yet been sufficient for developing multiscale calculation with electronic structure level.

It can be also understood by the readers the possibility for combining the continuum model with the extended cluster model. Although it is not so difficult process at basic concept levels of simulations, there has been appeared few reports on such extensions. Ogata et al. recently reported a hybrid finite-element/molecular-dynamics/ electronic-density-functional approach to materials simulations on parallel computing.<sup>31)</sup> The finite element method (FEM) for continuum mechanics is coupled with the molecular dynamics method for an atomic system that embeds a cluster of atoms described quantum-mechanically with the electronic density-functional method based on real-space multi-grids. There is the handshake region between the finite-element and molecular-dynamics regions, in which the finite element mesh is refined down to the atomic scale in such a way that each finite element node coincides a molecular-dynamics atom. The electronic state calculations using the electronic density functional method are performed based on the ONIOM method mentioned above. Here, the readers must pay an attention to the difference between this electronic-density-functional method and the density functional method appeared in the mesoscopic simulation mentioned in section 2,

although they have the same name. A hybrid simulation of the oxidation of a Si(111) surface demonstrated a seamless coupling of the continuum region with the classical and quantum atomic ones. The applicability of the hybrid method has been shown explicitly by Ogata et al. Unfortunately, there still remains the development of a method for counting mesoscopic structures in the hierarchical simulation process in the present progress of the material simulations.

## 4. Construction of the present issue

In the previous two sections, the necessities and the varieties of mesoscopic and multiscale methods for material simulations are briefly explained. While the classical continuum model simulations have been commonly used in macroscopic material analyses, the quantum mechanical and/or atomistic simulations are now applicable also for practical usages. However, there has been a lack of mesoscopic simulation techniques in the wide region of spatial and temporal scales of material structures. The lack of mesoscopic simulation techniques has been started to be compensated within the previous decade. There are now several new and useful techniques of the mesoscopic material simulations. These new methods can be applied not only for the simulation of particular mesoscopic structures but also for compensation of the distance between macroscopic and microscopic techniques. The progresses of mesoscopic simulation techniques are indispensable for realizing the multiscale simulation of materials. The realization of multiscale simulation of materials is an important subject on material sciences and technologies because there are many kinds of physical theories suitable for different spatiotemporal scales of phenomena. Especially for the scale, in which the quantum mechanics plays an important role, special attentions should be paid for the realization of multiscale simulation techniques.

In the present issue of "Multiscale simulation for materials", three original papers on the application of mesoscopic simulations and attempts to multiscale simulations, especially related to atomistic levels on natural hierarchy, are appeared. Additionally, a commentary to a problem on cooperative simulation of quantum and classical simulation techniques is also appeared.

Dr. Yamamoto's paper deals with a hierarchical procedure for compensating the gap between mesoscopic and atomistic simulations mainly for polymer systems. The process appeared here is basically similar to that reported by Aoyagi et al.<sup>22)</sup> Both of them introduced a Monte Carlo method for mapping the molecular configurations into mesoscopic scale structures. The advantage of Yamamoto's method is that the construction of the mesoscopic structure from the atomistic model and the reconstruction of the atomistic configuration from the mesoscopic structure are inversely applicable through identical process each other. The basis of this reversible construction technique can be derived from the characteristics of the DPD method. Applications are shown for an ideal polymer blend system and a practical polyelectrolyte membrane system.

The second paper of this special issue, written by Dr. Hayashi, deals with the foundations of the LBM and its application to flow analyses in practical porous media. The readers can see the efficiency of the LBM in comparing with usual numerical methods for solving the Navier-Stokes equation in complex porous structures. An application of the LBM based on the mesoscopic structure which derived from the DPD simulations for polyelectrolyte membrane will be a good example of the multi-physics treatment of material simulations. Based on this application, a mesoscopic structure derived from atomistic information will be able to be transferred into the characteristic behavior of a macroscopic flow in porous media. An important basis for multiscale material simulations from microscopic to macroscopic scales can be seen here.

The last research paper reports a possible method for electronic state calculations under a mesoscopic inhomogeneous environment. The flexibility of the basis functions for usual quantum chemical calculations might not be enough for electronic state calculations in inhomogeneous fields. As a fully flexible basis function, the shape function of the FEM is introduced here. Because the FEM must take huge amounts of spatial grid points for steeply varying quantities, such as a wavefunction near nuclei, a primitive application of the FEM is

unsatisfactory technique to electronic state calculations at the molecular level unfortunately. A mixed basis function with Gaussian basis functions and the shape functions of the FEM are introduced as a new technique on a usage of basis functions in the electronic state theory. This method can be classified as one of the multiscale techniques for the simultaneous treatment of different-scale spatiallyvarying quantities. The slowly varying wavefunctions around whole system and the steeply varying wavefunctions near nuclei are simultaneously treatable with different types of basis functions in a self-consistent-field calculation. An application of this method to the simplest electron system, hydrogen atom, in an inhomogeneous field derived from a complex mesoscopic structure is introduced here. Although there have been reported many models for calculating electronic states in extended surrounding medium explained in section 3, the study on the paper of Yamakawa and Hyodo is possibly the first application on the electronic state calculation in explicit complex mesoscale structures.

Lastly, a commentary to a problem on cooperative simulation of quantum and classical simulation techniques is also included. This problem relates to what is called the problem of measurement for a quantum mechanical system, which has not yet been completely solved since the beginnings of the quantum mechanics. Most chemists and physicists in the material science field have paid little attention to this problem previously. With the advance of material science in new areas of research, typically nano-science and nano-technology, hierarchical concepts for the basis of theoretical treatments have gained interest. Following this situation, the problems on the quantum theory of measurement must be addressed, because the correct understanding on the interaction between quantum and classical systems must be taken. A recent way for avoiding these problems is given here as a commentary, although no final conclusion has been established yet.

The present issue of "Multiscale simulation for materials" introduces parts of works on the applications of advanced mesoscopic simulations and about their attempts to multiscale simulations, progressing at Toyota Central R & D Labs., Inc., especially those related to atomistic levels on natural hierarchy. These works do not, of course, fully cover the whole of the related simulation methods. However, they are expected to show some important and extendable approaches in this field. The previous lack of mesoscopic simulation techniques in the wide region of spatiotemporal scales of material structures is thought to cause an unfortunate restriction on practical applications of quantum mechanical and/or atomistic simulation techniques. It is expected to be understood the present feature of mesoscopic and multiscale material simulations from these present papers. Techniques for the practical prediction of macroscopic material characters have progressed on the basis of microscopic information, and the promising advances in the field of practical material designs will be realized.

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