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Hierarchical and large-scale atomistic simulations for practical materials

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To realize practical material design based on atomistic and/or molecular level of information, the hierarchical concept will make very promising procedure. The present paper reported the present status of such hierarchical material simulations according to the recent attempts progressed at the present author's group. As examples, amphiphile aqueous solutions as self-assembly systems, polyelectrolyte membrane as a proton conducting medium for fuel cells, and thick oil films as lubricating systems were reviewed for important applications of mesoscopic coarse-graining, hierarchical and large-scale all-atom molecular dynamics simulations, respectively, from their recent investigations. In spite of practical meanings of these results, there are some strict restrictions in these simulation techniques. Such issues to be solved are indicated according to the results of these practical applications. As one possible approach to the improvement, newly derived coarse-graining equation of motion is exhibited.

Keywords: Hierarchical material simulation; Large-scale atomistic simulation; Mesoscopic structure of amphiphile aqueous solutions; Hydrated polyelectrolyte membrane; Lubricant oil

1. Introduction

Many concepts of new types of advanced materials have recently been proposed, i.e.; nano-materials, porous/mesoporous materials, multilayered membranes, self-assembled materials, biomimetic materials, structure/morphology controlled materials, etc. Most of them are based on a characteristically describable structure within the scale of the assembly of molecules. This scale is typically 10–100 nm, possibly including 100 or more numbers in terms of small molecules and they construct larger scale structures or morphologies. Because the characteristics of the above advanced materials strongly depend on the structure in such a scale, the medium focused on should not be considered as a homogeneous one. When the lifetime or the degradation of real materials is considered, the inhomogeneity would be an indispensable term. Considering destruction by metal fatigue as a typical example, it is easy to find the importance of the inhomogeneity in usually available materials. We should investigate the mesoscale inhomogeneity as an important factor for studying characteristic structure in not only advanced materials but also conventional real ones.

Recently, trends in research on theoretical computation at a molecular level seem to be changing. Molecular computation has thus far pursued the extension of the scale by developing the theory and method and improving performance of computer architecture. Now an effective computational forecasting will be possible by developing models with an awareness of the hierarchy in the nature. Atoms and/or molecules construct the characteristic structure on the scale of the molecular assembly by themselves, even if substances can be treated homogeneously on a macroscopic scale. Such a characteristic structure is smeared out to become homogeneous on the macroscopic scale of space. The problem is the composition of a material that appears differently depending on the scale of the space under observation. Standard computation methods and/or general concepts have been proposed for several systems of materials [1–6].

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. The system design based on information from these numerical calculations is commonly proceeding

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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 deduced from material constants. They can determine only the requested condition of material under consideration. Synthesis chemists could not choose what kinds of materials should be synthesized within only such information. Syntheses based on trial and error processes are frequently challenged, and the sufficiency for given conditions is checked in realistic systems, step by step. The names of elements or molecules should be explicitly proposed in such a design process. For this purpose, the electronic structure is likely understood to be the most fundamental property of noticed materials. 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. We should, therefore, notice that information on the electronic state is strongly needed for completeness, general applicability and the requirement for fundamental knowledge on a realistic material design [6].

Previously, we reported an example of cooperative simulation at the microscopic and mesoscopic levels for hydrated polyelectrolyte (Nafion[®]) membranes [7,8]. This hierarchical simulation was performed from the structural formula of the Nafion[®] molecule to the electronic state of a hydronium ion in the hydrated Nafion[®] membrane through the mesoscopic structure of the membrane. This example represents a practical one of an electronic structure calculation within a mesoscopic inhomogeneous structural environment. Unfortunately, the connection between the polyelectrolyte molecular structure and the mesoscopic structure in polyelectrolyte membrane has still stayed at an example of “*modeling*” [9] for mesoscopic structural simulations. It is, therefore, required to develop coarse-graining methods which present a definite relationship between molecular and mesoscopic levels. In order to make sure an explicit process of hierarchical structural simulation of materials, on the other hand, very large-scale molecular simulation should be performed so that its results are directly compared with ones derived from simulations of upper hierarchical level.

In this paper, the present situations on mesoscopic coarse-graining, hierarchical and large-scale atomistic simulations would be reviewed mainly based on our recent investigations. Amphiphile aqueous solutions as self-assembly systems, polyelectrolyte membrane as a proton-conducting medium for fuel cells, and thick oil films as lubricating systems are reported as important applications of each simulation, respectively. In spite of practical

meanings of these results, some improvement should be made on these simulation techniques. As one possible approach to the improvement, newly derived coarse-graining equation of motion is exhibited here. This equation of motion has explicit relation to information at the atomistic scale and comprehends a couple of another well-known equation of motions.

2. Coarse-graining dynamics simulation for mesoscopic structure formation

The dissipative particle dynamics (DPD) [10–12] method is noticed as one useful simulation technique to reproduce mesoscale structure formations. Simultaneously, several artifacts have been also indicated on its temporal development and been ascribed them to the nature of assemblies constructed by soft repulsive potentials [13–15]. 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 other particles by a soft repulsive interaction force, and in addition, extra noise and friction are incorporated. If this is done in a well-specified way, the time evolution yields the correct equilibrium statistical mechanics in the NVT ensemble and all hydrodynamic interactions [11,16,17]. The DPD can be naturally applicable to the analysis of many component systems based on its foundation. For example, the simulation of vesicle formation was applied as a problem, which has not been simulated explicitly with the technique of molecular dynamics level calculations [18]. The interaction parameters of each DPD particle can be constructed by interatomic interaction parameters based on explicit molecular structures. Several methods to overcome the artifacts originating from time integration have been recently proposed [19–21].

Amphiphilic molecule solutions are typical examples of self-assembly systems. They can form spherical micelles, rod-like or spheroidal micelles, bilayer membranes, and vesicles (or liposomes). A stable type and shape of aggregates depend on the temperature, pressure, concentration and molecular structure of the amphiphile. In these structures, vesicles are biologically important in terms of separability of the solution for various applications such as drug delivery systems and artificial cells. They are also indispensable chemicals as molds (or templates) for mesoporous materials [22,23]. The amount of molecules is so large that atomistic simulation is hard to be adopted. To investigate the nature of such systems, therefore, coarse-graining approaches are seemingly helpful.

We have tried to apply the DPD to investigate self-assembly processes of vesicle forming [18], budding and fission dynamics of two-component vesicles [24], and the mechanism in crossing dynamics at an entanglement point of amphiphilic threadlike micelles [25]. In most of the previous theoretical studies on bilayer membranes and vesicles, coarse-grained surface models have been used in which the membranes are treated as smooth and

continuous thin surfaces [26–29]. Shape transformation of the vesicles is successfully understood by these continuum models based on the minimum bending energy of the membrane. However, in these models, the molecular structures of the amphiphile are not taken into account explicitly. On the other hand, molecular dynamics approaches have been attempted to investigate the structure and dynamics of lipid bilayers [30–36]. Though an atomistic approach is a powerful tool for understanding the structures and dynamics of bilayer membranes, they are restricted to a relatively small number of molecules due to the limitation of computation time. Instead of atomistic models, the coarse-grained amphiphilic molecules are adopted to investigate self-assembly into various types of micelles and vesicles.

Our DPD simulations essentially followed the Groot and Warren procedure [11]. Careful attention is of course paid to dynamical simulation conditions. Especially on threadlike micelle system, the parameters of conservative force and initial velocities were carefully chosen because the simulations were performed on weak collision process of two threadlike micelles under the periodic boundary condition [25]. Amphiphilic molecules were modeled by one hydrophilic head group and several hydrophobic tail groups. Characteristics of amphiphilic molecules are depicted by hydrophobicity of each DPD coarse-grained particle. The mesoscopic structures of amphiphile assemblies were essentially described by length and shape of hydrophobic tail groups.

Figure 1 shows the dynamics of aggregation and the vesicle formation process from the randomly dispersed systems at 9.7 vol% of A_1B_3 , A_2B_5 and $A_2(B_3)_2$ type amphiphiles aqueous solutions. Here, A indicates hydrophilic head groups, while B denotes hydrophobic tail groups. The behaviour of the largest cluster for all three types of amphiphiles and the number of water particles encapsulated in the cluster are drawn. The aggregation process with two-tailed amphiphiles $A_2(B_3)_2$ is faster because their radius of gyration is larger and the probability to meet with other amphiphiles is higher than with the single-tailed model. This feature was also observed in Monte Carlo simulation by Bernardes [37].

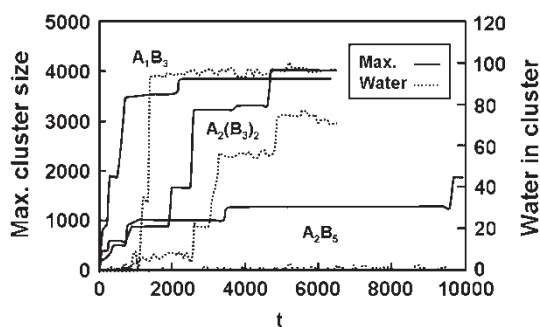


Figure 1. Dynamics of the aggregation process of amphiphiles in aqueous solution at 9.7 vol% of A_1B_3 , A_2B_5 , and $A_2(B_3)_2$ type amphiphiles aqueous solutions, showing the number of the largest clusters of amphiphiles and that of the water particles encapsulated in the cluster.

In contrast with this, the relatively large single-tailed model A_2B_5 shows slow dynamics of aggregation, and it seems that a much larger number of amphiphiles should be required to form the vesicle. From this figure, it is understood that, after several steps in which the number of cluster sizes reaches a critical value that is sufficient to form a transitory stable structure, vesicle is spontaneously formed. We performed additional simulations from different initial distributions of amphiphiles, and results similar to these described above were obtained. Our results show spontaneous formation of vesicle in every case investigated here. This means that each initial condition is under non-equilibrium one. Many sampling is required for quantitative investigations in such cases, but it is very difficult to meet sufficient conditions. The readers should pay attention to that the exact values of the number of aggregation and aggregation times have less meaning but qualitative estimations.

The internal degree of freedom in each coarse-grained particle is not usually considered in DPD simulations. This means that systems having multi-component order parameter, such as the orientation of a micro-crystal, etc. are difficult to calculate via DPD, although they make simple and useful process for calculating the time-development of multi-component density distribution. The phase-field method (PFM) [38,39] can be also taken account as another candidate for a simulation of mesoscopic structural formation [6]. 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 [40] and the domain structure of liquid crystals [41], etc. can be applied by this method. Multi-components of order parameters can be considered via PFM by assigning them to each lattice point on a numerical spatial grid. We should, therefore, select a suitable technique for simulation of mesoscopic structure formation for each objective system.

3. Hierarchical simulation of proton-conducting polyelectrolyte membrane

Previously, we demonstrated a DPD simulation coupled with realistic coarse-graining interaction parameters for binary polymer blends in order to examine a procedure for cooperation of atomistic and mesoscopic simulations [6,42]. A molecular configuration was generated based on the obtained mesoscopic structure by mapping atoms to the concentration profile of each DPD component using a Monte Carlo technique. This process was also applied to reproduce the atomistic structure of a water channel based on the mesoscopic structure of hydrated Nafion[®] membrane [43]. Aoyagi *et al.* reported the molecular mechanism of the strain–stress behaviour of the ABA type triblock copolymer using the similar procedure, combining mesoscopic self-consistent field calculation and molecular dynamics simulation [44]. Although such a

process can adequately reproduce the atomistic configuration restricted by the mesoscopic structure, it does not provide information on the constrained condition operating directly upon electronic states. Electronic state calculations under a mesoscopic inhomogeneous environment must be performed involving this type of constrained condition when charge distribution or the distribution of dielectric constant varies spatially to an appreciable extent. Electronic state calculations for a subsystem of a hydrated Nafion[®] membrane is a possible example in which such a calculation process is necessary, as the dielectric constants of the Nafion[®] and water regions differ considerably.

A result of electronic state calculation of a hydronium ion in a hydrated Nafion[®] membrane [8] is represented here. Electrostatic potential applied on a hydronium ion was calculated explicitly, accounting for the ambient electrostatic energy imparted by the mesoscopic structure. The electrostatic potential was treated as an additional potential of an electronic state Kohn–Sham equation [45], and the electronic state was then calculated for the hydronium ion based on the Gaussian-FE mixed basis method [46]. The distribution of dielectric constants was defined on the basis of the mesoscopic structure, and the hydronium ion was then placed in the water region. In figure 2, a hydronium ion is set at position A which is 0.14 nm distant from the nearest point on the surface of a DPD particle which contains a sulfonic acid group, or at position B with 1.5 nm distance. By iteratively solving the Poisson equation for the electrostatic potential and the Kohn–Sham equation for the electronic state, the energy of the hydronium ion was obtained. We compared the stability of hydronium ion in the mesoscopic structure and found that position B is more 48 kcal/mol stable than position A due to the dielectric polarization effect of the

mesoscopic structure. Notice here, hydration of each ion hinders direct connection of ions in general. The Gauss-FE mixed basis method is one promising technique of molecular electronic-structure calculations under the conditions in mesoscopic inhomogeneous environments [47] using the shape functions of the finite element method as sufficiently flexible basis functions, developed in our laboratory [46].

In order to perform a multi-scale or a hierarchical simulation for hydrated polyelectrolyte membrane, first we must divide the polymer molecule into coarse-grained particles having preferable compositions of atoms. If the level of coarse-graining is too large, the characteristics of molecular structure will be smeared out and such a simulation gives no meaning on material designs at molecular levels. The way of dividing a molecular structure strongly depends on chemical sense of each person. After the composition of each particle is decided, we must deduce the interaction parameters of particles based on the atomistic compositions. It is reasonable that such parameters should be defined by the average of interatomic interactions among all pairs of atoms belonging to each neighbouring coarse-grained particle. This assumption forces us to consider every meaningful configurations appearing in each coarse-grained particle. We, therefore, performed molecular dynamics or Monte Carlo simulation to deduce the average interatomic forces under sufficient amounts of configurations of atoms [7,8,42,43]. This process needs suitable skill for molecular simulations. The present situation of such a coarse-graining procedure cannot be called as well established process for general usage. We should think that the hierarchical procedure still stays at an example of “*modeling*” on mesoscopic structural simulations. We are trying to develop coarse-graining methods which present definite relationship between atomistic and mesoscopic levels as one possible treatment and will briefly discuss it in a latter section.

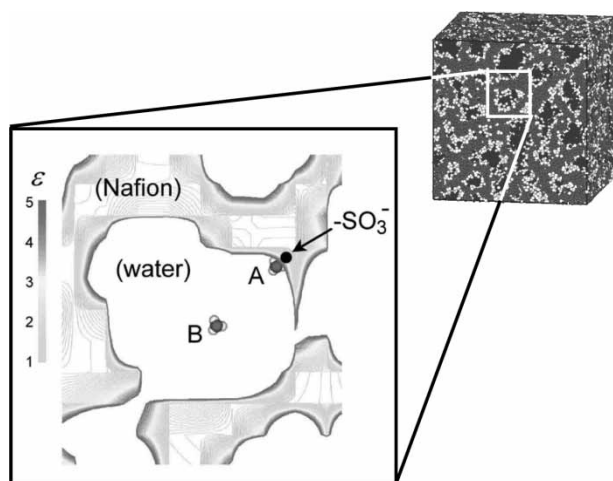


Figure 2. Hydronium ions in the water cluster of the hydrated Nafion[®] membrane for the water content $\text{H}_2\text{O}/\text{SO}_3\text{H} = 11.8$. The distribution of the dielectric constant in the Nafion[®] region is indicated by the contours. A cube at right hand side indicates mesoscale structure of Nafion[®] membrane reproduced via a DPD simulation. Dark regions show water clusters, while light gray regions indicate aggregates of polymer. White circles mean hydrophilic parts of Nafion[®] molecules.

4. Large-scale atomistic simulation of lubricating oil film

Machine elements in which large loads are transmitted such as traction drive continuously variable transmission (CVT) work in the elastohydrodynamic lubrication (EHL) regime [48]. Molecular dynamic behaviour of oil film under EHL has not been well understood since long trajectories of ensembles of large number of fluid molecules are required to analyze drastic phase transition invoked by high pressure [49]. Typical practical EHL condition is in film thickness of submicron order and in shear rate of under 10^6 s^{-1} . Although this film thickness exceeds the range of van der Waals force of solid wall, behaviour of fluid layer differs from bulk, i.e. traction coefficients (tractional horizontal force divided by normal load) cannot easily deduce from bulk shear viscosity.

Washizu and coworkers found that intramolecular degrees of freedom played important role on EHL mechanism by analyzing momentum transfer on typical fluid molecules of *n*-hexane, cyclohexane and dicyclohexyl via all-atom molecular dynamics simulation under the condition on film thicknesses and shear rates are 1–10 nm and 10^7 – 10^9 s⁻¹, respectively, [50]. Conditions of their numerical analyses were not consistent with realistic ones, i.e. several 100 nm film thickness and 10^6 s⁻¹ shear rate. Although they found the simulated traction coefficients were approaching to realistic ones by decreasing film thickness and by increasing shear rate, numerical confirmations for larger scale lubricant systems are still required to understand realistic EHL mechanism. Unfortunately, the role of intramolecular degrees of freedom on such high pressure systems avoids usual coarse-graining treatments on mesoscale dynamics simulations. Usual ways in coarse-graining completely ignore internal degree of freedom, therefore, it is required to develop coarse-graining methods which present a definite relationship between molecular and mesoscopic levels. In order to make sure an explicit process of such coarse-graining simulations, very large-scale molecular simulation should be performed so that its results are directly compared with ones derived from simulations of upper hierarchical levels. Therefore, we performed large-scale all-atom molecular dynamics simulations of EHL lubricating film of submicron thickness [51].

Fluid layer is confined between two confronting solid α -Fe walls under constant normal force. Traction simulations are performed by applying relative sliding motion on the walls. The *n*-hexane fluid molecules are treated dynamically using AMBER force field. RESPA was used to integrate the equations of motion. The temperatures are controlled to 350 K using Nosé-Hover formalism. Solver was parallelized by MPI and MD run was done via up to 24 nodes of HITACHI SR11000 of NAREGI project [52].

In fluid simulation with film thickness of 430 nm (figure 3), the mean traction coefficient was found to reach

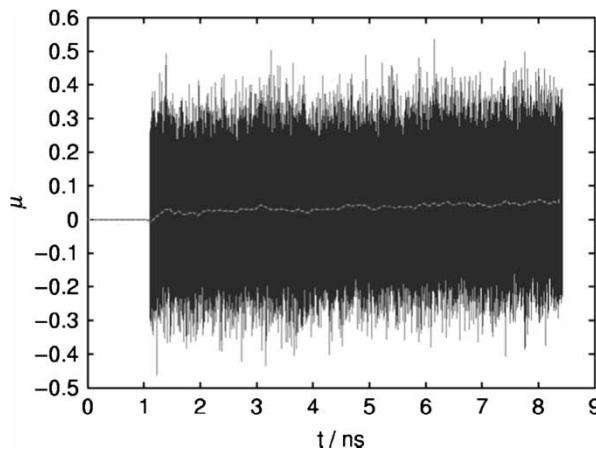


Figure 3. Time evolution of traction coefficient μ of *n*-Hexane fluid at thickness of about 430 nm and at a sliding speed of 1 m/s. Black line is the result of the simulation and the gray line represents the fitting curve.

0.04. While there still remains a slight difference from experimental value of 0.02, we can find that our result is comparable with experiment. Saturation from high traction coefficients in the range of small film thickness and high shear rate were analyzed in context of wall effect. Figure 4 shows pressure dependence on traction coefficients. Transition of traction behaviour is observed around 0.5–1.0 GPa which corresponds to viscoelastic region to plastic–elastic region which are experimentally observed [50].

5. Coarse-grained equation of motion based on atomistic picture

We already know that the choice of ensemble is very important to deduce conservative force parameters in the DPD simulation based on atomistic information. The hierarchical procedure explained in section 3 still stays at an example of “modeling” on mesoscopic structural simulations. The role of intramolecular degrees of freedom in EHL systems avoids usual coarse-graining treatments on mesoscale dynamics simulations as is introduced in section 4. It is, therefore, required to develop coarse-graining methods which present definite relationship between atomistic and mesoscopic levels.

We derived an equation of motion for the coarse-grained particles by using projection operator method [53,54] and calculated the mean force between coarse-grained particles by molecular dynamics simulations [55]. The idea of coarse-graining we adopt here is to divide the total N_t molecules into N groups (or clusters) which consist of n_α ($\alpha = 1, \dots, N$) molecules, and regard each molecular group as a coarse-grained particle. To derive the equation of motion for the coarse-graining particles, we introduce projection operator [54] P and $Q = I - P$ and divide Liouville equation for the phase space density for coarse-graining particles, $f_S(\hat{\Gamma}_S(t); \Gamma_S)$, as;

$$\frac{\partial}{\partial t} f_S(\hat{\Gamma}_S(t); \Gamma_S) = P i L f_S(\hat{\Gamma}_S(t); \Gamma_S) + Q i L f_S(\hat{\Gamma}_S(t); \Gamma_S) \quad (1)$$

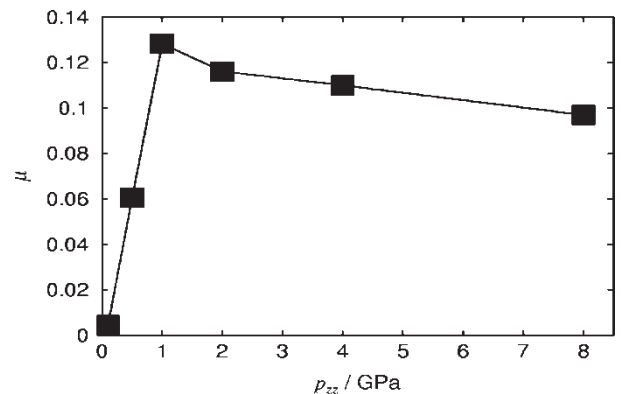


Figure 4. Effect of normal pressure p_{zz} on the traction coefficient μ of *n*-Hexane fluid at thickness of 10 nm and at a sliding speed of 1 m/s.

where $\hat{\Gamma}_S \equiv \{\hat{\mathbf{R}}_\alpha, \hat{\mathbf{P}}_\alpha\}$ denotes the positions and momenta of the center of mass of the coarse-graining particles. We obtained the equation of motion for the coarse-grained particles by integration of a derived equation from equation (1) with multiplying \mathbf{P}_σ ,

$$\begin{aligned} \frac{d}{dt} \hat{\mathbf{P}}_\sigma(t) = & \sum_{\alpha \neq \sigma} \langle \mathbf{F}_{\sigma\alpha} \rangle_{\Gamma_S} \\ & - \frac{\beta}{2} \sum_{\eta \neq \sigma} \sum_{\alpha} \sum_{\beta} \int_0^t ds \langle \delta \mathbf{F}_{\sigma\eta}^Q(t-s)^T \delta \mathbf{F}_{\alpha\beta}^Q(0) \rangle \mathbf{V}_{\alpha\beta} \\ & + \sum_{\alpha \neq \sigma} \delta \mathbf{F}_{\sigma\alpha}^Q(t), \end{aligned} \quad (2)$$

where $\langle \cdots \rangle_{\Gamma_S}$ denotes an average with fixed $\hat{\Gamma}_S$. The meaning of the first, second and third terms are the mean force, the friction force and the fluctuation force, respectively. We also showed correspondence of equation (2) to Brownian dynamics [56] and DPD. In equation (2), all the terms are related to the atomistic information. Then we performed molecular dynamics simulation with such constraint to calculate the mean force. All resulting forces show peaks at some distances and do not diverge even at close distance. Because amount of the mean force should depend on the size of coarse-graining particles, it is appropriate to scale the force and distance. The scaled mean forces show universality which correspond to that of the conventional conservative force in DPD.

The projection operator method is a useful technique to eliminate fast variables [53,57,58]. Although general formulation is given for the coarse-graining via the projection operator, explicit knowledge on the linkage between these formulations and conventional coarse-grained simulation methods has still not been satisfied. Kampen and Oppenheim derived the equation for Brownian motion for single Brownian particle from first principles [59]. Coarse-grained equations for single chain in polymer melt [60], a one-dimensional harmonic chain [61] and three-dimensional harmonic lattices [62] have been also derived using the projection operator method. These derivations are for specific systems, hence farther extension should be advanced. Our resultant equation of motion, equation (2), shows explicit linkage between atomistic and mesoscale coarse-grained simulation methods. The information needed to execute the coarse-graining simulations can be directly calculated by using MD simulations [63].

6. Concluding remarks

As examples to show the present situations on material simulations based on information at the molecular scale, amphiphile aqueous solutions as self-assembly systems, polyelectrolyte membrane as a proton conducting medium for fuel cells, and thick oil films as lubricating systems were

reviewed for important applications of mesoscopic coarse-graining, hierarchical, and large-scale all-atom molecular dynamics simulations, respectively, from our recent investigations. In spite of practical meanings of these results, there are some strict restrictions in these simulation techniques. Such issues to be solved are indicated according to the results of these practical applications. As one possible approach to the improvement, newly derived coarse-graining equation of motion is exhibited here. This equation of motion has explicit relation to information at the atomistic scale and comprehends Brownian dynamics and DPD equation of motions.

The present report describes our group's attempts on material simulations based on information at the molecular scale, including a procedure for calculating electronic states at the molecular level for inhomogeneous materials. The use of such a procedure can be expected to yield useful information regarding material structures and properties via various suitable simulation methods for mesoscopic structure formation.

Finding a procedure to make a connection between meso- and macro-scale phenomena is also an indispensable issue on practical material simulations. Macroscopic boundary conditions must affect mesoscopic structures and properties in practical inhomogeneous materials. Manifold active investigations should be required for improving the method of hierarchical material simulations.

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- [9] In general, modeling in theoretical/computational studies is of coarse important because that it can introduce a realistic and/or essential description to the nature of the problem. However, a success of introducing a special procedure to describe a specific feature in the problem sometimes makes misleading as it has general applicability to related problems. Such a procedure frequently contains adjusting processes on parameter fixing or term selection in an approximate equation. Keeping proper conditions is very difficult, and the result sometimes depends on the person selected and that it requires a lot of chemical sense. In such a situation, modeling in theoretical expression and/or computation procedure cannot have any generality in its descriptions. The author would like to express such a feature of modeling by the quoted term of ‘modeling’ here.
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