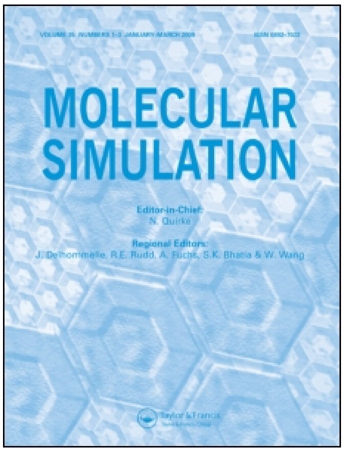

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Shi-Aki Hyodo[a]
[a] Computational Physics Laboratory, Toyota Central R&D Labs., Inc., Nagakute, Aichi, Japan

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A Procedure for Molecular Electronic State Calculation in Inhomogeneous Materials

SHI-AKI HYODO*

Computational Physics Laboratory, Toyota Central R&D Labs., Inc., Nagakute, Aichi 480-1192, Japan

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A possible procedure for calculating the molecular electronic states in mesoscopic inhomogeneous structures is explained based on the results of simulations on different spatial scales. Electrostatic potential is discussed as an essential factor to connect the electronic characteristics of different scales. The procedure is demonstrated by applying the results of hierarchical simulations on the structural formula of a polyelectrolyte (Nafion, a DuPont trademark) molecule to the electronic state calculations for a hydronium ion in a hydrated Nafion membrane via the mesoscopic structure of the membrane. The mesoscopic simulation method adopted here is dissipative particle dynamics (DPD), which is a coarse graining simulation method with dissipative and randomly fluctuating force terms. A mixed basis function method is introduced for electronic state calculations in inhomogeneous fields as a combination of Gaussian basis functions and shape functions of the finite element method (FEM) for expressing electronic wavefunctions. The procedure of the multi-scale simulation represents a practical example of ones reproducing electronic structural information within a mesoscopic inhomogeneous structure.

Keywords: Multi-scale simulation; Electronic state calculation; Mesoscopic structure; Hydrated polyelectrolyte membrane

INTRODUCTION

It is now accepted that information regarding the electronic state of a material is of real practical use in the development of new materials. However, while the calculable size of molecular systems has increased dramatically through the development of new theories and methods for calculation and modeling and ever-increasing computing power, electronic state calculations for complex structures still require simplification of the theoretical or structural expressions in order to allow computation. For example, electronic state calculations are impossible for an entire material with nanometer-scale inhomogeneity by straightforward molecular orbital calculation. It should therefore be accepted that the current techniques for performing electronic state calculations are insufficient for practical materials design.

Quantum mechanical calculations and simulations based on classical physics represent effective means of determining electronic states and macroscopic properties, respectively. However, when such different types of calculation are applied directly and separately to each suitable problem, the electronic state information cannot be related directly to the macroscopic properties, rendering it impossible to rationally predict suitable elements for the construction of materials from the macroscopic property information. In this context, the synthesis of materials for specific applications has in general been performed by trial and error. This situation clearly gives rise to the necessity to investigate new methods for performing molecular electronic state calculations for inhomogeneous materials.

Numerous procedures for multi-scale or hierarchical simulations of material structures have been reported [1–3]. However, even though the information on an electronic structural level is essential for evaluating material properties, explicit trials of multi-scale or hierarchical simulations involving electronic states have been less well studied. Hybrid quantum mechanics/molecular dynamics simulation based on an efficient method of molecular dynamics simulations for large systems has been directed towards obtaining electronic structural information for

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*Tel.: +81-561-63-4646. Fax: +81-561-63-5426. E-mail: e0668@mosk.tytlabs.co.jp

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inhomogeneous structures [4]. On the other hand, a process of simulation has been attempted based on the extraction of quantities that can be used to define the parameters of the model operatively on a larger scale from a smaller-scale simulation [5]. Unfortunately, the investigation of explicit procedures for calculating the electronic structure at a molecular level in materials with mesoscopic inhomogeneity does not appear to have been reported to date.

Previously, the concept of "meso-scale fusion" was introduced as a useful means of relating macroscopic information with microscopic information [6]. The conditions of macroscopic simulation can be deduced from the information at a microscopic level or from the electronic structure through an intermediate "meso-scale" via several transformation steps, and vice versa. The effectiveness of such a procedure was demonstrated through application to some discrete examples of calculations for different parts of the entire procedure [6], including (a) a mesoscopic structural simulation based on a component molecular structure, (b) a method for defining the atomistic configuration inversely from the mesoscopic structure, (c) an electronic state calculation under a hypothetical mesoscopic structure, and (d) an alternative electronic state calculation under a complex large-scale structure derived from a mesoscopic simulation.

The present paper reviews the progress made since the previous report and provides an example of cooperative simulation at the microscopic and mesoscopic levels for a hydrated polyelectrolyte (Nafion, a DuPont trademark) membrane. This multi-scale simulation was performed hierarchically, from the structural formula of the Nafion molecule to the electronic state of a hydronium ion in the hydrated Nafion membrane via the mesoscopic structure of the membrane. This multi-scale simulation represents a practical example of an electronic structure calculation under a mesoscopic inhomogeneous structural environment. The basis for the use of quantum mechanical calculations and classical physics simulations separately for the determination of the electronic states and mesoscopic structure is addressed first based on the density functional theory of electronic states.

BASIS FOR SEPARATION OF CLASSICAL AND QUANTUM SUBSYSTEMS

In order to perform hierarchical material simulations in combination with quantum mechanical calculations, it is necessary to consider the relationship between the quantum and classical subsystems within the region of interest. A quantum system is basically described in terms of a wavefunction, and exhibits long-range correlation originating from the coherent character of the wavefunction.[†] A classical system, on the other hand, can be described without information concerning wavefunction and does not show the coherency referred to in quantum theory. These two different subsystems must be related consistently.

In terms of density functional theory, exchange and correlation potentials can be defined by the local density. This means that the spatial correlations of exchange and correlation interactions are omitted within the framework of this theory. Therefore, the interaction between separate spatial points can only be considered to be classical Coulomb interactions. If the charge distribution of an objective system is defined explicitly in some way, the local electron distribution can definitely be described in terms of classical Coulomb potential, which is derived from the charge distribution, and local exchange-correlation potential. While the electron distribution on the microscopic scale must be described quantum mechanically using wavefunctions, macroscopic charge distribution can be defined by classical electrostatics under given boundary conditions. In other words, if a convergent electron density distribution for a macroscopic system was obtained by self-consistently solving a Kohn-Sham type differential equation [7] under density functional theory, the distribution would be identical to that derived by classical electrostatic calculation, except for microscopic fine structures. Although this represents a simple derivation from Hohenberg-Kohn theory [8] under local density and/or gradient expansion approximations, the concept is very important for separating a system into classical and quantum subsystems. Different methods of calculations can then be applied separately to different scales of structural information, and the structural information for larger scales based on classical Coulomb potential can be reflected to structures at smaller scales. If this conclusion could not be reached, the whole system might have to be calculated at a quantum mechanical level, which could only be performed when accurate information of the effects of the environment has been acquired. In this instance, the procedure of such calculations separately will be just a model to reduce computational cost. Thanks to the Hohenberg-Kohn theory,

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[†] A fundamental characteristic of macroscopic systems is that the system has a large degree of freedom and irreversibility. In the present text, only the problem of large degree of freedom is discussed, focusing on the multi-scale simulation procedure at different spatial scales. The term "long-range timescale" has meaning in a system with irreversibility, because the correlation of motion on a short-range time-scale will be smeared out for motions in a system having a large degree of freedom.

investigations using different types of separate calculations for different scales of phenomena can be progressed. Here, it must be stressed that explicit criterion for deciding the scale of a region in which the quantum mechanical picture should be applied has not been derived for the purpose of the qualitative discussion here. Such a problem is left for future investigation.

SIMULATION OF MESOSCOPIC STRUCTURE FORMATION

For mesoscopic-scale simulations, a calculation method premised on the analysis of a many-component system is necessary. Dissipative particle dynamics (DPD) [9,10,11] and the phase-field method (PFM) [12] are employed by our research group for the simulation of mesoscopic structure formation.

As an example of DPD simulation, the mesoscopic structure of hydrated Nafion membrane [13] is presented briefly. Nafion is a typical material used for polyelectrolyte membranes. The Nafion polymer molecule is modeled by connecting soft spherical particles that each corresponds to a group of several atoms and which are roughly 0.5 nm in diameter (Fig. 1a). The Flory-Huggins interaction parameters for DPD simulation are estimated based on the cohesive energies between DPD particles via a molecular simulation technique. DPD simulation reveals the spontaneous formation of a sponge-like structure, in which water particles and hydrophilic particles of Nafion side-chains form aggregates or clusters and become embedded in the hydrophobic phase of the Nafion backbone (Fig. 1b). The size and spacing of water clusters for 10–30 vol% water-content by this simulation are in agreement with experimental reports [13].

The PFM [12] can also be used in the simulation of mesoscopic structures. The PFM is a numerical method for solving the time-dependent Ginzburg-Landau equations, and for calculating the dynamics of many degrees of order parameters. For example, the morphology of polycrystals [14] and the domain structure of liquid crystals [15] can be analyzed by this method.

The microscopic and mesoscopic expressions can be intuitively related by a coarse graining process in DPD, as one DPD particle will correspond to a group of several atoms. In PFM, on the other hand, a variable in the basic equation is quite difficult to relate to microscopic quantities. The basic equation in PFM is based on phenomenological theory and is not derived explicitly from the microscopic structure within the coarse-grained region. Despite this difficulty, the PFM has the advantage of accounting for the internal degrees of freedom for each coarse-grained region, differing from DPD. An example application of PFM is presented in section "Electronic State Calculations in Mesoscopic Inhomogeneous Fields" for the construction of a mesoscopic inhomogeneous structure as an environment for a local electronic state calculation.

GAUSSIAN-FINITE ELEMENT MIXED BASIS METHOD FOR ELECTRONIC STATE CALCULATION AS A FLEXIBLE BASIS FUNCTION IN INHOMOGENEOUS FIELDS

The flexibility of the basis functions for usual quantum chemical calculations will be insufficient for electronic state calculations in inhomogeneous fields. The shape function of the finite element method (FEM) is therefore introduced here as a fully flexible basis function. As the FEM requires large numbers of spatial grid points for rapidly varying quantities such as wavefunctions near nuclei, a primitive application of the FEM is unfortunately unsatisfactory for electronic state calculations at the molecular level. A mixed basis function combining Gaussian basis functions and FEM shape functions (FE basis functions) is introduced as a new technique by which basis functions can be used in electronic

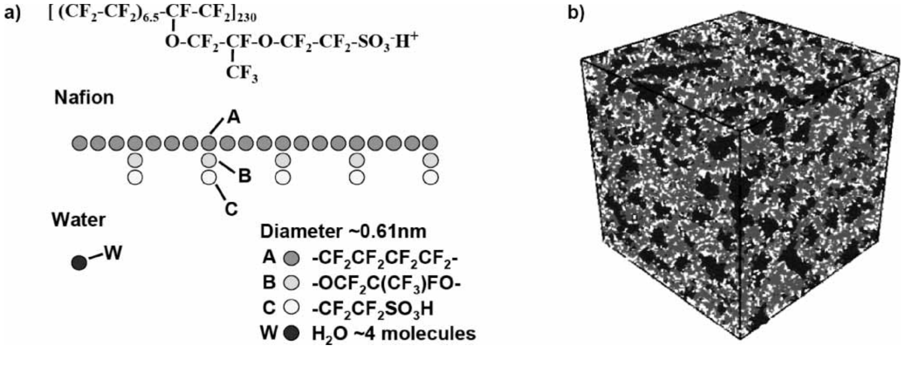

FIGURE 1 (a) DPD model for Nafion molecule and water, and (b) mesoscopic structure of Nafion membrane simulated by DPD.

state theory [16]. This method can be classified as a multi-scale technique for simultaneously treating spatially varying quantities of different scales. The slowly varying wavefunctions around an entire system and the steeply varying wavefunctions near nuclei can be treated simultaneously using different types of basis functions in a self-consistent-field calculation.

The Gaussian–FE mixed basis function method has been tested on H_2, AlH and Al_2 diatomic molecules and Al_4H clusters [16]. In these examples, Gaussian basis functions are used to express the steeply varying part and FE basis functions are employed to express the spreading part of the molecular orbital. The FE basis functions have also been shown to automatically compensate for parts of the wavefunction in the middle of chemical bonds, which cannot be expressed unerringly using Gaussian basis functions alone.

The example of H_2, in which both Gaussian basis functions and FE basis functions would effectively contribute, is considered here. The number of nodal points per dimension is 23, and the element width is set to 0.7 Bohr (1 Bohr ≈ 0.05291 nm) for all spatial elements. The calculation region is cubic with dimension of 15.4 Bohr, and the H—H distance is set at 1.4 Bohr. The Gaussian basis functions used here are defined as several parts of the usual 6-311G split valence type contracted Gaussian basis [17]. The contribution of the FE basis functions to the various Gaussian basis functions is then investigated. The electron energy of the 3G-FE mixed basis functions (3G of 6-311G and FE) is equivalent to that of the 311G** Gaussian basis functions alone. This is because the 3G basis functions express a steeply varying part and the FE basis functions express a spreading part, as shown in Fig. 2. The applicability of FEM to arbitrary boundary conditions can be maintained in the Gaussian–FE mixed basis technique by selecting suitable Gaussian basis components. Following the discussion in section "Basis for Separation of Classical and Quantum Subsystems", electronic state calculations should preferably be performed based on density functional theory. Application of the FEM to electronic state calculations is therefore convenient because the local properties of density functionals are suitable for constructing a sparse matrix for solving eigenvalue problems.

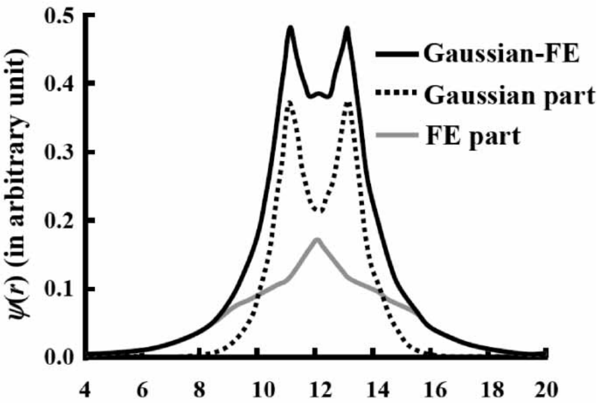

FIGURE 2 Molecular orbital $\psi(r)$ (arbitrary units) on a molecular axis of H_2 using 3G-FEM mixed basis functions. The abscissa n_{FEM} denotes the number of nodal points.

These test calculations demonstrate that the FE basis functions automatically compensate for the wavefunction part, which cannot be expressed by Gaussian basis functions alone. The molecular orbital, which spreads widely in the calculation space, is expected to be significantly influenced by the configuration of the inhomogeneous electrostatic field. In this method, FE basis functions, which are applicable to arbitrary boundary conditions, express the spreading part of the molecular orbital, while Gaussian basis functions express the steeply varying part. This mixed basis method is also available for electrostatic potential calculations in inhomogeneous charge distributions.

ELECTRONIC STATE CALCULATIONS IN MESOSCOPIC INHOMOGENEOUS FIELDS

After constructing a mesoscopic structure, the structure should be transformed into an inhomogeneous field and electronic state calculations should then be performed in that field. It is better to choose a sufficiently flexible method of electronic state calculation in order to respond to the inhomogeneity of the field.

The effectiveness of the Gaussian–FE mixed basis method for the purpose of calculating the electronic state in an inhomogeneous electrostatic field is investigated here. A model in which a hydrogen atom is positioned between two conductors is applied to discuss the electronic state of atoms/molecules at the grain boundary of the polycrystalline metal [18]. Spherical conductors and crystal grains are adopted as nanometer-scale conductors. The crystal grains were extracted from the polycrystalline structure by PFM simulation (Fig. 3). Here, the numerical method for solving the PFM equation is based on a finite difference with five-point reference sites with 100 × 100 × 100 grid points. The eigenvalue of the hydrogen atom was found to depend on the diameter of the spherical conductors when the diameter was less than 5 nm, and the wavefunction of the hydrogen atom was distorted due to the complex grain configuration (Fig. 4). The FE basis functions effectively represented the distortion of the wavefunction due to the existence of the inhomogeneous electrostatic field.

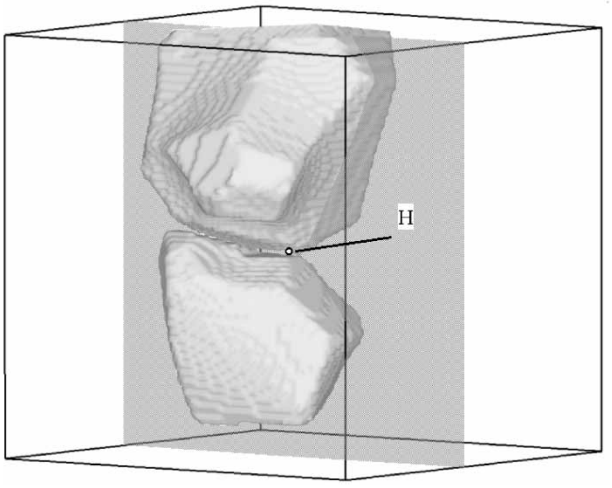

FIGURE 3 Polycrystalline model derived by the PFM. Small particle denotes the position of the H atom for the calculation in Fig. 4.

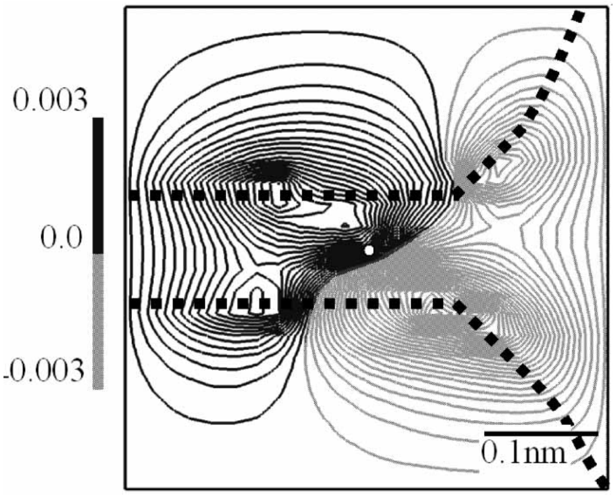

FIGURE 4 Contour map of wavefunction difference, (2 nm spherical conductor)—(Phase-Field grain). Broken lines denote the interface between grain and boundary regions.

MULTI-SCALE SIMULATION OF PROTON-CONDUCTING PERFLUORINATED SULFONIC ACID POLYELECTROLYTE (NAFION) MEMBRANE

A DPD simulation using realistic Flory-Huggins interaction parameters was shown in the previous report for binary polymer blends in order to derive a procedure for the cooperation of atomistic and mesoscopic simulations [6,19]. 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 can also be applied to the reproduction of the atomistic structure of a water channel based on the mesoscopic structure of a hydrated Nafion membrane (e.g. Fig. 1b) [20]. 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 on the electronic states. This type of constrained condition is typically described in terms of electrostatics, as was discussed in section "Basis for Separation of Classical and Quantum Subsystems" regarding the separation of a system into classical and quantum subsystems. Electronic state calculations under a mesoscopic inhomogeneous environment will involve this type of constrained condition when charge distribution or the distribution of dielectric constants varies spatially to an appreciable extent. Electronic state calculations for a subsystem of a hydrated Nafion membrane is an example in which such a calculation process is necessary, as the dielectric constants of the Nafion and water regions differ considerably.

The method is applied here to the electronic state calculations for a hydronium ion in a hydrated Nafion membrane [20] as an example. The electrostatic potential for a hydronium ion can be calculated explicitly, accounting for the ambient electrostatic energy imparted by the mesoscopic structure. The electrostatic potential can then be treated as an additional potential of an electronic state Kohn-Sham equation, and the electronic state can be calculated for the hydronium ion based on the Gaussian–FE mixed basis method. The distribution of dielectric constants is defined on the basis of the mesoscopic structure, and the hydronium ion is placed in the water region (Fig. 5). In this example, the distance

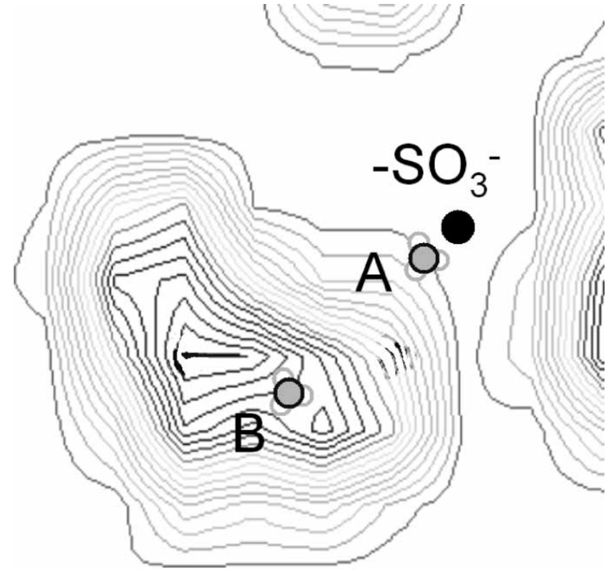

FIGURE 5 Hydronium ions in the water cluster of a hydrated Nafion membrane for a water content of $[H_2O]/[SO_3H] = 11.8$. The distribution of dielectric constants in the water region is indicated by the contours. A and B indicate the position of the hydronium ion calculated here.

from the sulfonic acid group is 0.14 nm at position A, and 1.5 nm at position B (Fig. 5). 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 can be obtained. Comparison of the stability of the hydronium ion in the mesoscopic structure reveals that a hydronium ion at position B is 48 kcal/mol more stable than at position A due to the dielectric polarization effect of the mesoscopic structure.

Although the above example represents a successful multi-scale or hierarchical simulation for a hydrated polyelectrolyte membrane, the electronic energy of each individual position in the inhomogeneous environment cannot be confirmed by experiment. Therefore, other quantities will need to be experimentally determined as a means of verification. Calculations of the diffusion constants of the hydronium ion and water in the water channel of a hydrated Nafion membrane are in reasonable agreement with experimental values as a preliminary investigation, and detailed analysis on this basis will be presented in a future report [21]. Although the possibility of including a calculation that treats an atomistic structure combining with an electrostatic constrained condition remains to be investigated, the multi-scale simulation presented in this report demonstrates that it is possible to extract electronic structural information in an inhomogeneous system.

SUMMARY

A simulation method that combines microscopic and mesoscopic levels was presented and applied to the simulation of a hydrated polyelectrolyte (Nafion) membrane. This report described the current state of multi-scale materials simulation in the author's research group.

The grounds on which quantum mechanical calculations and simulations of classical physics can be used separately for simulation of the electronic state and mesoscopic structure were discussed briefly based on the density functional theory of electronic states. A DPD simulation of the mesoscopic structure of a hydrated polyelectrolyte (Nafion) membrane was then presented, and the electronic structure of a hydronium ion in an inhomogeneous electrostatic field was calculated based on the mesoscopic structure derived by DPD simulation. A Gaussian–FE mixed basis method was introduced as a technique for calculating the electronic state of a molecule and local structure in an inhomogeneous environment. Availability of this mixed basis function method was examined by an electronic state calculation under a complex inhomogeneous electrostatic field derived from a mesoscopic structure determined by PFM. Calculations for a hydronium ion in the mesoscopic structure of a hydrated polyelectrolyte membrane were performed using the mixed basis function method.

The present report describes our group's attempts to construct 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.

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References

[1] Doi, M. (2002) "Material modeling platform", *J. Comput. Appl. Math.* **149**, 13.

[2] Aizawa, T., Prawoto, Y. and Tsumori, F. (2002) "Coupled, macro-micro modeling for hot deformation and sintering", *J. Comput. Appl. Math.* **149**, 307.

[3] Terada, K. and Kikuchi, N. (2001) "A class of general algorithms for multi-scale analyses of heterogeneous media", *Comput. Meth. Appl. Mech. Eng.* **190**, 5427.

[4] Ogata, S., Shimojo, F., Kalia, R.K., Nakano, A. and Vashishta, P. (2002) "Hibrid quantum mechanical/molecular dynamics simulation on parallel computers: density functional theory on real-space multigrids", *Comput. Phys. Commun.* **149**, 30.

[5] Nieminen, R.M. (2002) "From atomistic simulation towards multiscale modeling of materials", *J. Phys.* (Condensed matter) **14**, 2859.

[6] Hyodo, S. (2002) "Meso-scale fusion: a method for molecular electronic state calculation in inhomogeneous materials", *J. Comput. Appl. Math.* **149**, 101.

[7] Hohenberg, P. and Kohn, W. (1964) "Inhomogeneous electron gas", *Phys. Rev.* **136**, B864.

[8] Kohn, W. and Sham, L.J. (1965) "Self-consistent equations including exchange and correlation effects", *Phys. Rev.* **140**, A1133.

[9] Hoogerbrugge, P.J. and Koelman, J.M.V.A. (1992) "Simulating microscopic hydrodynamic phenomena with dissipative particle dynamics", *Europhys. Lett.* **19**, 155.

[10] Koelman, J.M.V.A. and Hoogerbrugge, P.J. (1993) "Dynamic simulations of hard-sphere suspensions under steady shear", *Europhys. Lett.* **21**, 363.

[11] Groot, R.D. and Warren, P.B. (1997) "Dissipative particle dynamics: bridging the gap between atomistic and mesoscopic simulation", *J. Chem. Phys.* **107**, 4423.

[12] Chen, L.-Q. (2002) "Phase-field models for microstructure evolution", *Annu. Rev. Mater. Res.* **32**, 113.

[13] Yamamoto, S. and Hyodo, S. (2003) "A computer simulation study of the mesoscopic structure of the polyelectrolyte membrane Nafion", *Polym. J.* **35**, 519.

[14] Chen, L.-Q. and Yang, W. (1994) "Computer simulation of the domain dynamics of a quenched system with a large number of nonconserved order parameters: the grain-growth kinetics", *Phys. Rev. B* **50**, 15752.

[15] Toth-Katona, T., Borzsonyi, T., Varadi, Z., Szabon, J., Buka, A., Gonzalez-Cinca, R., Ramirez-Piscina, L., Casademunt, J. and Hernandez-Machado, A. (1996) "Pattern formation during mesophase growth in a homologous series", *Phys. Rev. E* **54**, 1574.

[16] Yamakawa, S. and Hyodo, S. (2003) "Electronic state calculation of hydrogen in metal clusters based on

Gaussian–FEM mixed basis function", *J. Alloys Comp.* **356–357**, 231.

[17] Krishnan, R., Binkley, J.S., Seeger, R. and Pople, J.A. (1980) "Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions", *J. Chem. Phys.* **72**, 650.

[18] Yamakawa, S. and Hyodo, S. (2003) "Electronic state calculation for hydrogen atom under inhomogeneous field", *R & D Rev. Toyota CRDL* **38**, 26.

[19] Yamamoto, S. (2003) "Hierarchical procedure bridging the gap between mesoscopic and atomistic simulations for materials design", *R & D Rev. Toyota CRDL* **38**, 10.

[20] Yamamoto, S., Jinnouchi, R., Yamakawa, S. and Hyodo, S. "Atomistic simulation based on the mesoscopic structure of a polyelectrolyte membrane for fuel cells", (submitted).

[21] Yamamoto, S. and Hyodo, S. (in preparation).