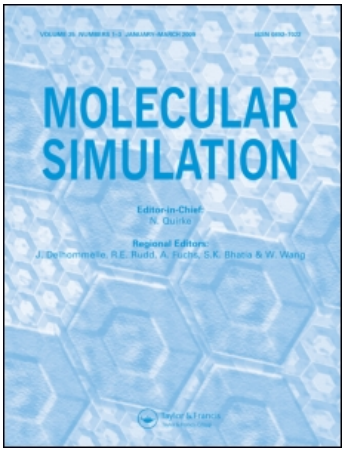

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Kinjo, T. and Hyodo, S.(2007) 'Linkage between atomistic and mesoscale coarse-grained simulation', Molecular Simulation, 33: 4, 417 — 420
To link to this Article: DOI: 10.1080/08927020601155436
URL: http://dx.doi.org/10.1080/08927020601155436

Molecular Simulation, Vol. 33, Nos. 4–5, 15–30 April 2007, 417–420

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Linkage between atomistic and mesoscale coarse-grained simulation

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(Received June 2006; in final form October 2006)

To reduce computational cost in large scale molecular simulations and to adjust the simulation methods to multiscale nature of complex materials, it is effective to treat several atoms (or molecules) as one element. Dissipative particle dynamics (DPD) and Brownian dynamics (BD) simulations are typical examples of such coarse-graining methods. In the coarse-grained (CG) simulation methods, linkage between molecular and mesoscale parameters is important to assess accuracy and applicability of these methods. For that purpose, we derived equation of motion for the CG particles by using projection operator method which will be appeared on a subsequent paper. In the derived equation, the force acting on the CG particles is divided into the mean force, friction force and random force. In this study, we calculated the mean force between CG particles by molecular dynamics (MD) simulations with constraints. We also showed the universality of the calculated mean forces.

Keywords: Coarse-graining; Mean force; Molecular dynamics simulation; Projection operator

1. Introduction

Many interesting phenomena in complex materials often span a range of length and time scales far beyond the molecular scale. For this reason, molecular dynamics (MD) simulation is presently incapable of handling whole perspective of the phenomena in complex materials. Coarse-graining of the description of the complex materials is a potent candidate to tackle such phenomena. In the case that a set of degrees of freedom (DOF) in the molecular system is thought to be unessential in the phenomena of interest, the set of DOF may be eliminated by averaging out. The elimination of the uninterested DOF is common starting point of coarse-grained (CG) simulation. In recent years, CG simulations such as Brownian dynamics (BD) and dissipative particle dynamics (DPD) have been widely used to various complex materials [1–3]. These coarse-graining methods are based on physical considerations; however, most of these methods are *ad hoc* in nature. For awareness of applicable scope and useful extension of the CG simulations, derivations of CG equations for the CG simulations should be evident.

The projection operator method is a useful tool for coarse-graining as an elimination of fast variables [4–6]. Although general formulation is given for the coarse-graining by the projection operator, there seems to be a lack of linkage between these formulations and conventional CG simulation methods. Kampen and Oppenheim [7] derived the equation for Brownian motion for single Brownian particle from first principles. CG equations for single chain in polymer melt [8], a one-dimensional harmonic chain [9] and three-dimensional harmonic lattices [10] are also derived using the projection operator method. These derivations are for specific systems; hence farther discussion should be advanced. In this paper, we investigate linkage between atomistic and mesoscale CG simulation methods. In our method, the information needed to execute the CG simulations can be calculated by using MD simulations.

2. Equation of motion for coarse-grained particles

Recently, we derived a CG equation of motion by using a projection operator. In this section, we describe the derivation briefly. Details of the derivation will be given in other paper [11]. The idea of coarse-graining we adopt here is to divide the total N_t atoms into N groups (or clusters) which consist of $n_\alpha, (\alpha = 1, \ldots, N)$ atoms and

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Molecular Simulation
ISSN 0892-7022 print/ISSN 1029-0435 online © 2007 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/08927020601155436

regard an atom group as a CG particle, as shown in figure 1. For classical systems, trajectories of the system $\hat{\mathbf{\Gamma}}(t) \equiv \{\hat{\mathbf{r}}_{\alpha i}(t), \hat{\mathbf{p}}_{\alpha i}(t)\}$ are determined completely by Hamilton's equation of motion. If the full atomistic information is not required, we may use a description of the system by coordinates and momenta of the center of mass (COM) of the CG particles.

$$\hat{\mathbf{R}}_\alpha \equiv \frac{\sum_i m_{\alpha i}\hat{\mathbf{r}}_{\alpha i}}{M_\alpha} \tag{1}$$

$$\hat{\mathbf{p}}_\alpha \equiv \sum_i \hat{\mathbf{p}}_{\alpha i} \tag{2}$$

$$\mathbf{M}_\alpha \equiv \sum_i m_{\alpha i} \tag{3}$$

where $m_{\alpha i}$ is mass of i-th atom in α-th CG particle. We define the phase space density for these variables as follows

$$f_s(\hat{\mathbf{\Gamma}}_s(t);\mathbf{\Gamma}_s) \equiv \delta(\hat{\mathbf{\Gamma}}_s(t) - \mathbf{\Gamma}_s) \equiv \prod_\alpha \delta(\hat{\mathbf{R}}_\alpha(t) - \mathbf{R}_\alpha)\delta(\hat{\mathbf{P}}_\alpha(t) - \mathbf{P}_\alpha), \tag{4}$$

where $\hat{\mathbf{\Gamma}}_s(t) \equiv \{\hat{\mathbf{R}}_\alpha, \hat{\mathbf{P}}_\alpha\}$ is a phase point in the phase space of COM and $\hat{\mathbf{\Gamma}}_s(t) \equiv \{\mathbf{R}_\alpha, \mathbf{P}_\alpha\}$ is a "relevant field variable" [12,13]. The phase space of the atomistic coordinates and the COM coordinates are referred to as Γ-space and Γ_s-space, respectively. The time evolution of $f_s(\hat{\mathbf{\Gamma}}_s(t);\mathbf{\Gamma}_s)$ along the trajectory in the Γ-space is written as

$$\left(\frac{\mathrm{d}}{\mathrm{d}t}\right)_\Gamma f_s = iL_s f_s. \tag{5}$$

In this form, the Liouville operator in the Γ_s-space is defined as

$$iL_s \equiv -\sum_\alpha \left\{\hat{\mathbf{F}}_\alpha \cdot \frac{\partial}{\partial \mathbf{P}_\alpha} + \frac{\hat{\mathbf{P}}_\alpha}{M_\alpha}\cdot\frac{\partial}{\partial \mathbf{R}_\alpha}\right\}, \tag{6}$$

where

$$\hat{\mathbf{F}}_\alpha \equiv \sum_{i=1}^{n_\alpha} \hat{\mathbf{f}}_{\alpha i} = -\sum_{i=1}^{n_\alpha} \frac{\partial U}{\partial \hat{\mathbf{r}}_{\alpha i}} \tag{7}$$

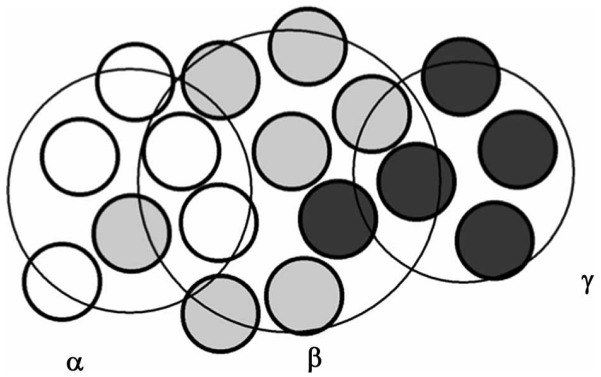

Figure 1. Schematic picture of CG particles. In this figure, three clusters as coarse grained particles, white (α), gray (β) and black (γ) are shown.

is sum of the force acting on atoms belonging to the CG particle α.

We introduce the projection operator P of an phase function $g(\hat{\mathbf{\Gamma}}(t))$ onto the Γ_s-space in the form [12,13],

$$Pg(\mathbf{\Gamma}(t)) = \int d\mathbf{\Gamma}'_s \int d\mathbf{\Gamma}''_s f_s(\hat{\mathbf{\Gamma}}_s(t_0);\mathbf{\Gamma}'_s)\langle f_s(\hat{\mathbf{\Gamma}}_s(t_0);\mathbf{\Gamma}'_s) f_s(\hat{\mathbf{\Gamma}}_s(t_0);\mathbf{\Gamma}''_s)\rangle^{-1} \times \langle f_s(\hat{\mathbf{\Gamma}}_s(t_0);\mathbf{\Gamma}''_s) g(\mathbf{\Gamma}(t))\rangle. \tag{8}$$

We divide the right-hand side of the equation of time evolution (5) by P and $Q \equiv 1 - P$.

$$\left(\frac{\mathrm{d}}{\mathrm{d}t}\right)_\Gamma f_s(\hat{\mathbf{\Gamma}}_s(t);\mathbf{\Gamma}_s) = PiLf_s(\hat{\mathbf{\Gamma}}_s(t);\mathbf{\Gamma}_s) + QiLf_s(\hat{\mathbf{\Gamma}}_s(t);\mathbf{\Gamma}_s). \tag{9}$$

Note that P is the projection onto a functional space which consists of "basis functions" f_s at time t. Straightforward arithmetic yields the time evolution equation for the phase space density $f_s(t)$. The result is in the form

$$\left(\frac{\mathrm{d}}{\mathrm{d}t}\right)_\Gamma f_s(\hat{\mathbf{\Gamma}}_s(t);\mathbf{\Gamma}_s) = \int d\Gamma'_s f_s(\hat{\mathbf{\Gamma}}_s(t);\mathbf{\Gamma}'_s) i\Omega(\mathbf{\Gamma}_s,\mathbf{\Gamma}'_s) + \int_0^t \mathrm{d}\tau \int d\Gamma'_s f_s(\hat{\mathbf{\Gamma}}_s(t-\tau);\mathbf{\Gamma}'_s) \times M(\mathbf{\Gamma}'_s,\mathbf{\Gamma}_s;\tau) + F(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}), \tag{10}$$

where $i\Omega$, M and F are frequency matrix, memory function and generalized random force, respectively.

The equation of motion for the coarse grained particles is obtained by integration of equation (10) with multiplying $\mathbf{P}_\sigma$.

$$\frac{\mathrm{d}}{\mathrm{d}t}\hat{\mathbf{P}}_\sigma = \frac{1}{\beta}\frac{\partial}{\partial \hat{\mathbf{R}}_\sigma}\ln\omega(\hat{\mathbf{R}}) - \beta\int_0^t \mathrm{d}s \left\langle \left[\delta\mathbf{F}^{\mathrm{Q}}_\sigma(t-\mathrm{s})\right]\left[\delta\mathbf{F}^{\mathrm{Q}}_\alpha(0)\right]^T\right\rangle \times \frac{\hat{\mathbf{P}}_\alpha(\mathrm{s})}{M_\alpha} + \delta\mathbf{F}^{\mathrm{Q}}_\sigma(t), \tag{11}$$

where

$$\omega(\mathbf{R}) \equiv \frac{\int \mathrm{d}\hat{\mathbf{r}}\,\delta(\hat{\mathbf{R}} - \mathbf{R})\,\mathrm{e}^{-\beta U}}{\int \mathrm{d}\hat{\mathbf{r}}\,\mathrm{e}^{-\beta U}}, \tag{12}$$

and

$$\delta\mathbf{F}^{\mathrm{Q}}_\sigma(t) \equiv \mathrm{e}^{-\mathrm{Q}iLt}\left[\hat{\mathbf{F}}_\sigma - \frac{1}{\beta}\frac{\partial}{\partial \mathbf{R}_\sigma}\ln\omega(\hat{\mathbf{R}})\right]. \tag{13}$$

In the above equations, we use notations $\hat{\mathbf{r}} \equiv \{\hat{\mathbf{r}}_{\alpha i}\}$and $\hat{\mathbf{R}} \equiv \{\hat{\mathbf{R}}_\alpha\}$. In the CG equation (11), the first, second and third terms of the right hand side are the mean force, friction force and random force, respectively.

3. Calculation of mean force between coarse-grained particles

All the terms of derived equation (11) are related to the inter-atomic forces clearly. Then, in principle, we can calculate them from the atomistic level information. The mean force between CG particles is especially important to execute a CG simulation. In this study, we calculate the mean force by using a MD simulation.

The mean force is written in the form,

$$\frac{1}{\beta}\frac{\partial}{\partial \mathbf{R}_\sigma}\ln\omega(\mathbf{R}) = \frac{1}{\beta}\frac{\left(\frac{\partial\omega}{\partial \mathbf{R}_\sigma}\right)}{\omega(\mathbf{R})} = \frac{\int \mathrm{d}\hat{\mathbf{r}}\,\delta(\hat{\mathbf{R}}-\mathbf{R})\left(-\frac{\partial U}{\partial \hat{\mathbf{R}}_\sigma}\right)}{\int \mathrm{d}\hat{\mathbf{r}}\,\delta(\hat{\mathbf{R}}-\mathbf{R})\mathrm{e}^{-\beta U}}$$

$$= \langle \mathbf{F}_\sigma\rangle_{\Gamma_\mathrm{s}} \tag{14}$$

where $\langle\cdots\rangle_{\Gamma\mathrm{s}}$ denotes an average with fixed $\hat{\mathbf{\Gamma}}_\mathrm{s}$. Because the mean force depends on the COM coordinates $\{\mathbf{R}_\alpha\}$, it is a multi-body force about the COM coordinates. In the particle-based simulation, calculation of multi-body forces is extremely expensive; therefore effective two-body forces are usually adopted. In this context, we assume that the mean force is decomposed to pair-wise additive terms as follows,

$$\langle \mathbf{F}_\sigma\rangle_{\Gamma_\mathrm{s}} = \sum_{\alpha\neq\sigma}\langle \mathbf{F}_\sigma\rangle_{R_{\alpha\sigma}}, \tag{15}$$

where

$$\langle \mathbf{F}_\sigma\rangle_{R_{\alpha\sigma}} \equiv \frac{\int \mathrm{d}\hat{\mathbf{r}}\,\delta(\hat{R}_{\alpha\sigma}-R_{\alpha\sigma})\mathbf{F}_\sigma\,\mathrm{e}^{-\beta U}}{\int \mathrm{d}\hat{\mathbf{r}}\,\delta(\hat{R}_{\alpha\sigma}-R_{\alpha\sigma})\,\mathrm{e}^{-\beta U}}. \tag{16}$$

is a statistical average with fixed $R_{\alpha\beta}$. With this assumption, we can calculate the mean force by MD simulation with such constraints. To calculate the mean force, we employ following constraints,

$$\frac{1}{N_\alpha}\sum_{i-1}^{n_\alpha}\mathbf{s}_{\alpha i}^2 = R_\mathrm{g}^2 = (\text{constant}) \tag{17}$$

$$(R_\alpha - R_\beta)^2 = (\text{constant}) \tag{18}$$

where

$$\mathbf{s}_{\alpha i} \equiv \mathbf{r}_{\alpha i} - \mathbf{R}_\alpha.$$

The first constraint is to avoid diffusion of constituent atoms of the CG particles. The dynamics under the constraints is different from the real dynamics of the system. In our calculations, the constraints are employed just to sample configurations of the constituent atoms. Using the constraints, we calculate the mean force for a Lennard–Jones fluid, inter-atomic potential of which is

$$\phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{20}$$

The mean force in the effective pairwise form can be calculated by averaging radial component of force acting on a CG particle which is in the form,

$$\mathbf{F}_\mathrm{eff}(R_{\alpha\beta}) = \left\langle \mathbf{F}_\alpha\cdot\frac{\mathbf{R}_{\alpha\beta}}{R_{\alpha\beta}}\right\rangle_{R_{\alpha\beta}} = -\left\langle \mathbf{F}_\beta\cdot\frac{\mathbf{R}_{\alpha\beta}}{R_{\alpha\beta}}\right\rangle_{R_{\alpha\beta}} \tag{21}$$

The results for various conditions are shown in figure 2. Degree of coarse-graining is indicated by number of constituent atoms n which are varied from $n = 4$ to 20 in this study. We introduce a packing parameter $d \equiv n/R_\mathrm{g}^3$ and execute calculations for the cases of $d = 6.0$ (a) and $d = 6.78$ (b). All calculated forces show peaks at some distances and do not diverse even in close distance. This "softness" of the potentials of mean force is quite different from inter-atomic forces most of which have hard repulsive core. The soft potential of mean force is studied by some authors. For the static properties of polymer solutions, Louis *et al.* showed that a "soft colloid" picture of polymer coils can be built on a "first principles" statistical mechanics foundation. They calculated the effective potential by Monte Carlo (MC) simulation of self-avoiding walks on a simple cubic lattice and the hyper-netted-chain (HNC) approximation [14]. Klapp *et al.* [15] investigated the origin of the "softness" of the effective potentials by MC simulation of two-dimensional rigid polymers. They showed that the origin of "softness"

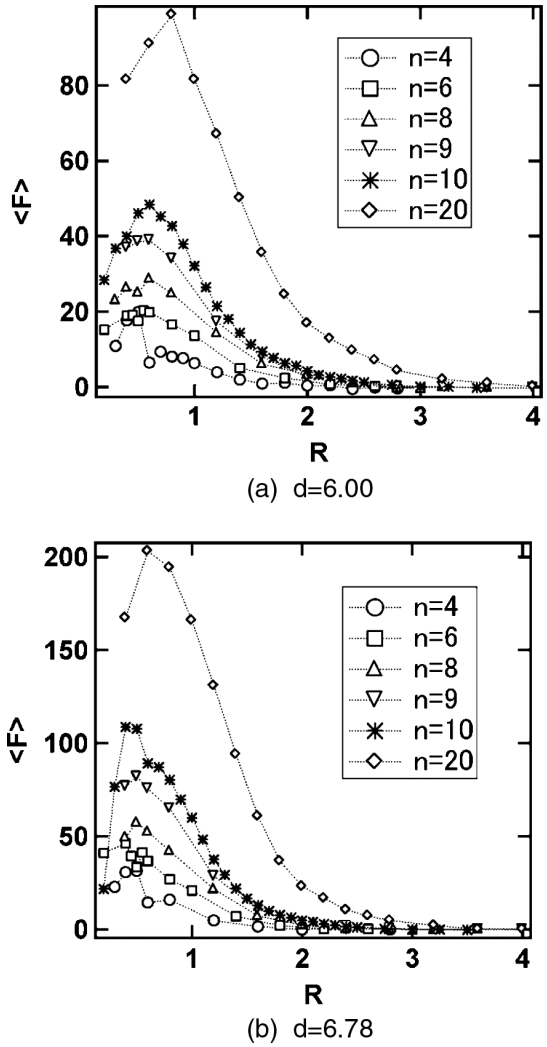

Figure 2. Mean force vs. distance are shown for (a) $d = 6.00$ and (b) $d = 6.78$. The larger number of constituent molecules indicates the larger force. The higher packing d also indicates the larger force.

can be explained roughly in terms of the free energy change occurring as the disc's overlap. Our method can treat off-lattice realistic molecular systems and take into account thermal fluctuation naturally.

Because the amount of the mean force should depend on the size of CG particles which is presented by the parameters n and R_g, it is appropriate to scale the force and distance by n and R_g, respectively. The scaled mean forces are shown in figure 3. In this figure, an universality of the mean forces are found for $R/R_g > 1$. This situation is correspond to the conventional conservative force in DPD in which [1],

$$\mathbf{F}^C(R_{\alpha\beta}) = \begin{cases} a\left(1 - \frac{R_{\alpha\beta}}{R_C}\right)\mathbf{e}_{\alpha\beta} & \text{for } R_{\alpha\beta} < R_C \\ 0 & \text{for } R_{\alpha\beta} \geq R_C \end{cases} \quad (22)$$

In this DPD model, differences in the properties of the CG particles appear only in the parameter a. Namely, for the both cases, the form of mean forces (or conservative forces) is independent of the degree of coarse-graining. As our calculations were done for a simple Lennard–Jones fluid, we should note that molecular fluid may exhibit more complex nature.

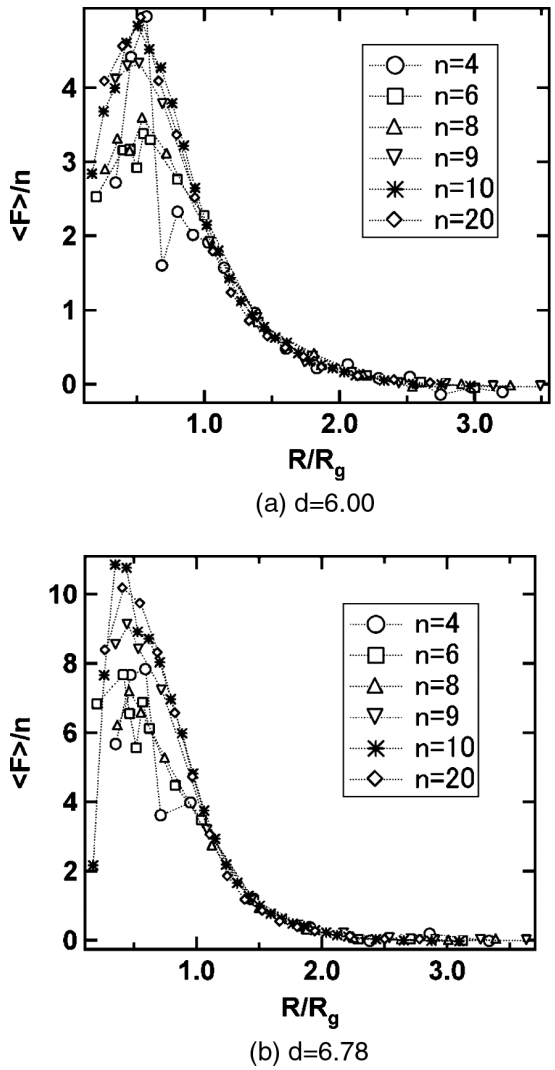

Figure 3. Scaled mean force vs. scaled distance are shown for (a) $d = 6.00$ and (b) $d = 6.78$. For the distance larger than gyration radius $R/R_g > 1$, all forces agree well in both cases.

4. Conclusions

We have extracted the mean forces by the projection operator method with an assumption that the time scales of COM motion and molecular motion are separable [11]. In this study, we calculated the mean force between two CG particles by MD simulations with the holonomic constraints. Although such mean forces have been calculated for some specific cases [14,15] elsewhere, our method of the MD simulation with the constraints allows us to calculate the mean forces for more general cases. Our calculation is for simple Lennard–Jones fluid, however, an extension to polymeric or molecular liquids is straightforward. By this calculation, the CG equation of motion is linked with atomistic description. Then the calculated mean forces can be used for a CG particle simulation which properly includes atomistic level information.

Acknowledgements

This work was supported by NAREGI Nanoscience Project from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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