Equation of motion for coarse-grained simulation based on microscopic description

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We have derived an equation of motion for coarse-grained particles by using a projection operator. Because the derived coarse-grained equation is based on microscopic description, it can be the basis for models of various coarse-grained simulations. We show that by substitution of random forces into fluctuating forces in the coarse-grained equation, the equations for Brownian dynamics and dissipative particle dynamics are reproduced.

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I. INTRODUCTION

Many concepts of new types of advanced materials have recently been proposed, i.e., nanomaterials, porous and mesoporous materials, multilayered membranes, self-assembled materials, biomimetic materials, structure and morphology controlled materials, etc. Most of them are based on a characteristic structure describable 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 can construct larger scale structures or morphologies. Because the characteristics of the above advanced materials strongly depend on the structure on such a scale, the medium focused on should not be considered as a homogeneous one. When the lifetime or the degradation of practical materials is considered, the inhomogeneity is 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. In addition to such an example, there are many interesting phenomena in complex materials which often span a range of length and time scales far beyond the molecular scales.

At the present time, full atomistic molecular dynamics (MD) simulations are mostly incapable of handling the entire perspective of the phenomena in complex materials. Coarse graining of the description of the complex materials is a potent candidate as a tool to tackle such phenomena. In the case where a set of degrees of freedom (DOF) in the molecular assembled system is thought to be unessential in the phenomena of interest, the set of DOFs may be eliminated by averaging out. The elimination of the uninteresting DOFs is a common starting point of the coarse-grained (CG) simulation. Recently, CG simulations such as dynamic density functional (or dynamic mean-field) (DMF), Brownian dynamics (BD), dissipative particle dynamics (DPD), and so on have been widely applied to various complex materials [1–9]. These coarse-graining methods are based on physical considerations; however, most of these methods are *ad hoc* in nature. For awareness of the applicable scope and useful extension of the CG simulations, derivations of coarse-grained equations for the CG simulations should be evident.

The term "coarse graining" has been regularly used to describe macroscopic properties of the objective system in standard statistical mechanics [10–12]. Let us divide here the hierarchy of phenomena in the system into two levels; the upper level and lower level; the upper one expresses rather extensive and coarse information on structures and/or states, and the lower one explicitly includes more detailed information on structures and/or states. We do not need all of the detailed information, but some kind of averaged information is needed to represent the quantity of material on the upper level. The procedure for obtaining such information is coarse graining, and it corresponds to extracting a DOF concerning the survey of physical properties for the investigation by averaging out the other DOFs. The procedure for coarse graining seems to have already been established in standard statistical mechanics. Unfortunately, the standard coarse-graining procedure in statistical mechanics has still not fulfilled the requirement for constructing a simulation method for mesoscopically inhomogeneous structures. Well-established procedures would be useful to analyze the entire macroscopic properties of the system based on a microscopic nature. In order to construct a procedure for mesoscopic structure simulations, it should be required to find a coarse-graining procedure having explicit relations between different regions at the hierarchy of the extensive (upper) level of mesoscopic structures. The standard Langevin equation expresses the motion of a Brownian particle but it includes unexplicit information about the correlation between different particles. BD is a method of simulating dynamics in assemblies of Brownian particles based on introducing a mean force term into the standard Langevin equation. Although it supplies a useful technique for simulating mesoscopically inhomogeneous structural formations, there is no explicit information about atomistic scale properties in this method.

Recently, many investigations on the characteristics of CG simulation, especially of the DPD, have been reported. Some of them focused on the origin of a "soft" force in its expression [13–15]. The others mentioned availability of its rather wider time steps [16,17]. While such investigations are progressing, the inevitability of those studies seems to be caused by the lack of knowledge of the explicit relation between different neighboring hierarchies.

Within the standard statistical mechanics, the projection operator method is a useful tool for coarse graining as an elimination of fast variables [10,18,19]. 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 coarse grained simulation

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methods. Kampen and Oppenheim derived the equation for Brownian motion for a single Brownian particle from first principles [20]. Coarse-grained equations for a single chain in a polymer melt [21], a one-dimensional harmonic chain [22], and three-dimensional harmonic lattices [23] are also derived using the projection operator method. Because these derivations are for specific systems and a part of them focuses on a local system without explicit information on the correlation between different CG particles, further discussion should be advanced.

In the present study, we derived the equation of motion for the coarse-grained particles from microscopic description via the projection operator method. The derived coarse-grained equation of motion consists of so-called mean-force and friction-force terms and a term originating from microscopic definite processes fluctuating around the most probable situations. When we assume that the last term can be expressed by some kind of random process, we can call this term a "random force" term. The resultant equation of motion is capable of retaining the relation between microscopic and coarse-grained equations of motion without making the assumption of random force. Any kind of statistical mechanical processes can be adopted here in the resultant CG equation of motion. To make sure of the generality of the resultant equation of motion, we examine the resultant equation in relation to the previous phenomenological equations of motion such as BD and DPD. As a conclusion, the resultant CG equation of motion comprehends several basic equations for previous CG simulation methods based on *a priori* coarse-grained particle models. The present expression is expectedly useful not only as a general formula of a CG equation of motion but also as a tool for analyzing the properties of several kinds of CG methods because it retains the explicit relation between microscopic and coarse-grained conditions.

This paper is organized as follows. In Sec. II, we present derivation of an equation of motion for CG particles. In Sec. III, we discuss the relation between the resultant equation and a conventional coarse-grained simulation such as Brownian dynamics and dissipative particle dynamics. Finally in Sec. IV, some concluding remarks are presented.

II. DERIVATION OF COARSE-GRAINED EQUATION OF MOTION

Our purpose is to derive the equation of motion for coarse-grained particles. For simplicity, we consider a system of monoatomic molecules. The idea of coarse graining is to divide the total N_t atoms into N groups (or clusters), which consist of n_α, $(\alpha=1,\ldots,N)$ atoms and to regard atom groups as coarse-grained particles. A schematic picture is shown in Fig. 1. In this section, we derive the equation of motion for the coarse-grained particles by using the projection operator method [10,11]. The outline of the derivation is similar to Schweizer's derivation of a generalized Langevin equation for a polymer in a melt [26]; however, the extracted degree of freedom in our derivation is different. In this study, we focus on center of mass of the coarse-grained particles.

We start from an atomistically well-defined N_t-particle system, the Hamiltonian of which is written by the all atomistic degree of freedom as follows:

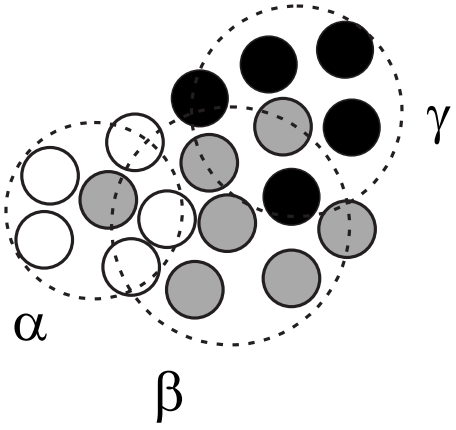

FIG. 1. Schematic picture of coarse-grained particles. Small and large circles show atoms and coarse-grained particles, respectively. In this figure, three clusters of atoms as coarse-grained particles, white (α), gray (β), and black (γ), are shown.

$$H = K + U, \tag{1}$$

$$K = \sum_{\alpha=1}^{N} \sum_{i=1}^{n_\alpha} \frac{\boldsymbol{p}_{\alpha i}^2}{2m_{\alpha i}}, \tag{2}$$

$$U = \frac{1}{2} \sum_{\substack{\alpha,\beta \\ (\alpha i)\neq(\beta j)}} \sum_{i,j} \phi(|\boldsymbol{r}_{\alpha i} - \boldsymbol{r}_{\beta j}|). \tag{3}$$

Hereafter, $\alpha,\beta,\ldots$ denote indices for coarse-grained particles, and $i,j,\ldots$ for atoms in coarse-grained particles, respectively. The trajectory of the system $\hat{\boldsymbol{\Gamma}}(t) \equiv \{\hat{\boldsymbol{r}}_{\alpha i}(t), \hat{\boldsymbol{p}}_{\alpha i}(t)\}$ is determined completely by Hamilton's equation of motion. We introduce the phase-space density for all the atoms,

$$f(\hat{\boldsymbol{\Gamma}}(t);\boldsymbol{\Gamma}) \equiv \delta(\hat{\boldsymbol{\Gamma}}(t) - \boldsymbol{\Gamma}) \equiv \prod_{\alpha,i} \delta[\hat{\boldsymbol{r}}_{\alpha i}(t) - \boldsymbol{r}_{\alpha i}]\delta[\hat{\boldsymbol{p}}_{\alpha i}(t) - \boldsymbol{p}_{\alpha i}], \tag{4}$$

which is a generalization of the phase-space density appearing in the kinetic theory for dilute and moderately dense gases [24–26]. $\hat{\boldsymbol{\Gamma}}$ denotes the phase-space coordinate of the system, and $\boldsymbol{\Gamma}$ the corresponding field variables [26,27]. If the full atomistic information is not required, a description of the system by coordinates and momenta of the center of mass (COM) of the coarse-grained particles can be employed,

$$\hat{\boldsymbol{R}}_\alpha \equiv \frac{\sum_i m_{\alpha i}\hat{\boldsymbol{r}}_{\alpha i}}{M_\alpha}, \tag{5}$$

$$\hat{\boldsymbol{P}}_\alpha \equiv \sum_i \hat{\boldsymbol{p}}_{\alpha i}, \tag{6}$$

$$M_\alpha \equiv \sum_i m_{\alpha i}. \tag{7}$$

For the description by $\hat{\mathbf{\Gamma}}_s(t) \equiv \{\hat{\boldsymbol{R}}_\alpha, \hat{\boldsymbol{P}}_\alpha\}$, we also define the phase-space density for the COMs,

$$f_s(\hat{\mathbf{\Gamma}}_s(t); \mathbf{\Gamma}_s) \equiv \delta(\hat{\mathbf{\Gamma}}_s(t) - \mathbf{\Gamma}_s) \equiv \prod_\alpha \delta(\hat{\boldsymbol{R}}_\alpha(t) - \boldsymbol{R}_\alpha)\delta(\hat{\boldsymbol{P}}_\alpha(t) - \boldsymbol{P}_\alpha). \tag{8}$$

The phase-space of the atomistic coordinates and the COM coordinates are referred to as Γ space and Γ_S space, respectively. The phase-space density $f_s(\hat{\mathbf{\Gamma}}_s(t); \mathbf{\Gamma}_s)$ depend on t via the phase point $\{\hat{\boldsymbol{r}}_{\alpha i}(t), \hat{\boldsymbol{p}}_{\alpha i}(t)\}$. The motion of them is determined by Hamilton's equation; $d\hat{\boldsymbol{r}}/dt = \partial H/\partial \hat{\boldsymbol{p}}, d\hat{\boldsymbol{p}}/dt = \partial H/\partial \hat{\boldsymbol{r}}$. Hence the time evolution of f_s along the trajectory in the Γ space is written as

$$\left(\frac{d}{dt}\right)_\Gamma f_s = -\sum_\alpha \sum_i \left\{ \frac{\partial H}{\partial \hat{\boldsymbol{r}}_{\alpha i}} \cdot \frac{\partial}{\partial \hat{\boldsymbol{p}}_{\alpha i}} - \frac{\partial H}{\partial \hat{\boldsymbol{p}}_{\alpha i}} \cdot \frac{\partial}{\partial \hat{\boldsymbol{r}}_{\alpha i}} \right\} f_s = \sum_\alpha \left\{ \hat{\boldsymbol{F}}_\alpha \cdot \frac{\partial}{\partial \hat{\boldsymbol{P}}_\alpha} + \frac{\hat{\boldsymbol{P}}_\alpha}{M_\alpha} \cdot \frac{\partial}{\partial \hat{\boldsymbol{R}}_\alpha} \right\} f_s = -\sum_\alpha \left\{ \hat{\boldsymbol{F}}_\alpha \cdot \frac{\partial}{\partial \boldsymbol{P}_\alpha} + \frac{\hat{\boldsymbol{P}}_\alpha}{M_\alpha} \cdot \frac{\partial}{\partial \boldsymbol{R}_\alpha} \right\} f_s \equiv iL_s f_s, \tag{9}$$

where

$$\hat{\boldsymbol{F}}_\alpha \equiv -\sum_{i=1}^{n_\alpha} \frac{\partial U}{\partial \hat{\boldsymbol{r}}_{\alpha i}} \tag{10}$$

is the sum of the force acting on atoms belonging to a coarse-grained particle α. The Liouville operator in the Γ_s space is defined as

$$iL_s \equiv -\sum_\alpha \left\{ \hat{\boldsymbol{F}}_\alpha \cdot \frac{\partial}{\partial \boldsymbol{P}_\alpha} + \frac{\hat{\boldsymbol{P}}_\alpha}{M_\alpha} \cdot \frac{\partial}{\partial \boldsymbol{R}_\alpha} \right\}. \tag{11}$$

We introduced a Hilbert space representation which consists of dynamical variables. To construct the Hilbert space, we must define the scalar product. A conventional definition of the scalar product is given by a correlation function in the canonical ensemble [11],

$$(A,B) \equiv \langle A(\hat{\mathbf{\Gamma}})B(\hat{\mathbf{\Gamma}})\rangle = \int d\hat{\mathbf{\Gamma}} A(\hat{\mathbf{\Gamma}})B(\hat{\mathbf{\Gamma}})\Psi(\hat{\mathbf{\Gamma}}), \tag{12}$$

where $\Psi(\hat{\mathbf{\Gamma}}) = e^{-\beta H}/Z$ is the equilibrium distribution function. Let us consider a dynamical variable $g(\hat{\mathbf{\Gamma}}(t))$. We divide $g(\hat{\mathbf{\Gamma}}(t))$ into two parts,

$$g(\hat{\mathbf{\Gamma}}(t)) = g_{\mathrm{P}}(\hat{\mathbf{\Gamma}}(t)) + g_{\mathrm{Q}}(\hat{\mathbf{\Gamma}}(t)), \tag{13}$$

and assume that $g_{\mathrm{P}}(\hat{\mathbf{\Gamma}}(t))$ can be expanded by a "basis set" $\{f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}_{\mathrm{S}})\}$ as follows:

$$g_{\mathrm{P}}(\hat{\mathbf{\Gamma}}(t)) = \int d\mathbf{\Gamma}'_{\mathrm{S}} C(\mathbf{\Gamma}'_{\mathrm{S}}) f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}'_{\mathrm{S}}), \tag{14}$$

where $C(\mathbf{\Gamma}_{\mathrm{S}})$ is the expansion coefficient. By taking the scalar product of both sides of the above equation with $f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}_{\mathrm{S}})$, we obtain the coefficient in the form

$$C(\mathbf{\Gamma}'_{\mathrm{S}}) = \int d\mathbf{\Gamma}_{\mathrm{S}} \langle f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}_{\mathrm{S}}) g_{\mathrm{P}}(\hat{\mathbf{\Gamma}}(t))\rangle \times \langle f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}_{\mathrm{S}}) f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}'_{\mathrm{S}})\rangle^{-1}. \tag{15}$$

Substitution of the expansion coefficient and using an assumption

$$\langle f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}_{\mathrm{S}}) g_{\mathrm{Q}}(\hat{\mathbf{\Gamma}}(t))\rangle = 0 \tag{16}$$

yields the definition of the projection operator $\mathcal{P}$ of a phase function $g(\hat{\mathbf{\Gamma}}(t))$ onto the Γ_s space in the form

$$\mathcal{P}g(\hat{\mathbf{\Gamma}}(t)) \equiv g_{\mathrm{P}}(\hat{\mathbf{\Gamma}}(t)) = \int d\mathbf{\Gamma}'_{\mathrm{S}} \int d\mathbf{\Gamma}''_{\mathrm{S}} f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}'_{\mathrm{S}}) \times \langle f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}'_{\mathrm{S}}) f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}''_{\mathrm{S}})\rangle^{-1} \times \langle f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}''_{\mathrm{S}}) g(\hat{\mathbf{\Gamma}}(t))\rangle. \tag{17}$$

Note that the resultant $\mathcal{P}g(\hat{\mathbf{\Gamma}}(t))$ depends only on the $\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t)$ explicitly. It is also worth noting that the time correlation $\langle f_{\mathrm{S}}(\hat{\mathbf{\Gamma}}_{\mathrm{S}}(t_0); \mathbf{\Gamma}''_{\mathrm{S}}) g(\hat{\mathbf{\Gamma}}(t))\rangle$ in the integrand is the origin of memory terms in the coarse-grained equation which will be derived in this paper. This form is a generalization of the projection operator in the kinetic theory [24–26]. The assumption (16) means that time scales of motion in the Γ_{S} space and Γ space are separable. For a proper definition of CG particles, this assumption can be reasonable.

The equilibrium distribution functions in the Γ_s space are defined as

$$\mu(\mathbf{\Gamma}_s) \equiv \frac{1}{Z} \int d\hat{\mathbf{\Gamma}}\, \delta(\hat{\mathbf{\Gamma}}_s - \mathbf{\Gamma}_s) e^{-\beta H} \tag{18}$$

$$= \omega(\boldsymbol{R})\Phi(\boldsymbol{P}), \tag{19}$$

where

$$\omega(\boldsymbol{R}) \equiv \frac{\int d^N\hat{\boldsymbol{r}}\, \delta(\hat{\boldsymbol{R}} - \boldsymbol{R}) e^{-\beta U}}{\int d^N\hat{\boldsymbol{r}} e^{-\beta U}}, \tag{20}$$

and

$$\Phi(\boldsymbol{P}) \equiv \frac{\int d^N\hat{\boldsymbol{p}}\, \delta(\hat{\boldsymbol{P}} - \boldsymbol{P}) e^{-\beta K}}{\int d^N\hat{\boldsymbol{p}} e^{-\beta K}}. \tag{21}$$

Thus we can write

$$\langle f_S(\hat{\Gamma}_S(t_0);\Gamma'_S) f_S(\hat{\Gamma}_S(t_0);\Gamma''_S)\rangle = \delta(\Gamma'_s - \Gamma''_s)\mu(\Gamma'_s). \quad (22)$$

Note that the inverse "matrix" is

$$[\delta(x-x')]^{-1} = \delta(x-x'). \quad (23)$$

Thus Eq. (17) can be written as

$$\mathcal{P}g(\hat{\Gamma}(t)) \equiv \frac{\int d\hat{\Gamma}'\, \delta(\hat{\Gamma}'_S - \hat{\Gamma}_S(t_0)) g(\hat{\Gamma}'(t)) e^{-\beta H(\hat{\Gamma}')}}{\int d\hat{\Gamma}'\, \delta(\hat{\Gamma}'_S - \hat{\Gamma}_S(t_0)) e^{-\beta H(\hat{\Gamma}')}}. \quad (24)$$

This expression shows that the projection onto the Γ_S space corresponds to an average under constraint which fixes $\hat{\Gamma}_S$. We divide the right side of the equation of time evolution (9) by the operators $\mathcal{P}$ and $\mathcal{Q} \equiv 1 - \mathcal{P}$ as follows:

$$\left(\frac{d}{dt}\right)_\Gamma f_S(\hat{\Gamma}_S(t);\Gamma_S) = \mathcal{P}iLf_S(\hat{\Gamma}_S(t);\Gamma_S) + \mathcal{Q}iLf_S(\hat{\Gamma}_S(t);\Gamma_S), \quad (25)$$

where $\mathcal{P}$ is the projection onto the phase-space density at time t. By using the definition of the projection operator, the first term of the right side of Eq. (25) is written as follows:

$$\begin{aligned}\mathcal{P}iLf_S(\hat{\Gamma}_S(t);\Gamma_S) = \int d\Gamma'_S \int d\Gamma''_S f_S(\hat{\Gamma}_S(t);\Gamma'_S) \\ \times \langle f_S(\hat{\Gamma}_S;\Gamma'_S) f_S(\hat{\Gamma}_S;\Gamma''_S)\rangle^{-1} \\ \times \langle f_S(\hat{\Gamma}_S;\Gamma''_S) iL_S f_S(\hat{\Gamma}_S;\Gamma_S)\rangle, \quad (26)\end{aligned}$$

where we omit t in the equilibrium averages. We should derive the form of the following term:

$$\begin{aligned}\langle f_S(\hat{\Gamma}_S;\Gamma''_S) iLf_S(\hat{\Gamma}_S;\Gamma'_S)\rangle = -\Bigg\langle f_S(\hat{\Gamma}_S;\Gamma''_S) \times \sum_\alpha \Bigg(\hat{F}_\alpha \cdot \frac{\partial}{\partial \boldsymbol{P}_\alpha} \\ + \frac{\hat{\boldsymbol{P}}_\alpha}{M_\alpha} \cdot \frac{\partial}{\partial \boldsymbol{R}_\alpha}\Bigg) f_S(\hat{\Gamma}_S;\Gamma'_S)\Bigg\rangle. \quad (27)\end{aligned}$$

At first, we transform the following term:

$$\begin{aligned}\left\langle f_S(\hat{\Gamma}_S;\Gamma''_S)\hat{F}_\alpha \cdot \frac{\partial}{\partial \boldsymbol{P}_\alpha} f_S(\hat{\Gamma}_S;\Gamma_S)\right\rangle \\ = \frac{\partial}{\partial \boldsymbol{P}_\alpha} \cdot \langle \hat{F}_\alpha f_S(\hat{\Gamma}_S;\Gamma''_S) f_S(\hat{\Gamma}_S;\Gamma_S)\rangle. \quad (28)\end{aligned}$$

To advance the derivation, we should consider the integration by $\{\hat{\boldsymbol{r}}_{\alpha i}\}$ in the equilibrium average $\langle\cdots\rangle$. The relevant integral in the average is

$$-\int d\hat{\boldsymbol{r}}_{\alpha 1}\cdots d\hat{\boldsymbol{r}}_{\alpha n_\alpha} \delta(\hat{\boldsymbol{R}}_\alpha - \boldsymbol{R}''_\alpha)\delta(\hat{\boldsymbol{R}}_\alpha - \boldsymbol{R}_\alpha) \times \left(\sum_i \frac{\partial H}{\partial \hat{\boldsymbol{r}}_{\alpha i}}\right)\Psi(\hat{\Gamma}). \quad (29)$$

For simplicity, we consider only the x component here. Other components can be treated in the same way. The integration can be executed as

$$\begin{aligned}-\int d\hat{x}_{\alpha 1}\cdots d\hat{x}_{\alpha n_\alpha} \delta(\hat{X}_\alpha - X''_\alpha)\delta(\hat{X}_\alpha - X_\alpha)\left(\sum_i \frac{\partial H}{\partial \hat{x}_{\alpha i}}\right)\Psi(\hat{\Gamma}) \\ = \frac{1}{\beta}\int d\hat{x}_{\alpha 1}\cdots d\hat{x}_{\alpha n_\alpha} \delta(\hat{X}_\alpha - X''_\alpha)\delta(\hat{X}_\alpha - X_\alpha)\left(\sum_i \frac{\partial \Psi(\hat{\Gamma})}{\partial \hat{x}_{\alpha i}}\right) \\ = -\frac{1}{\beta}\int d\hat{x}_{\alpha 1}\cdots d\hat{x}_{\alpha n_\alpha} \frac{\partial}{\partial \hat{X}_\alpha}[\delta(\hat{X}_\alpha - X''_\alpha)\delta(\hat{X}_\alpha - X_\alpha)]\Psi(\hat{\Gamma}).\end{aligned}$$

Using the following formula for the delta function:

$$\begin{aligned}\frac{\partial}{\partial \hat{X}_\alpha}[\delta(\hat{X}_\alpha - X''_\alpha)\delta(\hat{X}_\alpha - X_\alpha)] = -\left(\frac{\partial}{\partial X''_\alpha} + \frac{\partial}{\partial X_\alpha}\right) \\ \times \delta(\hat{X}_\alpha - X''_\alpha)\delta(\hat{X}_\alpha - X_\alpha), \quad (30)\end{aligned}$$

we obtain

$$\begin{aligned}\langle \hat{\boldsymbol{F}}_\alpha f_S(\hat{\Gamma}_S;\Gamma''_S) f_S(\hat{\Gamma}_S;\Gamma_S)\rangle &= \frac{1}{\beta}\left(\frac{\partial}{\partial \boldsymbol{R}''_\alpha} + \frac{\partial}{\partial \boldsymbol{R}_\alpha}\right) \\ &\quad \times \langle f_S(\hat{\Gamma}_S;\Gamma''_S) f_S(\hat{\Gamma}_S;\Gamma_S)\rangle \\ &= \frac{1}{\beta}\left(\frac{\partial}{\partial \boldsymbol{R}''_\alpha} + \frac{\partial}{\partial \boldsymbol{R}_\alpha}\right)\delta(\Gamma''_S - \Gamma_S)\mu(\Gamma_S) \\ &= \frac{1}{\beta}\delta(\boldsymbol{P}'' - \boldsymbol{P})\delta(\boldsymbol{R}'' - \boldsymbol{R})\Phi(\boldsymbol{P}) \\ &\quad \times \frac{\partial}{\partial \boldsymbol{R}_\alpha}\omega(\boldsymbol{R}). \quad (31)\end{aligned}$$

Thus Eq. (28) is written in the form

$$\begin{aligned}-\frac{\partial}{\partial \boldsymbol{P}_\alpha} \cdot \langle \hat{\boldsymbol{F}}_\alpha f_S(\hat{\Gamma}_S;\Gamma''_S) f_S(\hat{\Gamma}_S;\Gamma_S)\rangle \\ = -\frac{1}{\beta}\left(\frac{\partial}{\partial \boldsymbol{P}_\alpha}\delta(\boldsymbol{P}'' - \boldsymbol{P})\Phi(\boldsymbol{P})\right) \cdot \left(\delta(\boldsymbol{R}'' - \boldsymbol{R})\frac{\partial}{\partial \boldsymbol{R}_\alpha}\omega(\boldsymbol{R})\right). \quad (32)\end{aligned}$$

In the same way, we have

$$\begin{aligned}-\left\langle f_S(\hat{\Gamma}_S;\Gamma''_S)\frac{\hat{\boldsymbol{P}}_\alpha}{M_\alpha} \cdot \frac{\partial}{\partial \boldsymbol{R}_\alpha} f_S(\hat{\Gamma}_S;\Gamma_S)\right\rangle \\ = \frac{1}{\beta}\left(\frac{\partial}{\partial \boldsymbol{R}_\alpha}\delta(\boldsymbol{R}'' - \boldsymbol{R})\omega(\boldsymbol{R})\right) \cdot \left(\delta(\boldsymbol{P}'' - \boldsymbol{P})\frac{\partial}{\partial \boldsymbol{P}_\alpha}\Phi(\boldsymbol{P})\right). \quad (33)\end{aligned}$$

Thus the first term of Eq. (25) is written in the form

$$\mathcal{P}iL_s f_s = \int d\Gamma'_s f_s(\hat{\Gamma}(t);\Gamma'_s) i\Omega(\Gamma'_s,\Gamma_s), \quad (34)$$

where the "matrix" $i\Omega$ is called the "frequency matrix," the definition of which is

$$i\Omega(\mathbf{\Gamma}_s',\mathbf{\Gamma}_s) = -\frac{1}{\beta}\frac{1}{\Phi(\boldsymbol{P}')\omega(\boldsymbol{R}')} \times\sum_{\alpha=1}^{N}\left[\left(\frac{\partial}{\partial \boldsymbol{P}_\alpha}\delta(\boldsymbol{P}'-\boldsymbol{P})\Phi(\boldsymbol{P})\right)\cdot\left(\delta(\boldsymbol{R}'-\boldsymbol{R})\frac{\partial}{\partial \boldsymbol{R}_\alpha} \times\omega(\boldsymbol{R})\right) - \left(\frac{\partial}{\partial \boldsymbol{R}_\alpha}\delta(\boldsymbol{R}'-\boldsymbol{R})\omega(\boldsymbol{R})\right)\cdot\left(\delta(\boldsymbol{P}'-\boldsymbol{P}) \times\frac{\partial}{\partial \boldsymbol{P}_\alpha}\Phi(\boldsymbol{P})\right)\right]. \tag{35}$$

Next, we derive the expression for the $\mathcal{Q}iL_s f_s$. This term cannot be described in $\hat{\mathbf{\Gamma}}_S$ alone and depends on the (full atomistic) phase-space coordinate in the Γ space. We introduce the function

$$f_{\mathcal{Q}}(\hat{\mathbf{\Gamma}}(t);\mathbf{\Gamma}_s) \equiv \mathcal{Q}iL_s f_s(\hat{\mathbf{\Gamma}}_s(t);\mathbf{\Gamma}_s). \tag{36}$$

The time evolution of $f_{\mathcal{Q}}$ along the trajectory in Γ space is

$$\left(\frac{d}{dt}\right)_\Gamma f_{\mathcal{Q}}(\hat{\mathbf{\Gamma}}(t);\mathbf{\Gamma}_s) = -iLf_{\mathcal{Q}}(\hat{\mathbf{\Gamma}}(t);\mathbf{\Gamma}_s), \tag{37}$$

where iL is the Liouville operator in the Γ space,

$$iL \equiv \sum_\alpha\sum_i\left(\frac{\partial H}{\partial \hat{\boldsymbol{r}}_{\alpha i}}\cdot\frac{\partial}{\partial \hat{\boldsymbol{p}}_{\alpha i}} - \frac{\partial H}{\partial \hat{\boldsymbol{p}}_{\alpha i}}\cdot\frac{\partial}{\partial \hat{\boldsymbol{r}}_{\alpha i}}\right). \tag{38}$$

The formal solution of the time evolution is given by $f_{\mathcal{Q}}(t) = e^{-iLt}f_{\mathcal{Q}}(0)$. If the projection operator $\mathcal{P}$ represents the projection onto Γ_S at an arbitrary time $t_0 < t$ [we put $t_0=0$ and use a notation $\hat{\mathbf{\Gamma}}(0)=\hat{\mathbf{\Gamma}}$ for simplicity], we can divide $e^{-iLt}f_{\mathcal{Q}}(0)$ by using $\mathcal{P}$ and $\mathcal{Q}=1-\mathcal{P}$ as follows:

$$\begin{aligned} f_{\mathcal{Q}}(\hat{\mathbf{\Gamma}}(t);\mathbf{\Gamma}_S) &= e^{-iLt}f_{\mathcal{Q}}(\hat{\mathbf{\Gamma}};\mathbf{\Gamma}_S) \\ &= e^{-(\mathcal{P}+\mathcal{Q})iLt}f_{\mathcal{Q}}(\hat{\mathbf{\Gamma}};\mathbf{\Gamma}_S) \\ &= e^{-\mathcal{Q}iLt}f_{\mathcal{Q}}(\hat{\mathbf{\Gamma}};\mathbf{\Gamma}_S) \\ &\quad - \int_0^t d\tau e^{-iL(t-\tau)}\mathcal{P}iLe^{-\mathcal{Q}iL\tau}f_{\mathcal{Q}}(\hat{\mathbf{\Gamma}};\mathbf{\Gamma}_S). \end{aligned} \tag{39}$$

Here we used an identity for linear operators,

$$e^{(B+C)t} = e^{Bt} + \int_0^t d\tau e^{(B+C)(t-\tau)}Ce^{B\tau}. \tag{40}$$

We introduce the generalized fluctuating force,

$$\mathcal{F}(\hat{\mathbf{\Gamma}}(t);\mathbf{\Gamma}_S) \equiv e^{-\mathcal{Q}iLt}\mathcal{Q}iL_S f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S). \tag{41}$$

For $t=0$,

$$\mathcal{F}(\hat{\mathbf{\Gamma}},\mathbf{\Gamma}_S) = \mathcal{Q}iL_S f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S). \tag{42}$$

Then Eq. (39) is written as

$$f_{\mathcal{Q}}(\hat{\mathbf{\Gamma}}(t);\mathbf{\Gamma}_S) = \mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S) - \int_0^t d\tau e^{-iL(t-\tau)}\mathcal{P}iL\mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S). \tag{43}$$

According to the definition of the projection operator $\mathcal{P}$ (17), $\mathcal{P}iL\mathcal{F}$ is written as

$$\mathcal{P}iL\mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S) = \int d\mathbf{\Gamma}_S'\int d\mathbf{\Gamma}_S'' f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S') \times\langle f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S')f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S'')\rangle^{-1} \times\langle f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S'')iL\mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S)\rangle. \tag{44}$$

By using the Hermiticity of iL,

$$\langle f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S'')iL\mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S)\rangle = -\langle iL_S f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S'')\mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S)\rangle. \tag{45}$$

In the following derivation, we often use

$$iLf_S = iL_S f_S. \tag{46}$$

Because $\mathcal{P}$ and $\mathcal{Q}$ satisfy the relation

$$\langle\mathcal{P}A(\hat{\mathbf{\Gamma}})\mathcal{Q}B(\hat{\mathbf{\Gamma}})\rangle = 0, \tag{47}$$

we can write

$$\begin{aligned} \langle iL_S f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S'')\mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S)\rangle &= \langle\mathcal{Q}iL_S f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S'')\mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S)\rangle \\ &= \langle\mathcal{F}(\hat{\mathbf{\Gamma}},\mathbf{\Gamma}_S'')\mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}_S)\rangle. \end{aligned} \tag{48}$$

The final expression represents a time correlation function of the fluctuating force. Thus the second term of Eq. (39) is

$$\begin{aligned} &\int_0^t d\tau e^{-L(t-\tau)}\int d\mathbf{\Gamma}_S'\int d\mathbf{\Gamma}_S'' f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S')\delta(\mathbf{\Gamma}_S'-\mathbf{\Gamma}_S'') \\ &\quad\times\mu(\mathbf{\Gamma}_S')^{-1}\langle\mathcal{F}(\hat{\mathbf{\Gamma}},\mathbf{\Gamma}_S'')\mathcal{F}(\hat{\mathbf{\Gamma}}(\tau),\mathbf{\Gamma}_S)\rangle \\ &\quad= \int_0^t d\tau\int d\mathbf{\Gamma}_S' f_S(\hat{\mathbf{\Gamma}}_S(t-\tau);\mathbf{\Gamma}_S')M(\mathbf{\Gamma}_S',\mathbf{\Gamma}_S;\tau). \end{aligned} \tag{49}$$

Here $M(\mathbf{\Gamma}_S',\mathbf{\Gamma}_S;\tau)$ is a memory function,

$$M(\mathbf{\Gamma}_S',\mathbf{\Gamma}_S;\tau) \equiv [\mu(\mathbf{\Gamma}_S')]^{-1}\langle\mathcal{F}(\hat{\mathbf{\Gamma}},\mathbf{\Gamma}_S')\mathcal{F}(\hat{\mathbf{\Gamma}}(\tau),\mathbf{\Gamma}_S)\rangle. \tag{50}$$

Therefore we can write the time evolution equation for the phase-space density as follows:

$$\left(\frac{d}{dt}\right)_\Gamma f_S(\hat{\mathbf{\Gamma}}_S(t);\mathbf{\Gamma}_S) = \int d\mathbf{\Gamma}_S' f_S(\hat{\mathbf{\Gamma}}_S(t);\mathbf{\Gamma}_S')i\Omega(\mathbf{\Gamma}_S,\mathbf{\Gamma}_S') + \int_0^t d\tau\int d\mathbf{\Gamma}_S' f_S(\hat{\mathbf{\Gamma}}_S(t-\tau);\mathbf{\Gamma}_S') \times M(\mathbf{\Gamma}_S',\mathbf{\Gamma}_S;\tau) + \mathcal{F}(\hat{\mathbf{\Gamma}}(t),\mathbf{\Gamma}). \tag{51}$$

The equation of motion for the coarse-grained particles is obtained by integration of Eq. (51) by $\mathbf{\Gamma}_S$ with multiplying $\boldsymbol{P}_\sigma$. The left side is easily obtained as

$$\int d\mathbf{\Gamma}_S \left[\boldsymbol{P}_\sigma \left(\frac{d}{dt} \right)_\Gamma f_S(\hat{\mathbf{\Gamma}}_S(t);\mathbf{\Gamma}_S) \right] = \frac{d}{dt}\hat{\boldsymbol{P}}_\sigma. \tag{52}$$

The first term of the right side is

$$\int d\mathbf{\Gamma}_S \boldsymbol{P}_\sigma \int d\mathbf{\Gamma}'_S f_S(\hat{\mathbf{\Gamma}}_S(t);\mathbf{\Gamma}'_S) i\Omega(\mathbf{\Gamma}'_s,\mathbf{\Gamma}_s)$$
$$= \int d\mathbf{\Gamma}_S \boldsymbol{P}_\sigma i\Omega(\hat{\mathbf{\Gamma}}_s(t),\mathbf{\Gamma}_s). \tag{53}$$

Substitution of the definition of the frequency matrix $i\Omega$ into the above equation yields

$$\int d\mathbf{\Gamma}_S \boldsymbol{P}_\sigma i\Omega(\hat{\mathbf{\Gamma}}_s(t),\mathbf{\Gamma}_s) = \frac{1}{\beta} \frac{\partial}{\partial \boldsymbol{R}_\sigma} \ln \omega(\boldsymbol{R}) \Big|_{\boldsymbol{R}=\hat{\boldsymbol{R}}(t)}. \tag{54}$$

The generalized fluctuating force can be written as

$$\mathcal{F}(\hat{\mathbf{\Gamma}}(0),\mathbf{\Gamma}_S) = \mathcal{Q}iLf_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S)$$
$$= iLf_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S) - \mathcal{P}iLf_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S)$$
$$= iL_S f_S(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S) - i\Omega(\hat{\mathbf{\Gamma}}_S;\mathbf{\Gamma}_S). \tag{55}$$

By using the definition of the generalized fluctuating force, we can write

$$\mathcal{F}(\hat{\mathbf{\Gamma}}(0),\mathbf{\Gamma}_S) = -\sum_\alpha \left[\left\{ \hat{\boldsymbol{F}}_\alpha - \frac{\Phi(\boldsymbol{P})}{\Phi(\hat{\boldsymbol{P}})} \frac{1}{\beta} \frac{\partial}{\partial \boldsymbol{R}_\alpha} \right. \right.$$
$$\left. \times \ln \omega(\boldsymbol{R}) \right\} \cdot \frac{\partial}{\partial \boldsymbol{P}_\alpha} \delta(\hat{\mathbf{\Gamma}}_s - \mathbf{\Gamma}_s)$$
$$\left. + \left\{ \frac{\hat{\boldsymbol{P}}_\alpha}{M_\alpha} - \frac{\omega(\boldsymbol{R})}{\omega(\hat{\boldsymbol{R}})} \frac{\boldsymbol{P}_\alpha}{M_\alpha} \right\} \cdot \frac{\partial}{\partial \boldsymbol{R}_\alpha} \delta(\hat{\mathbf{\Gamma}}_s - \mathbf{\Gamma}_s) \right]. \tag{56}$$

Multiplying this term by $\boldsymbol{P}_\sigma$ and integrating over $\mathbf{\Gamma}_S$ yields the expression for the third term,

$$\int d\mathbf{\Gamma}_S \boldsymbol{P}_\sigma \mathcal{F}(\hat{\mathbf{\Gamma}}(0),\mathbf{\Gamma}_S) = \delta \boldsymbol{F}_\sigma \equiv \hat{\boldsymbol{F}}_\sigma - \frac{1}{\beta} \frac{\partial}{\partial \hat{\boldsymbol{R}}_\sigma} \ln \omega(\hat{\boldsymbol{R}}). \tag{57}$$

Integration of the second term is transformed into

$$\int d\mathbf{\Gamma}_S \boldsymbol{P}_\sigma \int d\mathbf{\Gamma}'_S \delta[\hat{\mathbf{\Gamma}}_S(t-\tau) - \mathbf{\Gamma}'_S] M(\mathbf{\Gamma}'_S,\mathbf{\Gamma}_S;\tau)$$
$$= \int d\mathbf{\Gamma}'_S \delta[\hat{\mathbf{\Gamma}}_S(t-\tau) - \mathbf{\Gamma}'_S] \int d\mathbf{\Gamma}_S \boldsymbol{P}_\sigma M(\mathbf{\Gamma}'_S,\mathbf{\Gamma}_S;\tau). \tag{58}$$

Thus integration over $\mathbf{\Gamma}_S$ is

$$\int d\mathbf{\Gamma}_S \boldsymbol{P}_\sigma M(\mathbf{\Gamma}'_S,\mathbf{\Gamma}_S;\tau) = \frac{1}{\mu(\mathbf{\Gamma}'_S)}$$
$$\times \int d\mathbf{\Gamma}_S \boldsymbol{P}_\sigma \langle \mathcal{F}(\hat{\mathbf{\Gamma}},\mathbf{\Gamma}'_S) \mathcal{F}(\hat{\mathbf{\Gamma}}(\tau),\mathbf{\Gamma}_S) \rangle$$
$$= \frac{1}{\mu(\mathbf{\Gamma}'_S)} \langle \mathcal{F}(\hat{\mathbf{\Gamma}},\mathbf{\Gamma}'_S) \delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(\tau) \rangle, \tag{59}$$

where $\delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(\tau) \equiv e^{-\mathcal{Q}iL\tau} \delta \boldsymbol{F}_\sigma$. Assuming that

$$\langle A(\hat{\mathbf{\Gamma}}_S) \delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(\tau) \rangle = 0 \tag{60}$$

for an arbitrary function $A(\hat{\mathbf{\Gamma}}_S)$, we can write

$$\langle \mathcal{F}(\hat{\mathbf{\Gamma}},\mathbf{\Gamma}'_S) \delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(\tau) \rangle = -\sum_\alpha \left\langle \hat{\boldsymbol{F}}_\alpha \cdot \frac{\partial}{\partial \boldsymbol{P}'_\alpha} \delta(\hat{\mathbf{\Gamma}}_S - \mathbf{\Gamma}'_S) \delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(\tau) \right\rangle$$
$$= -\beta \sum_\alpha \langle [\delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(\tau)][\delta \boldsymbol{F}^{\mathcal{Q}}_\alpha(0)]^{\mathrm{T}} \rangle \frac{\boldsymbol{P}'_\alpha}{M_\alpha}, \tag{61}$$

where $\boldsymbol{X}^{\mathrm{T}}$ denotes the transposed low vector of the column vector $\boldsymbol{X}$. Hence we obtain the second term in the form

$$-\beta \sum_\alpha \int_0^\tau d\tau \langle [\delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(\tau)][\delta \boldsymbol{F}^{\mathcal{Q}}_\alpha(0)]^{\mathrm{T}} \rangle \frac{\boldsymbol{P}'_\alpha(t-\tau)}{M_\alpha}. \tag{62}$$

Finally, we have the equation of motion for coarse-grained particles,

$$\frac{d}{dt}\hat{\boldsymbol{P}}_\sigma = \frac{1}{\beta} \frac{\partial}{\partial \hat{\boldsymbol{R}}_\sigma} \ln \omega(\hat{\boldsymbol{R}}) - \beta \sum_\alpha \int_0^t ds \langle [\delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(t-s)]$$
$$\times [\delta \boldsymbol{F}^{\mathcal{Q}}_\alpha(0)]^{\mathrm{T}} \rangle \frac{\hat{\boldsymbol{P}}_\alpha(s)}{M_\alpha} + \delta \boldsymbol{F}^{\mathcal{Q}}_\sigma(t). \tag{63}$$

The meaning of first, second, and third terms are the mean force, the friction force, and the fluctuating force, respectively.

III. DISCUSSION

A. Characteristics of resultant coarse-grained equation of motion

The resultant equation of motion for CG particles, Eq. (63), has a formula similar to the standard Langevin-type equation with an external force term. In the context of the present report, the external force should be considered as the mean force acting on a CG particle under every possible configuration of microscopic particles. Equation (20) assures the existence of an explicit procedure for reproducing such CG mean force based on a detailed microscopic expression. The origin and/or meaning of the soft potential in DPD has been discussed in several articles [13–15]. The explicit description of the CG mean force must be reproduced via Eq. (20), and the origin of the softness of it could be analyzed. In order to do a quantitative analysis, however, one must assume some explicit formula for the interparticle potential at the microscopic level. Therefore a distinct discussion may depend on the choice of the microscopic interaction poten-

tial, and then it would be reported in consequent papers [28].

In the case where the effective mean force term is zero, the formula corresponds to a standard Langevin equation but includes a correlation between fluctuating forces in different CG particles. The inclusion of such a correlation is capable of maintaining the effects like so-called hydrodynamic correlations in the dynamics of Brownian particles, because all the correlations between every microscopic particle can be basically expressed in this term. Note that randomness still has not been introduced here onto the fluctuating force term. The Rouse model [29], which is a famous fundamental theoretical basis for investigation of polymer solutions, has no effective mean force and also no correlation between microscopic particles (solvents) surrounding the tagged CG particle. An important extension of the Rouse model has been made by considering such effects as hydrodynamic correlations [29]. The resultant formula of Eq. (63) includes the correlation between microscopic particles even though the mean force term is assumed to be zero; therefore it can be an extension to dynamics in polymer solutions with a general formulation. Schweizer's theory on dynamics in polymer solutions [26] was derived via the projection operator method like that of our present treatment. The theory corresponds to a case without an effective mean force and focuses on dynamics within a region of one CG polymer. It can be assigned as a generalized extensive theory of the Rouse model for investigating microscopic dynamics in a coarse-grained environment. Because the focused DOF is different from our resultant equation of motion, it is accepted as another type of generalized Langevin equation.

The second term of Eq. (63) is expressed as proportional to velocity and the inverse of kinetic energy (k_BT) with a temporal correlation function of fluctuation force. This can be acceptable as a friction force term and seems to naturally correspond to a generalized relation of the fluctuation-dissipation theorem. Although the fluctuating force of $\delta \boldsymbol{F}^{Q}(t)$ is not necessarily random like in a standard explanation, this term formally shows a similar relation with fluctuation-dissipation theorem. This characteristic would support an expectation that Eq. (63), and other expressions derived from it, could naturally satisfy the fluctuation-dissipation theorem. Explicit discussions will appear in the latter subsections on correspondence to BD and DPD.

The third term of Eq. (63) shows a force acting on the CG particle, by every microscopic particle, fluctuating around a mean force value. This term includes the entire expression of potential energy between every pair of microscopic particles, in the form of differentiation respects to every coordinate of the microscopic particles within a CG particle σ. The explicit expression, except for the mean value and time dependency, can be found in Eq. (10). Here, we should remember again that the fluctuating force of $\delta \boldsymbol{F}_{\sigma}^{Q}(t)$ is not necessarily random. When the system to be investigated is decided, the formula of the microscopic interparticle potential can be explicitly given. Microscopic movements under a given potential must be understood traceably on the time scale of microscopic events. One of such movements should be expressed as an event understood as a possible one within all probabilities of realizing possible configurations at the upper extensive hierarchy. There is a room in which randomness penetrates mesoscopic phenomena with microscopic events. While mesoscopic conditions can be entirely constructed by microscopic information according to Eq. (63), a microscopic event should be understood as just one possible probability restricted by mesoscopic conditions on its time scale. We should note that an inverse prediction is not deterministic. Visualizing the case where there are several modes of corrective motions, such as the internal vibrations of a molecule, we can find that the traceability of microscopic movements on the time scale of microscopic events is very useful to investigate such a system even though inverse prediction is not deterministic. In this sense, we can say that our resultant equation of motion is capable of retaining the relation between microscopic and coarse-grained equations of motion without making *a priori* assumptions on the construction of an explicit simulation procedure.

B. Correspondence to Brownian dynamics

The derivation of Eq. (63) is quite general; therefore it naturally includes the other coarse-grained equations of motion such as Brownian dynamics and dissipative particle dynamics. In this section, we see the correspondence to the existent coarse-grained equations.

The equation of motion for Brownian particles is given as follows:

$$\frac{d}{dt}\boldsymbol{p}_i = \boldsymbol{F}_i^C - \frac{\gamma}{m}\boldsymbol{p}_i + \boldsymbol{F}_i^R, \tag{64}$$

where $\boldsymbol{F}_i^C$ is the mean force acting on the ith Brownian particle. $\boldsymbol{F}_i^R$ is the random force and γ is the friction coefficient. The random force satisfies

$$\langle F_{i\mu}^R(t) F_{j\nu}^R(s)\rangle = \sigma^2 \delta_{ij}\delta_{\mu\nu}\delta(t-s), \tag{65}$$

$$\langle F_{i\mu}^R(t)\rangle = 0. \tag{66}$$

The Fokker-Planck equation for the Brownian particles (so called Kramers equation) is [12,30]

$$\frac{\partial}{\partial t}P(\boldsymbol{r},\boldsymbol{p},t) = \sum_{i=1}^{N}\left(-\frac{\boldsymbol{p}_i}{m}\cdot\frac{\partial}{\partial \boldsymbol{r}_i} - \boldsymbol{F}_i\cdot\frac{\partial}{\partial \boldsymbol{p}_i} + \frac{\gamma}{m}\frac{\partial}{\partial \boldsymbol{p}_i}\cdot\boldsymbol{p}_i + \frac{\sigma^2}{2}\frac{\partial^2}{\partial p_i^2}\right) \times P(\boldsymbol{r},\boldsymbol{p},t), \tag{67}$$

where $P(\boldsymbol{r},\boldsymbol{p},t)$ is the probability distribution of the Brownian particles. The steady state solution for Eq. (67) with $\partial_t P=0$, gives the equilibrium distribution P^{eq}. If we assume that the equilibrium distribution is the Gibbs canonical ensemble for the Hamiltonian,

$$H(\boldsymbol{r},\boldsymbol{p}) = \sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{2m} + U(\boldsymbol{r}), \tag{68}$$

where $U(\boldsymbol{r})$ is the potential of mean force, the distribution function is

$$P^{\mathrm{eq}}(\boldsymbol{r},\boldsymbol{p}) = \frac{1}{Z}\exp\left[-\beta\left(\sum_i \frac{\boldsymbol{p}_i^2}{2m} + U(\boldsymbol{r})\right)\right], \tag{69}$$

where $\beta=1/k_BT$. Substitution of Eq. (69) and $\partial_t P^{\mathrm{eq}}=0$ into Eq. (67) leads to the relation between σ and γ,

$$\gamma = \frac{\sigma^2}{2k_B T}. \tag{70}$$

This is the fluctuation-dissipation theorem for Brownian dynamics.

The characteristics of the equation appeared in the treatment of random force. In the Brownian dynamics, the random force $\delta \boldsymbol{F}_\alpha^{\mathcal{Q}}$ is modeled as

$$\delta F_{\alpha\mu}^{\mathcal{Q}}(t) = \sigma \theta_{\alpha\mu}(t), \tag{71}$$

where $\theta_{\alpha\mu}(t)$ is a random number with unit variance which satisfies

$$\langle \theta_{\alpha\mu}(t)\theta_{\beta\nu}(0)\rangle = \delta_{\alpha\beta}\delta_{\mu\nu}\delta(t) \tag{72}$$

and

$$\langle \theta_{\alpha\mu}(t)\rangle = 0. \tag{73}$$

μ, ν denotes the x, y, or z component. Substitution of Eq. (71) into Eq. (63) yields

$$\frac{d}{dt}\hat{\boldsymbol{P}}_\sigma(t) = \frac{1}{\beta}\frac{\partial}{\partial \hat{\boldsymbol{R}}_\sigma} \ln \omega(\hat{\boldsymbol{R}}) - \gamma \hat{\boldsymbol{V}}_\sigma(t) + \delta \boldsymbol{F}_\sigma^{\mathcal{Q}}. \tag{74}$$

This equation has the same form as the Brownian dynamics and satisfies the fluctuation-dissipation relation $\sigma^2 = 2\gamma k_B T$ naturally.

C. Correspondence to dissipative particle dynamics

The equation of motion for DPD is written as [31]

$$\frac{d}{dt}\boldsymbol{p}_i = \boldsymbol{F}_i^C - \gamma \sum_{j\neq i} \omega_D(r_{ij})(\boldsymbol{e}_{ij}\cdot \boldsymbol{v}_{ij})\boldsymbol{e}_{ij} + \sum_{j\neq i} \boldsymbol{F}_{ij}^R, \tag{75}$$

where $\boldsymbol{e}_{ij} \equiv (\boldsymbol{r}_i - \boldsymbol{r}_j)/r_{ij}$ is the unit vector between particles i and j, and $\omega_D(r)$ is the weight function for the drag force. The random force $\boldsymbol{F}_{ij}^R$ satisfies

$$\langle F_{ij}^R(t) F_{kl}^R(t)\rangle = [\sigma \omega_R(r_{ij})]^2(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})\delta(t-s), \tag{76}$$

and

$$\langle F_{ij}^R(t)\rangle = 0, \tag{77}$$

where $\omega_R(r)$ is the weight function for the random force. The Fokker-Planck equation for the DPD equation is given as [31]

$$\frac{\partial}{\partial t}P(\boldsymbol{r},\boldsymbol{p},t) = L_C P(\boldsymbol{r},\boldsymbol{p},t) + L_D P(\boldsymbol{r},\boldsymbol{p},t), \tag{78}$$

where

$$L_C \equiv -\sum_i \left(\frac{\boldsymbol{p}_i}{m}\cdot\frac{\partial}{\partial \boldsymbol{r}_i} + \boldsymbol{F}_i \cdot \frac{\partial}{\partial \boldsymbol{p}_i}\right) \tag{79}$$

$$L_D \equiv \sum_i \sum_{j\neq i} \boldsymbol{e}_{ij}\cdot\frac{\partial}{\partial \boldsymbol{p}_i}\left[\gamma \omega_D(r_{ij})(\boldsymbol{e}_{ij}\cdot\boldsymbol{v}_{ij}) + \frac{\sigma^2}{2}\omega_R^2(r_{ij})\boldsymbol{e}_{ij}\cdot\left(\frac{\partial}{\partial \boldsymbol{p}_i} - \frac{\partial}{\partial \boldsymbol{p}_j}\right)\right]. \tag{80}$$

In the same way in the case of BD, the equilibrium distribution function (69) and steady state condition $\partial_t P = 0$ requires the relation

$$\omega_D(r) = [\omega_R(r)]^2 \tag{81}$$

$$\gamma = \frac{\sigma^2}{2k_B T}. \tag{82}$$

This is the fluctuation-dissipation theorem for the dissipative particle dynamics.

If the interatomic potential is pairwise, the random force is also expressed as

$$\delta \boldsymbol{F}_\alpha^{\mathcal{Q}} = \sum_{\beta\neq\alpha} \delta \boldsymbol{f}_{\alpha\beta}^{\mathcal{Q}}. \tag{83}$$

A possible form of the random force in DPD is pairwise,

$$\delta \boldsymbol{f}_{\alpha\beta}^{\mathcal{Q}} = \sigma w(R_{\alpha\beta})\theta_{\alpha\beta}(t)\boldsymbol{e}_{\alpha\beta}, \tag{84}$$

where

$$\boldsymbol{e}_{\alpha\beta} \equiv \frac{\boldsymbol{R}_{\alpha\beta}}{R_{\alpha\beta}}, \tag{85}$$

and

$$\langle \theta_{\alpha\beta}(t)\theta_{\epsilon\eta}(s)\rangle = (\delta_{\alpha\epsilon}\delta_{\beta\eta} + \delta_{\alpha\eta}\delta_{\beta\epsilon})\delta(t-s), \tag{86}$$

$$\langle \theta_{\alpha\beta}(t)\rangle = 0. \tag{87}$$

This relation means that the random forces assigned to different pairs do not correlate. By substitution of Eq. (84) into the second term of the right side of Eq. (63), we obtained

$$\begin{aligned}
&\sum_\alpha \langle \delta \boldsymbol{F}_\eta^{\mathcal{Q}}(t-s)\delta \boldsymbol{F}_\alpha^{\mathcal{Q}}(0)^T\rangle \boldsymbol{V}_\alpha(s) \\
&= \sum_\alpha \sum_{\lambda\neq\eta}\sum_{\epsilon\neq\alpha} \langle \delta \boldsymbol{f}_{\eta\lambda}^{\mathcal{Q}}(t-s)\delta \boldsymbol{f}_{\alpha\epsilon}^{\mathcal{Q}}(0)^T\rangle \boldsymbol{V}_\alpha(s) \\
&= \sum_\alpha \sum_{\lambda\neq\eta}\sum_{\epsilon\neq\alpha} \langle \theta_{\eta\lambda}(t-s)\theta_{\alpha\epsilon}(t)\rangle \sigma^2 w(R_{\eta\lambda})w(R_{\alpha\epsilon}) \\
&\quad \times [\boldsymbol{e}_{\eta\lambda}\boldsymbol{e}_{\alpha\epsilon}^T]\boldsymbol{V}_\alpha(s) \\
&= \sum_{\lambda\neq\eta} \delta(t-s)[\sigma w(R_{\eta\lambda})]^2(\boldsymbol{e}_{\eta\lambda}\boldsymbol{e}_{\eta\lambda}^T)[\boldsymbol{V}_\eta(s) - \boldsymbol{V}_\lambda(s)] \\
&= \sum_{\lambda\neq\eta} \delta(t-s)[\sigma w(R_{\eta\lambda})]^2[\boldsymbol{e}_{\eta\lambda}\cdot\boldsymbol{V}_{\eta\lambda}(s)]\boldsymbol{e}_{\eta\lambda}.
\end{aligned} \tag{88}$$

Here we use the following relations:

$$\boldsymbol{e}_{\alpha\beta} = -\boldsymbol{e}_{\beta\alpha},$$

$$(\boldsymbol{A}\boldsymbol{B}^T)\boldsymbol{C} = \boldsymbol{A}(\boldsymbol{B}\cdot\boldsymbol{C}). \tag{89}$$

The second term of the right side of Eq. (63) is in the form

$$\begin{aligned}
&-\beta \sum_\alpha \int_0^t ds \langle \delta \boldsymbol{F}_\eta^{\mathcal{Q}}(t-s)\delta \boldsymbol{F}_\eta^{\mathcal{Q}}(0)^T\rangle \\
&= -\frac{1}{2k_B T}\sum_{\lambda\neq\eta}[\sigma w(R_{\eta\lambda})]^2[\boldsymbol{e}_{\eta\lambda}\cdot\boldsymbol{V}_{\eta\lambda}(t)]\boldsymbol{e}_{\eta\lambda}.
\end{aligned} \tag{90}$$

Thus we obtained the equation for DPD (75). The fluctuation dissipation theorem is also satisfied naturally.

IV. CONCLUSIONS

In this paper, we derived the equation of motion for coarse-grained particles by using the projection operator. Because all the terms of the equation are expressed microscopically, we can connect the dynamics of coarse-grained particles to microscopic information (e.g., force field). Especially, the mean force acting on the CG particles can be calculated by molecular dynamics simulation straightforwardly. In this derivation, the conventional form of the mean force is straightforwardly obtained. We can easily see that

$$\frac{1}{\beta}\frac{\partial}{\partial \boldsymbol{R}_\sigma}\ln \omega(\boldsymbol{R}) = \frac{1}{\beta}\frac{\left(\frac{\partial \omega}{\partial \boldsymbol{R}_\sigma}\right)}{\omega(\boldsymbol{R})} = \frac{1}{\omega(\boldsymbol{R})}\int d\hat{\boldsymbol{r}}\,\delta(\hat{\boldsymbol{R}}-\boldsymbol{R})\left(-\frac{\partial U}{\partial \hat{\boldsymbol{R}}_\sigma}\right) \times e^{-\beta U} = \langle \boldsymbol{F}_\sigma \rangle_{\Gamma_s} = \sum_{\alpha\neq\sigma}\langle \boldsymbol{f}_{\sigma\alpha}\rangle_{\Gamma_s}. \tag{91}$$

Usually, the mean force is introduced by a static picture of averaged force acting on a coarse-grained particle. In the present derivation, it naturally appeared in the CG equation (63). The calculation of the mean force is underway by the present authors and will appear in a subsequent paper. The mean force based on the microscopic information may improve the quality of coarse-grained simulations which usually use an *ad hoc* model for interparticle interactions.

We also investigated the correspondence of the derived CG equation to the conventional CG simulation such as Brownian dynamics and dissipative particle dynamics. We showed that the difference in these method appears in a characteristic of the model of the random force. The random forces assigned to each molecule and the random forces to each pair of molecules correspond to the BD and DPD, respectively. The derived equation can give the microscopic basis of coarse-grained simulations and the suggestions for possible extension of it.

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