A Brownian Dynamics Method for Systems of Nonspherical Brownian Particles

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A Brownian dynamics method is proposed for simulating the coupled translational and rotational diffusive motions of nonspherical Brownian particles. Results of test simulations to assess the accuracy of the algorithm are presented.

Introduction

Since the pioneering work of Simon and Zimm,[1] the stochastic dynamics (SD) method has been a rapidly growing branch of computer simulation methods for many-particle systems, including liquids, solids, and macromolecules. The algorithm used by Simon and Zimm neglected the inertia term in the Langevin equation and assumed that the random force remains constant during each time step, Δt. Obviously, physical situations that satisfy these two conditions simultaneously are quite rare. More rigorous algorithms were obtained for the case, $\Delta t \ll \gamma^{-1}$, by Weiner and Forman[2], and for the case, $\Delta t \gg \gamma^{-1}$, by Ermak[3]; here γ^{-1} is the velocity relaxation time of a Brownian particle. Subsequently, Ermak and Buckholtz[4] derived an algorithm in which Δt is not restricted with respect to the magnitude of γ^{-1}. However, all the algorithms cited so far are restricted by the condition that the systematic force upon a Brownian particle does not change appreciably during Δt. Allen[5] and independently van Gunsteren *et al.*[6] proposed third order algorithms which allow linear variation of the systematic force during Δt. However, at least in the diffusive regime (*i.e.*, $\Delta t \gg \gamma^{-1}$), these third order algorithms may lead to erroneous results.[7] Other lines of generalization of the SD methods have been to include the effects of hydrodynamic interactions between Brownian particles[8] or memory effects in the correlation of stochastic forces upon the Brownian particles.[4,9-11] Algorithms based on the ordinary Langevin equations are called Brownian dynamics (BD) methods, and those based on the generalized Langevin equations are called generalized Brownian dynamics (GBD) methods. All these methods are valid for the cases where the Brownian particles are more massive than the solvent molecules, although for GBD this restriction is relaxed. Montgomery *et al.*[12] derived an impulsive stochastic dynamics method that is applicable to the case where the particles of primary interest are less massive than solvent molecules.

In this paper, we present a BD method for simulating the dynamical behavior of a system of N interacting nonspherical Brownian particles in the diffusive regime [*i.e.*, for the case in which the time step size is much larger than the relaxation times of translational and rotational velocities]. Although hydrodynamic interactions between Brownian particles are incorporated into the algorithm, the lack of any explicit expression for the hydrodynamic interaction tensor for nonspherical particles will enforce the neglect of them in actual applications. However, the hydrodynamic interactions between parts of a Brownian particle which result in the coupling between translational and rotational diffusion of the particle[13] are included. Recently, Dickinson *et al.*[14] proposed a similar BD algorithm for systems of spherical particles with spin. However, their algorithm for rotational motion is incomplete. The three "moving-on" angles in their algorithm are the angles of rotations around the three body-fixed axes. Such angles are meaningful only for the infinitesimal rotation. In this paper, we present two algorithms for simulating the finite rotational movements that occur in the diffusive regime. In one algorithm, Euler angles are used as the orientational coordinates, and in the other nine components of the three body-fixed orthonormal vectors are used together with six orthonormality conditions among them. Detailed descriptions of the algorithms are presented in the next section, and results of test simulations to assess the accuracy of both methods are given in the final section.

BD Algorithms

A. Coupled Translational and Rotational Langevin Equations. The system under consideration consists of N Brownian particles with arbitrary shape which are immersed in a viscous incompressible solvent continuum. The particles may be subject to configuration-dependent force due to interparticle interactions or external fields. The particles are also subject to velocity-dependent hydrodynamic interactions. The coupled translational and rotational Langevin equations governing the dynamics of this system are[15,16]

$$m_i(dv_i/dt)_{lab} = m_i(dv_i/dt)_i + \omega_i \times m_i v_i \tag{2.1}$$
$$= -\sum_{j=1}^{N} \xi_{ij}^{TT} \cdot v_j - \sum_{j=1}^{N} \xi_{ij}^{TR} \cdot \omega_j + F_i^T + R_i^T$$

$$(dL_i/dt)_{lab} = (dL_i/dt)_i + \omega_i \times L_i \tag{2.2}$$
$$= -\sum_{j=1}^{N} \xi_{ij}^{RT} \cdot v_j - \sum_{j=1}^{N} \xi_{ij}^{RR} \cdot \omega_j + F_i^R + R_i^R$$

Here m_i, v_i, ω_i, and L_i are the mass, velocity, angular velocity, and the angular momentum of the i-th particle, respectively. $(d/dt)_{lab}$ denotes the rate of change in v_i or L_i measured in the space-fixed coordinate system, and $(d/dt)_i$ denotes the corresponding quantity measured in the body-fixed coordinate system attached to the particle i. Terms involving the configuration-dependent friction-tensors ξ_{ij}^{TT}, ξ_{ij}^{TR}, ξ_{ij}^{RT}, and ξ_{ij}^{RR} represent the frictional retardation of the particle velocities due to the viscous medium. F_i^T (F_i^R) is the sum of interparticle and external forces (torques) acting on the i-th particle. R_i^T (R_i^R) represents the randomly fluctuating force (torque) exerted on the i-th particle by the surrounding fluid.

The statistical properties of these random forces and torques are related to the friction tensors by fluctuation-dissipation theorem[15,16]:

$$<\boldsymbol{R}_i^T(t)>=<\boldsymbol{R}_i^R(t)>=0 \tag{2.3}$$

$$<\boldsymbol{R}_i^\alpha(t)\widetilde{\boldsymbol{R}}_j^\beta(t')>=2k_BT\xi_{ij}^{\alpha\beta}\delta(t-t') \quad (\alpha,\beta=T,R) \tag{2.4}$$

where the tilde over $\boldsymbol{R}_j^\beta$ denotes the transpose and thus $\widetilde{\boldsymbol{R}}_j^\beta$ is a row vector. The notation $\boldsymbol{R}_i\widetilde{\boldsymbol{R}}_j^\beta$ represents a dyad product. In the presence of systematic forces $\boldsymbol{F}_i^T$ and $\boldsymbol{F}_i^R$, a term involving the correlation function between the systematic forces and the velocities v_j and ω_j should perhaps be added to the right hand side of Eq. (2.4).[17] For spherical particles, however, it has been shown numerically that the contribution from this additional term is negligible.[18]

In the diffusive regime (*i.e.*, in a highly viscous medium), the inertial terms in Eqs. (2.1) and (2.2) can be neglected, and we have

$$v_i=\sum_{j=1}^{N}(k_BT)^{-1}\ D_{ij}^{TT}\cdot(\boldsymbol{F}_j^T+\boldsymbol{R}_j^T)$$
$$+\sum_{j=1}^{N}(k_BT)^{-1}D_{ij}^{TR}\cdot(\boldsymbol{F}_j^R+\boldsymbol{R}_j^R) \tag{2.5}$$

$$\omega_i=\sum_{j=1}^{N}(k_BT)^{-1}D_{ij}^{RT}\cdot(\boldsymbol{F}_j^T+\boldsymbol{R}_j^T)+\sum_{j=1}^{N}(k_BT)^{-1}D_{ij}^{RR}\cdot(\boldsymbol{F}_j^R+\boldsymbol{R}_j^R) \tag{2.6}$$

Here the various diffusion tensors are related to the friction tensors by the generalized Einstein relation[15,16]:

$$D_{ij}^{\alpha\beta}=k_BT(\xi^{-1})_{ij}^{\alpha\beta} \tag{2.7}$$

where the matrix inverse is defined by

$$\sum_{\gamma k}(\xi^{-1})_{ik}^{\alpha\gamma}\cdot\xi_{kj}^{\gamma\beta}=1\delta_{\alpha\beta}\delta_{ij} \tag{2.8}$$

and the labels α, β, and γ refer to translation(T) and rotation (R). **1** in the 3×3 unit matrix.

B. Derivation of the BD Algorithm in the Diffusive Regime. In the present algorithm, we are concerned with calculating the changes in positions and orientations of the particles over a short time step Δt during which $\boldsymbol{F}$ remains essentially constant. However, Δt must be much larger than the correlation times of velocities v_i and ω_i for Eqs. (2.5) and (2.6) to provide a valid description of the dynamical behavior of the system on the time scale longer than Δt.

First, it is convenient to introduce the grand velocity vector $\boldsymbol{V}$, grand force vectors $\boldsymbol{F}$, and $\boldsymbol{R}$, and grand diffusion matrix $\boldsymbol{D}$ as follows:

$$\boldsymbol{V}=\begin{pmatrix}v_1\\ \omega_1\\ \vdots\\ v_N\\ \omega_N\end{pmatrix}\quad \boldsymbol{F}=\begin{pmatrix}\boldsymbol{F}_1^T\\ \boldsymbol{F}_1^R\\ \vdots\\ \boldsymbol{F}_N^T\\ \boldsymbol{F}_N^R\end{pmatrix}\quad \boldsymbol{R}=\begin{pmatrix}\boldsymbol{R}_1^T\\ \boldsymbol{R}_1^R\\ \vdots\\ \boldsymbol{R}_N^T\\ \boldsymbol{R}_N^R\end{pmatrix} \tag{2.9}$$

$$\boldsymbol{D}=\begin{pmatrix}D_{11}^{TT} & D_{11}^{TR} & D_{12}^{TT} & D_{12}^{TR}\cdots & D_{1N}^{TT} & D_{1N}^{TR}\\ D_{11}^{RT} & D_{11}^{RR} & D_{12}^{RT} & D_{12}^{RR}\cdots & D_{1N}^{RT} & D_{1N}^{RR}\\ D_{21}^{TT} & D_{21}^{TR} & D_{22}^{TT} & D_{22}^{TR}\cdots & D_{2N}^{TT} & D_{2N}^{TR}\\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots\\ D_{N1}^{RT} & D_{N1}^{RR} & D_{N2}^{RT} & D_{N2}^{RR}\cdots & D_{NN}^{RT} & D_{NN}^{RR}\end{pmatrix} \tag{2.10}$$

Then we can rewrite Eqs. (2.3)-(2.8) in the form

$$\boldsymbol{V}=(k_BT)^{-1}\boldsymbol{D}\cdot(\boldsymbol{F}+\boldsymbol{R}) \tag{2.11}$$

$$<\boldsymbol{R}(t)>=\boldsymbol{0} \tag{2.12}$$

$$<\boldsymbol{R}(t)\widetilde{\boldsymbol{R}}(t')>=2k_BT\Xi\delta(t-t') \tag{2.13}$$

$$\boldsymbol{D}\cdot\Xi=\Xi\cdot\boldsymbol{D}=k_BT\boldsymbol{I} \tag{2.14}$$

Here the $6N\times6N$ grand friction matrix Ξ has N^2 blocks, each of which is a 6×6 matrix; e.g., the ij-block has the following elements

$$\begin{pmatrix}\xi_{ij}^{TT} & \xi_{ij}^{TR}\\ \xi_{ij}^{RT} & \xi_{ij}^{RR}\end{pmatrix}$$

and I is the $6N\times6N$ unit matrix.

Generation of the Displacement Vector $\Delta\chi(t_n)$

We define the displacement vector $\Delta\chi(t_n)$ by

$$\Delta\chi(t_n)\equiv\int_{t_n}^{t_{n+1}}V(t')\,dt' \quad \text{with } t_{n+1}=t_n+\Delta t \tag{2.15}$$

Here it must be noted that, of the 6N components of $\Delta\chi$, the 3N components related to angular displacements of particles are physically meaningful only if they are much smaller than π. Then from Eqs. (2.11)-(2.15), we can show that

$$\Delta\chi(t_n)\equiv\Delta\chi^S(t_n)+\Delta\chi^R(t_n) \tag{2.16}$$

$$\Delta\chi^S(t_n)\equiv<\Delta\chi(t_n)> \tag{2.17}$$
$$=(k_BT)^{-1}\boldsymbol{D}(t_n)\cdot\boldsymbol{F}(t_n)\Delta t+O[(\Delta t)^2]$$

$$<\Delta\chi^R(t_n)>=\boldsymbol{0} \tag{2.18}$$

$$<\Delta\chi^R(t_n)\Delta\widetilde{\chi}^R(t_n)>=2\boldsymbol{D}(t_n)\Delta t)+O[(\Delta t)^2] \tag{2.19}$$

The 6N components of the random displacement vector $\Delta\chi^R$ with the statistical properties given by Eqs. (2.18) and (2.19) can be obtained as follows.[8] First, we generate 6N Gaussian random deviates[19] A_i ($i=1,2,\ldots,6N$) with $<A_i>=0$ and $<A_iA_j>=2\Delta t\delta_{ij}$. We can then write

$$\Delta\chi^R(t_n)=\boldsymbol{S}\cdot\boldsymbol{A} \tag{2.20}$$

Here $\widetilde{\boldsymbol{A}}=(A_1,A_2,\ldots,A_{6N})$ and the components of $\boldsymbol{S}$ are given by

$$S_{ii}=\{[D(t_n)]_{ii}-\sum_{k=1}^{i-1}S_{ik}^2\}^{1/2} \tag{2.21}$$

$$S_{ij}=\begin{cases}\{[D(t_n)]_{ij}-\sum_{k=1}^{j-1}S_{ik}S_{jk}\}/S_{jj} & \text{for } i>j\\ 0 & \text{for } i<j\end{cases} \quad (2.22)$$

Move Algorithms for the Spatial Coordinates $\{r_i\}$

Since $dr_i/dt=v_i$, we have

$$r_i(t_{n+1})=r_i(t_n)+\int_{t_n}^{t_{n+1}}v_i(t')\,dt'$$

$$=r_i(t_n)+\begin{pmatrix}(\Delta\chi)_{6(i-1)+1}\\(\Delta\chi)_{6(i-1)+2}\\(\Delta\chi)_{6(i-1)+3}\end{pmatrix}+O[(\Delta t)^2] \quad (2.23)$$

$$(i=1,2,\cdots,N)$$

where we have used Eqs. (2.9) and (2.15) to obtain the second line.

Move Algorithms for the Orientational Coordinates

There are several alternatives for the choice of orientational coordinates. The most common choice makes use of the Euler angles[20] $(\alpha_i,\ \beta_i,\ \gamma_i)$ $(i=1,2,\ldots,N)$. The components of the angular velocities along the axes of space-fixed coordinate system are related to the rates of changes in the Euler angles by[21]

$$\begin{pmatrix}\dot{\alpha}_i\\ \dot{\beta}_i\\ \dot{\gamma}_i\end{pmatrix}=E_i\cdot\omega_i \qquad (i=1,2,\cdots,N) \quad (2.24)$$

where dots over the Euler angles denote the differentiation with respect to time, and $E_i(\alpha_i,\beta_i)$ is given by

$$E_i=\frac{1}{\sin\beta_i}\begin{pmatrix}-\cos\beta_i\cos\alpha_i & -\cos\beta_i\sin\alpha_i & \sin\beta_i\\ -\sin\beta_i\sin\alpha_i & -\sin\beta_i\cos\alpha_i & 0\\ \cos\alpha_i & \sin\alpha_i & 0\end{pmatrix} \quad (2.25)$$

Intergrating Eq. (2.24) over t from t_n to t_{n+1} and using Eqs. (2.9) and (2.15), we obtain

$$\begin{pmatrix}\alpha_i(t_{n+1})\\ \beta_i(t_{n+1})\\ \gamma_i(t_{n+1})\end{pmatrix}=\begin{pmatrix}\alpha_i(t_n)\\ \beta_i(t_n)\\ \gamma_i(t_n)\end{pmatrix}+E_i(t_n)\cdot\begin{pmatrix}(\Delta\chi)_{6(i-1)+4}\\(\Delta\chi)_{6(i-1)+5}\\(\Delta\chi)_{6(i-1)+6}\end{pmatrix}+O[(\Delta t)^2] \quad (2.26)$$

To avoid the divergence of $1/\sin\beta_i$ in E_i as β_i approaches 0 or π, we need to use two space-fixed coordinate systems which have the same y-axis but are rotated by $\pm\pi/2$ around the y-axis from each other, and then to change the space-fixed coordinate system associated with the i-th particle whenever β_i comes within $\pi/10$ of 0 or π[22].

Another choice for the orientational coordinates for the i-th particle consists of the nine components of the three body-fixed orthonormal vectors $(\hat{x}_i,\ \hat{y}_i,\ \hat{z}_i)$. These nine components are interdependent through the orthogonality and normalization relations; $\hat{\mu}_i\cdot\hat{\nu}_i=\delta_{\mu\nu}$ $(\hat{\mu},\nu=x,y,z)$. The time derivatives of these vectors are related to the angular velocity ω_i by[23]

$$d\hat{\mu}_i/dt=\omega_i\times\hat{\mu}_i \qquad (\mu=x,y,z) \quad (2.27)$$

Integrating Eq. (2.27) over t from t_n to t_{n+1} and using Eqs. (2.9) and (2.15), we obtain

$$\hat{\mu}_i(t_{n+1})=\hat{\mu}_i(t_n)+\begin{pmatrix}(\Delta\chi)_{6(i-1)+4}\\(\Delta\chi)_{6(i-1)+5}\\(\Delta\chi)_{6(i-1)+6}\end{pmatrix}\times\hat{\mu}_i(t_n)+O[(\Delta t)^2] \quad (2.28)$$

The orthonormality relations may not be satisfied after several moves due to the numerical inaccuracy for a finite size of Δt. To avoid this problem, the following move algorithm is used.

(i) Move $\hat{z}_i(t_n)$ and $\hat{x}_i(t_n)$ according to Eq. (2.28) to obtain $\hat{z}_i'(t_{n+1})$ and $\hat{x}_i'(t_{n+1})$.

(ii) Normalize $\hat{z}_i'(t_{n+1})$ to obtain $\hat{z}_i(t_{n+1})$.

(iii) Orthogonalize $\hat{x}_i'(t_{n+1})$ with respect to $\hat{z}_i(t_{n+1})$ by use of the relation, $\hat{x}_i''=\hat{x}_i'-\hat{z}_i(\hat{z}_i'\hat{x}_i')$.

(iv) Normalize $\hat{x}_i''(t_{n+1})$ to obtain $\hat{x}_i(t_{n+1})$.

(v) Find $\hat{y}_i(t_{n+1})$ from the relation, $\hat{y}_i=\hat{z}_i\times\hat{x}_i$.

Calculation of the Components of $D(t_n)$

In order to calculate $\Delta\chi(t_n)$, we need to know the components of $D(t_n)$ which are functions of the positions and orientations of the Brownian particles at t_n. General expressions for the interparticle diffusion tensors $D_{ij}^{\alpha\beta}(\alpha,\beta=T,R;\ i\neq j)$ for particles with arbitrary shape cannot be given, since they depend on the shape of particles as well as the relative separation and orientation of particles i and j. For spherical particles of uniform surface roughness, "Oseen's approximations" for the interparticle diffusion tensors which keep only the lowest order terms in the reciprocal of interparticle separation, r_{ij}^{-1}, were given by Wolynes and Deutch[16]. Higher order expressions have been presented recently by Mazur and van Saarloos.[24] Expressions for the self diffusion tensors, $D_{ii}^{\alpha\beta}(\alpha,\beta=T,R)$, also involve terms arising from interparticle hydrodynamic interactions.[24] Neglecting those terms which are higher order in r_{ij}^{-1}, we can write[25]

$$D_{ii}^{\alpha\beta}=\tilde{T}_i\cdot D_i^{\alpha\beta}\cdot T_i \qquad (\alpha,\beta=T,R) \quad (2.29)$$

Here $D_i^{\alpha\beta}$ is the representation of the diffusion tensor in the particle-fixed coordinate system and is independent of the position and orientation of particle i. It thus needs to be calculated only once before starting the simulation. Numerical procedures for calculating $D_i^{\alpha\beta}$ were reviewed by Garcia de la Torre and Bloomfield.[26] The orthogonal transformation matrix T_i is given by

$$T_i=\begin{pmatrix}\cos\alpha_i\cos\beta_i\cos\gamma_i-\sin\alpha_i\sin\gamma_i & \sin\alpha_i\cos\beta_i\cos\gamma_i+\cos\alpha_i\sin\gamma_i & -\sin\beta_i\cos\gamma_i\\ -\cos\alpha_i\cos\beta_i\sin\gamma_i-\sin\alpha_i\cos\gamma_i & -\sin\alpha_i\cos\beta_i\sin\gamma_i+\cos\alpha_i\cos\gamma_i & \sin\beta_i\sin\gamma_i\\ \cos\alpha_i\sin\beta_i & \sin\alpha_i\sin\beta_i & \cos\beta_i\end{pmatrix}$$

$$-\begin{pmatrix} (\hat{x}_i)_1 & (\hat{x}_i)_2 & (\hat{x}_i)_3 \\ (\hat{y}_i)_1 & (\hat{y}_i)_2 & (\hat{y}_i)_3 \\ (\hat{z}_i)_1 & (\hat{z}_i)_2 & (\hat{z}_i)_3 \end{pmatrix} \tag{2.30}$$

where $(\hat{\mu}_i)_1$, $(\hat{\mu}_i)_2$, and $(\hat{\mu}_i)_3$ are the component of $\hat{\mu}_i (\mu = x,y,z)$ with respect to the space-fixed coordinate system.

Test Simulations

To test the accuracies of the BD algorithms, we have calculated two long trajectories for an axially symmetric particle with $(D^{TT})_z = 43.1$ Å^2/ns, $(D^{TT}) = (D^{TT})_y = 37.7$ Å^2/ns, $(D^{RR})_z = 1.45$ ns^{-1}, and $(D^{RR})_x = (D^{RR})_y = 0.680$ ns^{-1}. These values correspond to those for a dimer made up of two spherical subunits with radii = 4 Å in water at room temperature. The reason for choosing this system is that any systematic errors due to inaccuracies of algorithms can be determined since we have exact expressions for the distributions of statistical errors in the translational diffusion coefficient and in the orientational correlation function of the symmetry axis calculated from BD trajectories[27]; these errors arising from the replacement of the ensemble average by a finite time average are unavoidable. The length of each of the two trajectories is 100 ns. One of them has been generated by using the Euler angle algorithm, and the other by using the body-fixed vector algorithm. For both trajectories, $\Delta t = 0.2$ ps has been used.

To examine the distributions of statistical errors, each of the trajectories was divided into 100 parts. From each part, we calculated the translational coefficient,

$$D_\tau(t) \equiv [r(t) - r(0)]^2_\tau / 6t \tag{3.1}$$

and the correlation function associated with reorientation of the symmetry axis,

$$C_\tau(t) \equiv [\hat{z}(0) \cdot \hat{z}(t)]_\tau \tag{3.2}$$

where the subscripts τ signify the time averages over a trajectory of finite length τ ($\simeq 1$ ns). If the BD algorithms are correct, as $\tau \to \infty$ these values should converge to

$$D_\infty(t) \equiv \lim_{\tau\to\infty} D_\tau(t) = (Tr\, D^{TT})/3 \tag{3.3}$$

$$C_\infty(t) \equiv \lim_{\tau\to\infty} C_\tau(t) = \exp(-2D^R_x t) \tag{3.4}$$

where $D^R_x = (D^{RR})_x$. For finite τ, the standard deviations of errors are given by[27]

$$\sigma_T = \langle [D_\tau(t) - D_\infty(t)]^2 \rangle^{1/2} = (2/3)\left[\frac{t}{\tau}\left(1 - \frac{t}{4\tau}\right)\right]^{1/2} \tag{3.5}$$

$$\sigma_R = \langle [C_\tau(t) - C_\infty(t)]^2 \rangle^{1/2} =$$

$$\frac{1}{24D^R_x\tau}\left\{\left(4 - \frac{1}{D^R_x\tau}\right) - \left(16 + \frac{8}{D^R_x\tau}\right)\exp(-6D^R_x t)\right.$$

$$\left. + \left[12\left(1 - \frac{t}{\tau}\right) - 48D^R_x t + \frac{24D^R_x t^2}{\tau} + \frac{9}{D^R_x\tau}\right)\exp(-4D^R_x t)\right| \tag{3.6}$$

Table 1. Distributions of Errors in $D_\tau(t)$ and $C_\tau(t)$ Calculated from the Trajectory Obtained by Using the Euler Angle Algorithm

t(ns)	% errors lying in the range[a]			
	$\Delta_T(t) \le \sigma_T$	$\sigma_T < \Delta_T(t) \le 2\sigma_T$	$2\sigma_T < \Delta_T(t) \le 3\sigma_T$	$3\sigma_T < \Delta_T(t) \le 4\sigma_T$
0.001	65	26	7	2
0.005	69	24	6	1
0.020	65	30	4	1
0.100	61	30	8	1
0.500	68	27	1	4
t(ns)	% erros lying in the range[b]			
	$\Delta_R(t) \le \sigma_R$	$\sigma_R < \Delta_R(t) \le 2\sigma_R$	$2\sigma_R < \Delta_R(t) \le 3\sigma_R$	$3\sigma_R < \Delta_R(t) \le 4\sigma_R$
0.001	56	31	9	4
0.005	70	22	8	0
0.020	65	27	8	0
0.100	62	33	4	1
0.500	68	25	7	0
Normal distribution	69.3	26.2	4.3	0.2

[a] $\Delta_T(t) \equiv |D_\tau(t) - D_\infty(t)|$. [b] $\Delta_R(t) \equiv |C_\tau(t) - C_\infty(t)|$.

Table 2. Distributions of Errors in $D_\tau(t)$ and $C_\tau(t)$ calculated from the Trajectory Obtained by Using the Body-Fixed Vector Algorithm.

t(ns)	% errors lysing in the range[a]			
	$\Delta_T(t) \le \sigma_T$	$\sigma_T < \Delta_T(t) \le 2\sigma_T$	$2\sigma_T < \Delta_T(t) \le 3\sigma_T$	$3\sigma_T < \Delta_T(t) \le 4\sigma_T$
0.001	66	25	9	0
0.005	74	19	6	1
0.020	64	31	4	1
0.100	60	31	8	1
0.500	68	27	1	4
t(ns)	% errors lying in the range[b]			
	$\Delta_R(t) \le \sigma_R$	$\sigma_R < \Delta_R(t) \le 2\sigma_R$	$2\sigma_R < \Delta_R(t) \le 3\sigma_R$	$3\sigma_R < \Delta_R(t) \le 4\sigma_R$
0.001	61	26	8	5
0.005	57	38	3	2
0.020	64	32	3	1
0.100	71	24	4	1
0.500	64	33	2	1
Normal distribution	69.3	26.2	4.3	0.2

[a] $\Delta_T(t) \equiv |D_\tau(t) - D_\infty(t)|$. [b] $\Delta_R(t) \equiv |C_\tau(t) - C_\infty(t)|$.

Table 1 and 2 show the distributions of errors in $D_\tau(t)$ and $C_\tau(t)$ calculated from the 100 parts of trajectory obtained by using the Euler angle algorithm and the body-fixed vector algorithm, respectively. We see that the error distributions are in quite good agreement with the normal distribution. These results confirm the accuracies of both algorithms.

Applications of the present BD algorithms to investigate the hydrodynamic properties of segmentally flexible macromolecules such as immunoglobulins and the reaction dynamics of diffusion-influenced enzyme-substrate reactions are the subjects of future work.

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Different Mode of Cytochrome *c* and Apocytochrome *c* Interactions with Phospholipid Bilayer

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Cytochrome *c* induces fusion of phosphatidylserine/phosphatidylethanolamine vesicles while apocytochrome *c* does not have a fusogenic capability despite the fact that the apoprotein binds to the vesicles more extensively. In order to see whether the difference in the fusogenic behavior comes from the topological variation in membrane bound proteins, the holoprotein and apoprotein were labeled with phenylisothiocyanate, a hydrophobic label, in the presence of its hydrophilic analogue *p*-sulfophenylisothiocyanate. Apocytochrome *c* was labeled with the hydrophobic probe more extensively than the cytochrome *c*, indicating that the apoprotein penetrates deeper into the bilayer than cytochrome *c* does. The translocation experiments of these proteins by trypsin entrapped vesicles further supported this conclusion.

Introduction

The studies on fusion of phosphatidylserine/phosphatidylethanolamine (PS/PE, 1:1, mol/mol) vesicles induced by α-lactalbumin[1-3] and lysozyme[4] suggested that surface penetration of small protein segments is important for the process. Apocytochrome *c* (Apo *c*) binds more extensively to PS/PE vesicles and a longer stretch of it is protected from the proteolysis of the protein-vesicle complex as compared

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