Brownian dynamics of rigid polymer chains with hydrodynamic interactions

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With the idea of a broad investigation of the flow behavior of dilute polymer solutions in mind, the dynamics of polymer chains with rigid constraints and hydrodynamic interactions is formulated in various equivalent ways. Starting from a very general diffusion equation of polymer kinetic theory, equivalent stochastic differential equations of motion both in terms of generalized coordinates and in terms of constraint conditions are derived. Then an efficient Brownian dynamics simulation algorithm is constructed rigorously, and a convenient expression for evaluating stresses in simulations is suggested. Furthermore, a modified simulation algorithm, which is appropriate for infinitely stiff rather than rigid systems, is discussed.

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I. INTRODUCTION

Mechanical models of polymers involving constraints play an important role in polymer kinetic theory [1]. Although models with constraints often impose fixed bond lengths or bond angles, they usually do not pretend to portray details of the chemical structure. The idea is rather to model molecules which exhibit considerable rigidity on much larger scales, such as the fashionable biological macromolecules or liquid crystal polymers.

There exist various delicate problems in modeling rigid or stiff polymer molecules by mechanical bead-rod-spring chains. For example, different results are obtained depending on whether bead inertia is neglected before or after introducing rigid constraints (Fixman [2] follows the former procedure while kinetic theory [1] implies the latter one), and rigid chains are different from very stiff elastic chains even in the limit of infinite stiffness [3]. Moreover, multiplicative noise unavoidably occurs in the stochastic differential equations of motion for polymer models with constraints, and the interpretation of the equations is then ambiguous (this ambiguity is known as the Itô-Stratonovich problem [4,5]). In view of all these delicacies it may be not surprising that in almost every paper on models with constraints errors in the previous literature are pointed out; we here follow that accredited tradition. In order to be on the safest possible ground we start from well-founded kinetic theory equations, and we consistently apply the mathematically rigorous Itô approach to stochastic calculus to avoid all ambiguities.

In this paper, bead-spring models with constraints and hydrodynamic interaction are approached in four steps. First, after introducing some notation (Sec. II), a very general diffusion equation of polymer kinetic theory is reformulated as a system of stochastic differential equations involving generalized coordinates (Sec. III). Second, from the stochastic equations of motion for the beads the generalized coordinates are eliminated in favor of constraint conditions (Sec. IV). Third, a numerical integration scheme (i.e., a Brownian dynamics simulation algorithm) is developed for the equations of motion in Cartesian coordinates (Sec. V). Fourth, an expression for the stress tensor which is particularly suitable for simulations is suggested (Sec. VI). A brief summary concludes the paper (Sec. VII).

II. BASIC NOTATION

Througout this paper, we assume that the constraints restrict only the internal configurations. It is hence useful to introduce the position vector of bead μ with mass M_μ ($\mu = 1, 2, \ldots, N$) with respect to the center of mass by $\mathbf{R}_\mu := \mathbf{r}_\mu - \mathbf{r}_c$, where $\mathbf{r}_\mu$ is the bead position vector with respect to an arbitrary point fixed in space and $\mathbf{r}_c$ is the center of mass position vector, $\mathbf{r}_c := \sum_\mu M_\mu \mathbf{r}_\mu / M_p$, $M_p := \sum_\mu M_\mu$ (by convention, the range of greek summation indices is always from 1 to N). We allow for beads having not only different masses M_μ but also different frictional properties described by symmetric friction tensors $\boldsymbol{\zeta}_\mu$. If the internal motions are restricted by d' time-independent constraints then we need $d = 3N-3-d'$ generalized coordinates $Q_1, Q_2, \ldots, Q_d$ in order to characterize the internal chain configurations. We assume that there exist smooth functions $\mathbf{R}_\mu(Q_1, Q_2, \ldots, Q_d)$ which specify the constrained internal configurations in terms of the generalized coordinates.

The influence of the constraints on inertial and frictional effects can most elegantly be described by means of two metric $d \times d$ matrices with components

$$\mathbf{g}_{jk} := \sum_\mu M_\mu \frac{\partial \mathbf{R}_\mu}{\partial Q_j} \cdot \frac{\partial \mathbf{R}_\mu}{\partial Q_k}, \tag{1}$$

$$\widetilde{\mathbf{g}}_{jk} := \sum_{\mu\nu} \frac{\partial \mathbf{R}_\mu}{\partial Q_j} \cdot \widetilde{\boldsymbol{\zeta}}_{\mu\nu} \cdot \frac{\partial \mathbf{R}_\nu}{\partial Q_k}, \tag{2}$$

which are only defined in the manifold characterized by the constraints (that is, in the space of constrained configurations). The tensors $\widetilde{\boldsymbol{\zeta}}_{\mu\nu}$ account not only for

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the bead friction but also for hydrodynamic interactions. More precisely, we assume that hydrodynamic interactions are described in terms of the tensors $\boldsymbol{\Omega}_{\mu\nu} := \boldsymbol{\Omega}(\mathbf{r}_\mu - \mathbf{r}_\nu) = \boldsymbol{\Omega}(\mathbf{R}_\mu - \mathbf{R}_\nu)$, where $\boldsymbol{\Omega}$ is a given function such as the Oseen-Burgers or Rotne-Prager-Yamakawa tensor [1]. We then introduce the effective friction tensors $\boldsymbol{\zeta}_{\mu\nu}$ by

$$\sum_\nu \boldsymbol{\zeta}_{\mu\nu} \cdot (\delta_{\nu\mu'} \boldsymbol{\zeta}_\nu^{-1} + \boldsymbol{\Omega}_{\nu\mu'}) = \delta_{\mu\mu'}\, \boldsymbol{\delta}\,, \tag{3}$$

where $\delta_{\mu\nu}$ is the Kronecker delta and $\boldsymbol{\delta}$ is the unit tensor. The modified effective friction tensors occurring in Eq. (2) are defined as

$$\tilde{\boldsymbol{\zeta}}_{\mu\nu} := \boldsymbol{\zeta}_{\mu\nu} - \boldsymbol{\lambda}_\mu^T \cdot \mathbf{Z} \cdot \boldsymbol{\lambda}_\nu\,, \tag{4}$$

where $\mathbf{Z} := \sum_{\mu\nu} \boldsymbol{\zeta}_{\mu\nu}$ is the total effective friction tensor and the $\boldsymbol{\lambda}_\nu := \mathbf{Z}^{-1} \cdot \sum_\mu \boldsymbol{\zeta}_{\mu\nu}$ are weight tensors with $\sum_\nu \boldsymbol{\lambda}_\nu = \boldsymbol{\delta}$. We thus obtain from Eq. (4),

$$\sum_\mu \tilde{\boldsymbol{\zeta}}_{\mu\nu} = \mathbf{0}\,. \tag{5}$$

As an immediate but very useful consequence of Eq. (3) we obtain the identity

$$\sum_\nu \tilde{\boldsymbol{\zeta}}_{\mu\nu} \cdot (\delta_{\nu\mu'} \boldsymbol{\zeta}_\nu^{-1} + \boldsymbol{\Omega}_{\nu\mu'}) = \delta_{\mu\mu'}\, \boldsymbol{\delta} - \boldsymbol{\lambda}_\mu^T\,. \tag{6}$$

III. FORMULATION OF STOCHASTIC DIFFERENTIAL EQUATIONS

The formulation of stochastic differential equations for the d generalized coordinates which are equivalent to the diffusion equation (16.2-6) of Ref. [1] is straightforward [4,5]. Formulation of the noise terms requires a decomposition of the diffusion matrix which is not unique. Rather than looking for a possible representation of the noise terms involving only d Wiener processes we here introduce N three-dimensional Wiener processes $\mathbf{W}_\mu$ ($3N > d$) corresponding to the noise terms for the individual beads [that is, the time-dependent random variables $\mathbf{W}_\mu(t)$ possess a Gaussian distribution with $\langle \mathbf{W}_\mu(t) \rangle = \mathbf{0}$ and $\langle \mathbf{W}_\mu(t)\, \mathbf{W}_\nu(t') \rangle = \delta_{\mu\nu} \min(t, t')\, \boldsymbol{\delta}$]. While this representation leads to unnecessarily complicated noise terms in the equations for the generalized coordinates, it yields the most natural form of the equations of motion in Cartesian space. One then needs the decomposition

$$\delta_{\mu\mu'} \boldsymbol{\zeta}_\mu^{-1} + \boldsymbol{\Omega}_{\mu\mu'} = \sum_\nu \mathbf{B}_{\mu\nu} \cdot \mathbf{B}_{\mu'\nu}^T\,, \tag{7}$$

for all $\mu, \mu' = 1, 2, \ldots, N$, which is independent of the constraints. When the tensors $\mathbf{B}_{\mu\nu}$ are used to represent the noise terms, the stochastic differential equations for the generalized coordinates are

$$dQ_j = \sum_{k=1}^d \sum_\mu \tilde{\mathsf{G}}_{jk} \frac{\partial \mathbf{R}_\mu}{\partial Q_k} \cdot \left\{ \left[\sum_\nu (\delta_{\mu\nu}\, \boldsymbol{\delta} - \boldsymbol{\lambda}_\mu^T) \cdot (\mathbf{F}_\nu + \mathbf{F}_\nu^{(e)}) + \sum_\nu \tilde{\boldsymbol{\zeta}}_{\mu\nu} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_\nu \right] dt + \sqrt{2k_BT} \sum_{\nu\nu'} \tilde{\boldsymbol{\zeta}}_{\mu\nu} \cdot \mathbf{B}_{\nu\nu'} \cdot d\mathbf{W}_{\nu'} \right\}$$
$$+ k_BT \frac{1}{\sqrt{\mathsf{g}}} \sum_{k=1}^d \frac{\partial}{\partial Q_k} \left(\tilde{\mathsf{G}}_{jk} \sqrt{\mathsf{g}} \right) dt\,, \tag{8}$$

where the velocity gradients $\boldsymbol{\kappa}$ characterize a given homogeneous flow field of the form $\mathbf{v}_0 + \boldsymbol{\kappa} \cdot \mathbf{r}$, $\mathbf{F}_\mu$ and $\mathbf{F}_\mu^{(e)}$ are the internal interaction and external forces on bead μ, k_B is Boltzmann's constant, T is the absolute temperature, g is the determinant of g_{jk}, and $\tilde{\mathsf{G}}_{jk}$ represents the inverse of $\tilde{\mathsf{g}}_{jk}$. With the results of Sec. II, it is straightforward to write the Fokker-Planck equation associated with Eq. (8) in the form of Eq. (16.2-6) of Ref. [1]. Only the weight tensors $\boldsymbol{\lambda}_\mu^T$, which we have introduced in front of the force terms, are delicate. For the intramolecular forces this has no effect since the additional term vanishes when the summation over ν is carried out. The same argument applies when $\mathbf{F}_\nu^{(e)}$ depends only on the internal configuration of the chain. If, however, the external forces depend on the center of mass position then Eq. (18.2-23) of Ref. [1] implies that the weight tensors need to be introduced in the above manner.

By transforming the equations of motion for the generalized coordinates by means of the Itô formula [4,5], we obtain stochastic differential equations for the position vectors $\mathbf{R}_\mu$,

$$d\mathbf{R}_\mu = \sum_{\mu'} \mathbf{H}_{\mu\mu'} \cdot \left\{ \left[\sum_\nu (\delta_{\mu'\nu}\, \boldsymbol{\delta} - \boldsymbol{\lambda}_{\mu'}^T) \cdot (\mathbf{F}_\nu + \mathbf{F}_\nu^{(e)}) + \sum_\nu \tilde{\boldsymbol{\zeta}}_{\mu'\nu} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_\nu \right] dt + \sqrt{2k_BT} \sum_{\nu\nu'} \tilde{\boldsymbol{\zeta}}_{\mu'\nu} \cdot \mathbf{B}_{\nu\nu'} \cdot d\mathbf{W}_{\nu'} \right\}$$
$$+ k_BT \sum_{j,k=1}^d \frac{1}{\sqrt{\mathsf{g}}} \frac{\partial}{\partial Q_j} \left(\sqrt{\mathsf{g}}\, \tilde{\mathsf{G}}_{jk} \frac{\partial \mathbf{R}_\mu}{\partial Q_k} \right) dt\,, \tag{9}$$

where

$$\mathbf{H}_{\mu\nu} := \sum_{j,k=1}^d \tilde{\mathsf{G}}_{jk} \frac{\partial \mathbf{R}_\mu}{\partial Q_j} \frac{\partial \mathbf{R}_\nu}{\partial Q_k}\,. \tag{10}$$

Derivation of the equations for $\mathbf{r}_\mu$ requires additional consideration of the center of mass motion. After a straightforward generalization of the kinetic theory derivations of Ref. [1] we obtain

$$d\mathbf{r}_\mu = \sum_\nu \mathbf{P}_{\mu\nu} \cdot \left\{ \left[\mathbf{v}_0 + \boldsymbol{\kappa} \cdot \mathbf{r}_\nu + \sum_{\nu'} (\delta_{\nu\nu'} \zeta_\nu^{-1} + \boldsymbol{\Omega}_{\nu\nu'}) \cdot (\mathbf{F}_{\nu'} + \mathbf{F}_{\nu'}^{(e)}) \right] dt + \sqrt{2k_BT} \sum_{\nu'} \mathbf{B}_{\nu\nu'} \cdot d\mathbf{W}_{\nu'} \right\}$$
$$+k_BT \sum_\nu (\delta_{\mu\nu}\,\boldsymbol{\delta} - \boldsymbol{\lambda}_\nu) \cdot \sum_{j,k=1}^{d} \frac{1}{\sqrt{\mathrm{g}}} \frac{\partial}{\partial Q_j} \left(\sqrt{\mathrm{g}}\, \widetilde{\mathrm{G}}_{jk} \frac{\partial \mathbf{R}_\nu}{\partial Q_k} \right) dt + k_BT \sum_{\mu'\nu\nu'} \mathbf{P}_{\mu'\nu}^T : \left(\frac{\partial}{\partial \mathbf{r}_{\mu'}} \boldsymbol{\Omega}_{\nu\nu'} \right) \cdot \boldsymbol{\lambda}_{\nu'}^T \, dt\,, \tag{11}$$

where

$$\mathbf{P}_{\mu\nu} := \boldsymbol{\lambda}_\nu + \sum_{j,k=1}^{d} \widetilde{\mathrm{G}}_{jk} \sum_{\mu'\nu'} (\delta_{\mu\mu'}\,\boldsymbol{\delta} - \boldsymbol{\lambda}_{\mu'}) \cdot \frac{\partial \mathbf{R}_{\mu'}}{\partial Q_j} \frac{\partial \mathbf{R}_{\nu'}}{\partial Q_k} \cdot \widetilde{\boldsymbol{\zeta}}_{\nu'\nu}\,, \qquad \sum_\nu \mathbf{P}_{\mu\nu} \cdot \mathbf{P}_{\nu\mu'} = \mathbf{P}_{\mu\mu'}\,, \tag{12}$$

is a projection operator and ":" implies a double contraction. Note that most of the terms in the second line of Eq. (11) are independent of μ and hence do not contribute to the internal motions. The consistency of Eqs. (9) and (11) can be checked by means of Eq. (6) and the identity

$$\sum_{\mu'} \left(\delta_{\mu\mu'} - \frac{M_{\mu'}}{M_p} \right) \mathbf{P}_{\mu'\nu} = \sum_{\mu'} \mathbf{H}_{\mu\mu'} \cdot \widetilde{\boldsymbol{\zeta}}_{\mu'\nu}\,. \tag{13}$$

IV. GENERALIZED COORDINATES VERSUS CONSTRAINT CONDITIONS

If Eq. (11) is used as a starting point for a simulation then the evaluation of the coefficients requires an explicit parametrization of the vectors $\mathbf{R}_\mu$ in terms of generalized coordinates. In many applications, and in particular in simulations [2,3], it is simpler to work directly with time-independent constraints of the form $g_j(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = 0$ for $j = 1, \ldots, d'$, where, for example, for constrained bond lengths and angles, only two or three bead positions are involved in each constraint equation. In general, we assume that only the internal configurations are constrained, that is,

$$\sum_\mu \frac{\partial g_j}{\partial \mathbf{r}_\mu} = \mathbf{0}\,. \tag{14}$$

In the next step, we express all coefficients in Eq. (11) in terms of the constraint conditions. Again we need two metric matrices accounting for inertial and frictional effects, but now these are $d' \times d'$ matrices obtained directly from the constraint conditions,

$$\hat{\mathrm{G}}_{jk} := \sum_\mu \frac{1}{M_\mu} \frac{\partial g_j}{\partial \mathbf{r}_\mu} \cdot \frac{\partial g_k}{\partial \mathbf{r}_\mu}\,, \tag{15}$$

$$\overline{\mathrm{G}}_{jk} := \sum_{\mu\nu} \frac{\partial g_j}{\partial \mathbf{r}_\mu} \cdot (\delta_{\mu\nu} \zeta_\mu^{-1} + \boldsymbol{\Omega}_{\mu\nu}) \cdot \frac{\partial g_k}{\partial \mathbf{r}_\nu}\,. \tag{16}$$

In the course of eliminating all generalized coordinates from Eq. (11), the projection operator $\mathbf{P}_{\mu\nu}$ can now be expressed in the form

$$\mathbf{P}_{\mu\nu} = \delta_{\mu\nu}\boldsymbol{\delta} - \sum_{j,k=1}^{d'} \bar{\mathrm{g}}_{jk} \sum_{\mu'} (\delta_{\mu\mu'} \zeta_\mu^{-1} + \boldsymbol{\Omega}_{\mu\mu'}) \cdot \frac{\partial g_j}{\partial \mathbf{r}_{\mu'}} \frac{\partial g_k}{\partial \mathbf{r}_\nu}\,, \tag{17}$$

where $\bar{\mathrm{g}}_{jk}$ represents the inverse of $\overline{\mathrm{G}}_{jk}$. Note that Eqs. (15)–(17) are not restricted to the space of constrained configurations. The equivalence of the expressions (12) and (17) in the space of constrained configurations can be shown by comparing

$$\sum_\nu \mathbf{P}_{\mu\nu} \cdot \boldsymbol{\delta}, \quad \sum_\nu \mathbf{P}_{\mu\nu} \cdot \frac{\partial \mathbf{R}_\nu}{\partial Q_j}\,,$$
$$\sum_{\nu\nu'} \mathbf{P}_{\mu\nu} \cdot (\delta_{\nu\nu'} \zeta_\nu^{-1} + \boldsymbol{\Omega}_{\nu\nu'}) \cdot \frac{\partial g_k}{\partial \mathbf{r}_{\nu'}}\,, \tag{18}$$

corresponding to checking the equivalent action on $d + d' + 3 = 3N$ independent base vectors. In the absence of hydrodynamic interaction, the linear independence of the base vectors follows from the assumption that the d' constraints are independent, that is, that $3N - 3 - d'$ generalized coordinates are sufficient for characterizing the internal configurations. The linear independence must then hold also for weak hydrodynamic interaction and hence constitutes the generic case. In evaluating the expressions (18) with $\mathbf{P}_{\mu\nu}$ given by Eqs. (12) and (17), the differentiation rule,

$$\sum_\mu \frac{\partial g_j}{\partial \mathbf{r}_\mu} \cdot \frac{\partial \mathbf{R}_\mu}{\partial Q_k} = 0\,, \tag{19}$$

and Eqs. (6) and (14) are very useful.

What remains to be done is to eliminate the second-order derivative terms with respect to generalized coordinates from Eq. (11). As one should expect for a sensible formulation of the dynamics of models with constraints, this term is independent of the choice of generalized coordinates. Inspired by a very common and helpful procedure in the general theory of relativity, namely, the introduction of locally inertial coordinates [6], we choose

a set of generalized coordinates in which this term can be handled most conveniently so that a relationship with the constraint conditions can readily be established. More precisely, we introduce generalized coordinates such that at a given point of the space of constrained configurations the following conditions hold:

$$\mathbf{g}_{jk} = \delta_{jk}\,, \tag{20}$$

$$\sum_{\mu} M_\mu \frac{\partial^2 \mathbf{R}_\mu}{\partial Q_j \partial Q_k} \cdot \frac{\partial \mathbf{R}_\mu}{\partial Q_l} = 0\,. \tag{21}$$

When the generalized coordinates satisfy Eq. (21), one can derive the explicit representation

$$\frac{\partial^2 \mathbf{R}_\mu}{\partial Q_j \partial Q_k} = -\sum_{l,n=1}^{d'} \hat{\mathbf{g}}_{ln} \left(\sum_{\mu'\nu'} \frac{\partial \mathbf{R}_{\mu'}}{\partial Q_j} \cdot \frac{\partial^2 g_n}{\partial \boldsymbol{r}_{\mu'} \partial \boldsymbol{r}_{\nu'}} \cdot \frac{\partial \mathbf{R}_{\nu'}}{\partial Q_k} \right) \times \frac{1}{M_\mu} \frac{\partial g_l}{\partial \boldsymbol{r}_\mu}\,, \tag{22}$$

where $\hat{\mathbf{g}}_{jk}$ represents the inverse of $\hat{\mathbf{G}}_{jk}$. The representation (22) is the key to eliminating the second-order derivative terms with respect to generalized coordinates from Eq. (11). For a coordinate system satisfying Eq. (21), the derivatives of $\mathbf{g}$ vanish; the derivatives of $\widetilde{\mathbf{G}}_{jk}$, when expressed in terms of the derivatives of its inverse (2), do not only lead to terms involving $\partial^2 \mathbf{R}_\mu / \partial Q_j \partial Q_k$ but also to additional derivatives of modified effective friction tensors and hence of $\boldsymbol{\Omega}_{\nu\nu'}$. By combining these results, we finally obtain

$$\begin{aligned} d\boldsymbol{r}_\mu = {} & \sum_\nu \boldsymbol{P}_{\mu\nu} \cdot \left\{ \left[\boldsymbol{v}_0 + \boldsymbol{\kappa} \cdot \boldsymbol{r}_\nu + \sum_{\nu'} (\delta_{\nu\nu'} \boldsymbol{\zeta}_\nu^{-1} + \boldsymbol{\Omega}_{\nu\nu'}) \cdot (\boldsymbol{F}_{\nu'} + \boldsymbol{F}_{\nu'}^{(e)} + \boldsymbol{F}_{\nu'}^{(m)}) \right] dt + \sqrt{2k_BT} \sum_{\nu'} \boldsymbol{B}_{\nu\nu'} \cdot d\boldsymbol{W}_{\nu'} \right\} \\ & - k_BT \sum_{j=1}^{d'} \sum_{\mu'\nu\nu'} \left[\boldsymbol{P}_{\nu\mu'} \cdot (\delta_{\mu'\nu'} \boldsymbol{\zeta}_{\mu'}^{-1} + \boldsymbol{\Omega}_{\mu'\nu'}) \right] : \frac{\partial^2 g_j}{\partial \boldsymbol{r}_{\nu'} \partial \boldsymbol{r}_\nu} \frac{\partial \mathbf{R}_\mu}{\partial g_j}\, dt \\ & - k_BT \sum_{j=1}^{d'} \sum_{\mu'\nu\nu'} \boldsymbol{P}_{\mu\mu'} \cdot (\delta_{\mu'\nu'} \boldsymbol{\zeta}_{\mu'}^{-1} + \boldsymbol{\Omega}_{\mu'\nu'}) \cdot \frac{\partial^2 g_j}{\partial \boldsymbol{r}_{\nu'} \partial \boldsymbol{r}_\nu} \cdot \frac{\partial \mathbf{R}_\nu}{\partial g_j}\, dt + k_BT \sum_{\mu'\nu\nu'} \boldsymbol{P}_{\mu'\nu}^T : \left(\frac{\partial}{\partial \boldsymbol{r}_{\mu'}} \boldsymbol{\Omega}_{\nu\nu'} \right) \cdot \boldsymbol{P}_{\mu\nu'}^T\, dt\,. \end{aligned} \tag{23}$$

In this equation we have introduced an extra force due to the constraints which depends on the determinant $\hat{\mathbf{G}}$ of the metric matrix $\hat{\mathbf{G}}_{jk}$,

$$\boldsymbol{F}_\mu^{(m)} := \frac{1}{2} k_BT \frac{\partial}{\partial \boldsymbol{r}_\mu} \ln \hat{\mathbf{G}}\,. \tag{24}$$

Equation (23), together with the representation (17) for $\boldsymbol{P}_{\mu\nu}$, constitutes the desired reformulation of Eq. (11) in which generalized coordinates are eliminated in favor of the constraint conditions.

V. NUMERICAL INTEGRATION SCHEMES

There are several possibilities for simulating models with constraints. One possibility is based on the numerical integration of the stochastic differential equations for the generalized coordinates Q_j. However, this possibility is feasible only if the number of generalized coordinates involved is small, that is, for almost rigid molecules. If there are many internal degrees of freedom and hence many generalized coordinates then, in general, handling of them is too complicated. For this situation we construct in the next step a numerical integration scheme for Eq. (23) which rigorously satisfies the constraints and is very well suited for Brownian dynamics simulations.

If the bead positions at some initial time are given by $\boldsymbol{r}_\mu$ then the positions after a time step of width Δt are constructed in two steps. First an unconstrained move is taken to calculate the auxiliary positions

$$\begin{aligned} \overline{\boldsymbol{r}}_\mu = {} & \boldsymbol{r}_\mu + \left[\boldsymbol{v}_0 + \boldsymbol{\kappa} \cdot \boldsymbol{r}_\mu + \sum_\nu (\delta_{\mu\nu} \boldsymbol{\zeta}_\mu^{-1} + \boldsymbol{\Omega}_{\mu\nu}) \cdot (\boldsymbol{F}_\nu + \boldsymbol{F}_\nu^{(e)} + \boldsymbol{F}_\nu^{(m)}) \right] \Delta t \\ & + \sqrt{2k_BT} \sum_\nu \boldsymbol{B}_{\mu\nu} \cdot \Delta \boldsymbol{W}_\nu\,, \end{aligned} \tag{25}$$

where $\boldsymbol{B}_{\mu\nu}$ was introduced in Eq. (7) and $\Delta \boldsymbol{W}_\nu$ is the increment of the Wiener process $\boldsymbol{W}_\nu$ for the time step under consideration (that is, the $\Delta \boldsymbol{W}_\mu$ for all time steps are independent Gaussian random variables with $\langle \Delta \boldsymbol{W}_\mu \rangle = \mathbf{0}$ and $\langle \Delta \boldsymbol{W}_\mu \Delta \boldsymbol{W}_\nu \rangle = \delta_{\mu\nu} \boldsymbol{\delta} \Delta t$). All the coefficients in Eq. (25) are evaluated with the configuration at the beginning of the time step. Then, the final bead positions are obtained as

$$\widetilde{\boldsymbol{r}}_\mu = \overline{\boldsymbol{r}}_\mu - \sum_{j=1}^{d'} \gamma_j \left[\sum_\nu (\delta_{\mu\nu} \boldsymbol{\zeta}_\mu^{-1} + \boldsymbol{\Omega}_{\mu\nu}) \cdot \frac{\partial g_j}{\partial \boldsymbol{r}_\nu} \right]_c\,, \tag{26}$$

where $[\,]_c$ indicates that the corresponding term is evaluated at the positions $(1-c)\boldsymbol{r}_\mu + c\overline{\boldsymbol{r}}_\mu$ with $c \in [0,1]$. The set of Lagrange multipliers γ_j is to be determined such that all the constraints are satisfied rigorously, that is, $g_j(\widetilde{\boldsymbol{r}}_1, \widetilde{\boldsymbol{r}}_2, \ldots, \widetilde{\boldsymbol{r}}_N) = 0$.

In order to derive the stochastic differential equation corresponding to the iteration scheme in Eqs. (25) and (26) we need the contributions to γ_j which are of order $(\Delta t)^{1/2}$ and Δt. The precise form of these contributions can be obtained by expanding $g_j(\widetilde{\boldsymbol{r}}_1, \widetilde{\boldsymbol{r}}_2, \ldots, \widetilde{\boldsymbol{r}}_N)$. If the results are combined with Eqs. (25) and (26) then it is

found that the above procedure provides a numerical integration scheme for Eq. (23) provided that $c = 1/2$. The convergence of arbitrary averages is of first order in time step width. The choice $c = 1/2$ is crucial for obtaining terms involving derivatives of hydrodynamic-interaction tensors.

In the absence of hydrodynamic interactions and for identical beads with isotropic friction tensors one has

$$k_B T \sum_{j=1}^{d'} \sum_{\nu} \frac{\partial^2 g_j}{\partial \mathbf{r}_{\nu'} \partial \mathbf{r}_{\nu}} \cdot \frac{\partial \mathbf{R}_{\nu}}{\partial g_j} = \mathbf{F}_{\nu'}^{(m)} , \tag{27}$$

so that the first term in the last line of Eq. (23) cancels the term involving $\mathbf{F}_{\nu'}^{(m)}$ [4]. In this situation, a valid simulation algorithm is obtained when the metric force $\mathbf{F}_{\nu'}^{(m)}$ in Eq. (25) is omitted and Eq. (26) is used with $c = 0$. Such an algorithm was employed by Liu for Kramers chains [7]. The SHAKE-HI algorithm suggested in Ref. [8] corresponds to setting $c = 0$ and neglecting $\mathbf{F}_{\nu'}^{(m)}$ even in the presence of hydrodynamic interactions; in general, this algorithm does not reproduce the corresponding kinetic theory models.

The Lagrange multipliers γ_j in Eq. (26) must be determined from a set of nonlinear equations and hence need to be calculated by an iterative procedure. For example, one can construct an iteration scheme by writing the constraints in the form

$$\gamma_j = \gamma_j + \sum_{k=1}^{d'} \left[\bar{\mathbf{g}}_{jk}\right]_{c'} g_k(\tilde{\mathbf{r}}_1, \tilde{\mathbf{r}}_2, \ldots, \tilde{\mathbf{r}}_N) , \tag{28}$$

where $c' \in [0,1]$. Starting with $\gamma_j = 0$, successive approximations for γ_j can be generated by evaluating the right-hand side of Eq. (28) with the current approximate Lagrange multipliers γ_j until all constraints are satisfied within a specified tolerance [the vectors $\tilde{\mathbf{r}}_\mu$ depend on γ_j according to the definition (26)]. Note that $[\bar{\mathbf{g}}_{jk}]_{c'}$ needs to be calculated only once in this iterative procedure. Liu [7] observed rapid convergence when he employed a special case of this iterative scheme in a simulation of Kramers chains. Fixman [2] had previously used the same idea for solving the quadratic constraint equations for models with fixed bond lengths and bond angles. The fact that $\bar{\mathsf{G}}_{jk}$ typically has a narrow band structure can be exploited to design very efficient algorithms for calculating metric forces and Lagrange multipliers [2].

A well-known alternative for solving the set of nonlinear equations for the Lagrange multipliers is used in the SHAKE-HI algorithm [8]. In that approach, only one Lagrange multiplier γ_j is determined at a time, such that the corresponding constraint $g_j = 0$ is enforced. Since the enforcement of a particular constraint partially destroys constraints that were enforced previously, it is necessary to repeat the cycle of enforcing all constraints until all constraint equations are satisfied with the specified tolerance [8].

We conclude the description of our simulation algorithm with some heuristic or mnemonic remarks. The unconstrained move (25) is of the Itô type because all coefficients are evaluated at the beginning of the time step. It can be shown that the Itô approach is most natural for models with hydrodynamic interaction [4]. Therefore, only the occurrence of the metric forces $\mathbf{F}_{\nu}^{(m)}$ needs to be justified. To this end, it is important to realize that the metric force defined in Eq. (24) is exactly the negative of the corrective force which needs to be applied in order to make a rigid system behave like a very stiff system when bead inertia is taken into account in evaluating the constraint forces (in Ref. [3], this was shown only in the absence of hydrodynamic interaction; the arguments of Ref. [9] suggest that the compensation of metric and corrective forces is not affected by hydrodynamic interaction). In other words, if the forces $\mathbf{F}_{\nu}^{(m)}$ in Eq. (25) are omitted then we obtain a simulation of an infinitely stiff system; the truly rigid system necessitates the occurrence of the metric forces $\mathbf{F}_{\nu}^{(m)}$ in the unconstrained move. In this sense, it is slightly easier to simulate infinitely stiff rather than rigid systems, and the simulation algorithm for infinitely stiff systems appears to be more natural. Use of $c = 1/2$ in Eq. (26) corresponds to a Stratonovich-type restoration of constraints; one may thus think of the mechanism for restoring constraints as being governed by the rules of deterministic calculus. It is most remarkable that these simple heuristic arguments on the level of a simulation algorithm reproduce the full complexity of the kinetic theory equations (11) or (23).

VI. STRESS TENSOR

In the final step we show how the stress tensor can be evaluated in a Brownian dynamics simulation. As for obtaining the diffusion equation, we rely on kinetic theory for obtaining the appropriate stress tensor for general bead-rod-spring models. Starting from the modified Kramers expression for the stress tensor, Eq. (16.3-11) of Ref. [1], one can derive for only one polymer species

$$\begin{aligned} \boldsymbol{\tau}^p = {} & n_p \sum_{\mu\nu} \left\langle \mathbf{R}_\mu \tilde{\boldsymbol{\zeta}}_{\mu\nu} \cdot (\mathbf{A}_\nu - \boldsymbol{\kappa} \cdot \mathbf{R}_\nu) \right\rangle \\ & - n_p k_B T \left[\boldsymbol{\delta} - \sum_{\mu} \langle \mathbf{P}_{\mu\mu} \rangle \right. \\ & \left. + \sum_{\mu\mu'\nu\nu'} \left\langle \mathbf{R}_\mu \mathbf{P}^T_{\mu'\nu} : \left(\frac{\partial}{\partial \mathbf{r}_{\mu'}} \boldsymbol{\Omega}_{\nu\nu'} \right) \cdot \tilde{\boldsymbol{\zeta}}_{\nu'\mu} \right\rangle \right] . \end{aligned} \tag{29}$$

In this equation, $\mathbf{A}_\nu$ is the drift velocity associated with $\mathbf{R}_\nu$; this deterministic contribution to $d\mathbf{R}_\nu/dt$ can be obtained in terms of generalized coordinates or constraint conditions by neglecting the noise terms in Eqs. (11) or (23), respectively, and by subtracting the center of mass contribution to the drift velocity. For example, we obtain the drift velocity in terms of generalized coordinates from Eq. (11) [or directly from Eq. (9)],

$$\mathbf{A}_\mu = \sum_{\mu'} \mathbf{H}_{\mu\mu'} \cdot \Big[\sum_{\nu} (\delta_{\mu'\nu}\,\boldsymbol{\delta} - \boldsymbol{\lambda}_{\mu'}^{T}) \cdot (\mathbf{F}_\nu + \mathbf{F}_\nu^{(e)}) + \sum_{\nu} \tilde{\boldsymbol{\zeta}}_{\mu'\nu} \cdot \boldsymbol{\kappa} \cdot \mathbf{R}_\nu \Big] + k_B T \sum_{j,k=1}^{d} \frac{1}{\sqrt{\mathrm{g}}} \frac{\partial}{\partial Q_j} \left(\sqrt{\mathrm{g}}\, \tilde{\mathrm{G}}_{jk} \frac{\partial \mathbf{R}_\mu}{\partial Q_k} \right) . \tag{30}$$

The combination $\mathbf{A}_\nu - \boldsymbol{\kappa} \cdot \mathbf{R}_\nu$ occurring in the first term of Eq. (29) may then be interpreted as a convected drift derivative of $\mathbf{R}_\nu$.

Some comments on the limitations and usefulness of this expression for the stress tensor seem to be appropriate. While the incorporation of external forces into the equations of motion is very natural, their presence is more problematic for the stress tensor. The deeper reason for this problem is that, in general, external forces lead to inhomogeneous concentrations. Since the kinetic theory in Ref. [1] is limited to homogeneous systems, Eq. (29) can safely be used only if the total external force on each molecule vanishes. The fact that external forces do not explicitly occur in Eq. (29) might indicate that this expression could also be useful in the presence of arbitrary external forces. The last term in Eq. (29) vanishes if hydrodynamic interactions are absent (or if they are treated by some averaging approximation). The term involving the projection operators $\mathbf{P}_{\mu\mu}$ implies that the constraints can lead to anisotropic momentum exchange due to internal bead motions.

In a numerical integration scheme the drift velocity $\mathbf{A}_\nu$ in Eq. (29) may be replaced by the discrete approximation $[\mathbf{R}_\nu(t+\Delta t) - \mathbf{R}_\nu(t)]/\Delta t$, provided that all other terms in the average involving the drift velocity are evaluated at time t. This statement follows from the fact that, except for terms that vanish as $\Delta t \to 0$, the difference between these expressions is proportional to increments of the Wiener process which are independent of the polymer configurations at time t and hence vanish after averaging.

VII. SUMMARY

In summary, we have shown (i) how the general diffusion equation for polymer molecules with constraints and hydrodynamic interaction can be reformulated as a system of stochastic differential equations, (ii) how rigorous Brownian dynamics simulation algorithms can be constructed after eliminating generalized coordinates, and (iii) how stresses can be evaluated in simulations.

The simulation algorithm derived here for polymer molecules with hydrodynamic interaction in the presence of rigid constraints can easily be modified to treat infinitely stiff rather than rigid systems; the algorithm then actually takes a slightly more natural form. The algorithms for either case deviate from the SHAKE-HI algorithm which has previously been used in the literature in order to simulate polymer molecules with constraints and hydrodynamic interaction. Even though the simulation algorithms for infinitely stiff and rigid systems and other algorithms considered in the literature may give qualitatively the same results it should be emphasized that the simulations developed here constitute a rigorous tool for treating well-defined kinetic theory models.

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