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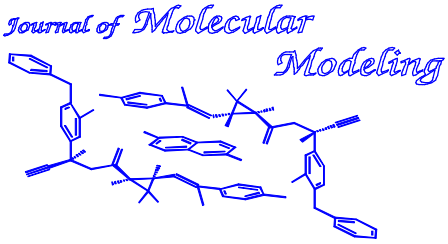

Sedimentation of Clusters of Spheres. II. Constrained Systems

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Abstract

Starting from the *N*-body friction matrix of an unconstrained system of *N* rigid particles immersed in a viscous liquid, we derive rigorous expressions for the corresponding friction and mobility matrices of a geometrically constrained dynamical system. Our method is based on the fact that geometrical constraints in a dynamical system can be cast in the form of linear constraints for the Cartesian translational and angular velocities of its constituents. Corresponding equations of motion for Molecular Dynamics simulations have been derived recently [1]. Using the concept of generalized inverse matrices, we find the form of the constrained friction and mobility matrix in Cartesian and in reduced coordinates. We show that the equations of motion for Stokesian Dynamics can be derived from a minimum principle which is similar to Gauß' principle of least constraint in classical mechanics.

We relate our approach for deriving constrained friction and mobility matrices to Kirkwood's method where holonomic constraints acting between point-like particles are described by generalized coordinates and tensor algebra in curvilinear space.

As an application, we perform a Stokesian Dynamics simulation of sedimentation of a small model polymer consisting of five spherical monomers connected by massless sticks and joints.

Keywords: hydrodynamic interactions, geometrical constraints, macromolecules

Introduction

The dynamics of chain molecules, such as polymers and proteins, in solution has been a subject of interest in statistical physics for many years [2, 3, 4]. In order to reduce the number of degrees of freedom of these complicated macromolecules, a number of simplified mechanical models involving geometrical constraints have been considered [3, 5, 6]. The idea is to describe the preservation of molecular structures or substructures by constraints instead of including the corresponding strong intramolecular forces explicitly in the model force field, which would be a formidable task, if not an impossible one. Various schemes for computer simulations on the atomic scale (Molecular Dynamics simulations) [7, 8] and on the mesoscopic scale (Brownian Dynamics simulations) [9 – 12] have been suggested. In Brownian Dynamics simulations, the solvent in which the molecules are immersed is treated

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in a continuum approximation and modelled by stochastic and hydrodynamic forces. It is well known that hydrodynamic interactions play an important role in the self-assembly of macromolecules as well as in their interactions [13, 14].

To be able to study the dynamics of realistic macromolecules one needs a simulation method which can

- handle complex chains,
- be applied to dense systems.

The method that is used almost exclusively to perform dynamical simulations of macromolecules with constraints is called SHAKE [7]. Originally, SHAKE was developed for Molecular Dynamics simulations of macromolecules, but it has also been used for Brownian dynamics simulations [11]. It works in cartesian coordinates and satisfies a set of interdependent bond constraints iteratively. The implementation in a Molecular Dynamics program is particularly simple. Later it was recognized that certain molecular geometries cannot be described by a set of bond constraints. Examples are planar rigid molecules with more than three atoms or three-dimensional molecules with more than four atoms. An extension to handle these cases has been developed [8], but is not in general use. In fact, it applies only to totally rigid molecules and cannot be used for topologically linked rigid structures as they frequently occur in macromolecules. Such systems can be treated using a method that we have developed recently [1, 15].

So far, hydrodynamic interactions in chain molecules have usually been approximated by pairwise additive interactions between 'beads' [2, 16, 11 – 13]. However, it is known that even in moderately dense systems with hydrodynamic interactions this approximation is not sufficient. Since molecular subunits in proteins and polymers are usually in close contact, the input friction matrix must describe hydrodynamic interactions in dense systems correctly. During the last few years, several authors have attacked the problem of computing friction and mobility matrices of dense systems such as colloids [17 – 19], going beyond the Oseen-Burger or Rotne-Prager descriptions [20] of hydrodynamic interactions. We use an efficient and precise method to compute the N-body friction and mobility matrices of spherical particles that has been published recently by Cichocki *et al.* [19]. This scheme is sufficiently accurate to describe even large closely packed assemblies of spheres; such mechanical models have already been used by Dwyer and Bloomfield to simulate the Brownian Dynamics of protein-DNA solutions [21]. We emphasize that the importance of an accurate description is not due to a desire for "correctness" at small distances; below a certain distance between particles, the assumption of length scale separation between solute and solvent breaks down. It is, however, necessary to include all long-range terms (i.e. those decaying as $1/R^3$ or slower) to obtain the correct hydrodynamic behaviour of the whole molecule or of large subunits. This has been demonstrated by Cichocki and Hinsen [22], who calculated the sedimentation coefficient of large conglomerates of spheres and compared with experimental data. It turns out that a level of accuracy that leads to the correct long-range terms also provides an already very good description for short-range interactions, but this fact is of little importance for simulations of macromolecules.

Here we concentrate on the aspect of describing hydrodynamic interactions in the presence of geometrical constraints. We present a rigorous and simple scheme for computing friction and mobility matrices of arbitrary chain molecules consisting of rigid constituents from the friction matrices describing the *freely moving* constituents. To derive expressions for constrained friction and mobility matrices, we start from the observation that geometrical constraints describing chain molecules can be cast in the form of linear constraints for the Cartesian translational and angular velocities of its constituents, extending an ansatz which has been employed recently to derive the equations of motion describing the classical Lagrangian mechanics of chain molecules [1]. Using the concept of generalized inverse matrices [23], we first construct a projector on the subspace of constrained Cartesian velocities. Then we derive the constrained friction and mobility matrices in full Cartesian space and in reduced space and show that the equations of motion for constrained Stokesian Dynamics can be derived from a minimum principle similar to Gauß' principle of least constraint in classical mechanics.

We also show that the relation between our constrained friction and mobility matrices in reduced space and in cartesian space can be expressed formally by appropriately defined coordinate transformations.

As an application we simulate the sedimentation of a pentamer by Stokesian Dynamics, modelling the monomers as rigid spheres linked by massless rods and joints placed between the monomers. Such a model is appropriate e.g. in the study of sedimentation of big proteins, where each monomer would represent a whole domain. The friction matrix of the unconstrained system is computed according to the scheme of Cichocki *et al.* [19, 22], using an implementation available from the CPC library [24]. To integrate the equations of motion, we employ a similar algorithm as in our previous article on Stokesian Dynamics simulations of unconstrained systems [25].

We have not yet tackled Brownian Dynamics simulations since they would require the evaluation of the divergence of the mobility matrix, $\nabla \cdot \boldsymbol{\mu}$ [26]. In the Oseen or Rotne-Prager approximations of hydrodynamic interactions, this term vanishes, but not for the mobility matrix computed according to [19]. The computation of $\nabla \cdot \boldsymbol{\mu}$ is still an unsolved problem.

Theory

Generalized inverse matrices

To derive expressions for constrained friction and mobility matrices, we will make use of *generalized inverse matrices*,

which are also called *pseudoinverse matrices* or *Moore-Penrose-Inverses* [23]. The generalized inverse of an arbitrary $m \times n$-matrix $\mathbf{A}$ is generally denoted by $\mathbf{A}^+$. It is uniquely determined by the four conditions

$$\mathbf{A}\mathbf{A}^+\mathbf{A} = \mathbf{A} \tag{2.1}$$

$$\mathbf{A}^+\mathbf{A}\mathbf{A}^+ = \mathbf{A}^+ \tag{2.2}$$

$$\left[\mathbf{A}^+\mathbf{A}\right]^T = \mathbf{A}^+\mathbf{A} \tag{2.3}$$

$$\left[\mathbf{A}\mathbf{A}^+\right]^T = \mathbf{A}\mathbf{A}^+ \tag{2.4}$$

The superscript ^{T} denotes a transposition. Obviously, $\mathbf{A}^+$ equals $\mathbf{A}^{-1}$ for a quadratic non-singular matrix $\mathbf{A}$. The relations (2.1) – (2.4) express the fact that $\mathbf{A}\mathbf{A}^+$ is a projector on the column space of $\mathbf{A}$ and $\mathbf{A}^+\mathbf{A}$ is a projector on its row space.

Consider now the set of linear equations $\mathbf{A}\mathbf{x} = \mathbf{b}$. A solution exists only if the *consistency condition* $\mathbf{A}\mathbf{A}^+\mathbf{b} = \mathbf{b}$ is fulfilled. Given that this is the case, the general form of the solution reads $\mathbf{x} = \mathbf{A}^+\mathbf{b} + (\mathbf{1} - \mathbf{A}^+\mathbf{A})\mathbf{y}$, where $\mathbf{y}$ is an arbitrary vector of length n. The unique solution of minimum length is given by $\mathbf{x}_0 = \mathbf{A}^+\mathbf{b}$.

If $\mathbf{A}$ can be written in the form $\mathbf{A} = \mathbf{F}\mathbf{G}$, where $\mathbf{F}$ is an $m \times f$ matrix of full column rank and $\mathbf{G}$ is an $f \times n$ matrix of full row rank, there is an explicit expression for $\mathbf{A}^+$ [23]:

$$\mathbf{A}^+ = \mathbf{G}^T\left(\mathbf{G}\mathbf{G}^T\right)^{-1}\left(\mathbf{F}^T\mathbf{F}\right)^{-1}\mathbf{F}^T \tag{2.5}$$

Generalized coordinates and velocities

Linear velocity constraints. We consider a system of N rigid particles i ($i = 1 \ldots N$) immersed in a viscous liquid. Each particle is assigned a translational velocity $\mathbf{v}_i$ and an angular velocity $\boldsymbol{\omega}_i$, yielding $6N$ degrees of freedom for the unconstrained system. Throughout this paper the angular velocities refer to a laboratory-fixed reference frame. The positions and the orientations of the particles are defined by the position vectors $\mathbf{r}_i$ and sets of angular variables $\mathbf{q}_i$, respectively. Examples for angular variables are Euler angles, $\mathbf{q} = (\alpha, \beta, \gamma)$, or quaternions, $\mathbf{q} = (q_0, q_1, q_2, q_3)$ with $\mathbf{q} \cdot \mathbf{q} = 1$. In contrast to translational motion, where $\mathbf{v} = \dot{\mathbf{r}}$, the relation between the angular velocities and the time derivatives of the angular variables reads $\boldsymbol{\omega} = \mathbf{A}(\mathbf{q})\dot{\mathbf{q}}$, and the inverse relation is given by $\dot{\mathbf{q}} = \mathbf{B}(\mathbf{q})\boldsymbol{\omega}$. The form of the matrices $\mathbf{A}$ and $\mathbf{B}$ depends on the choice of angular variables. For Euler angles and similar variable sets, $\mathbf{A}$ and $\mathbf{B}$ are mutually inverse 3×3 matrices, of which $\mathbf{A}$ is singular for certain angles. For quaternions, $\mathbf{A}$ is a 3×4 matrix and $\mathbf{B}$ is a 4×3 matrix, with $\mathbf{A}\mathbf{B} = \mathbf{1}$ and $\mathbf{B}\mathbf{A}\mathbf{q} = \mathbf{q}$, if $\mathbf{q} \cdot \mathbf{q} = 1$. Both $\mathbf{A}$ and $\mathbf{B}$ depend linearly on $\mathbf{q}$. Using the normalization constraint $\mathbf{q} \cdot \mathbf{q} = 1$, a non-singular relation between $\boldsymbol{\omega}$ and $\dot{\mathbf{q}}$ can be derived. This is the reason why quaternions have become popular for computer simulations [27, 28, 1].

To maintain a compact notation, we collect all translational and angular velocities into the vector $\mathbf{v} = (\mathbf{v}_1, \boldsymbol{\omega}_1, \ldots, \mathbf{v}_N, \boldsymbol{\omega}_N) = (v^1, \ldots, v^{6N})$. Correspondingly, we introduce the vector $\mathbf{x} = (\mathbf{r}_1, \mathbf{q}_1, \ldots, \mathbf{r}_N, \mathbf{q}_N) = (x^1, \ldots, x^M)$, where $M = 6N + s$ and s is the number of normalization conditions. Introducing appropriately defined supermatrices $\mathbf{A}$ and $\mathbf{B}$, the relations between the cartesian velocities and the time derivatives of the coordinates can be cast in the form

$$v^i = A^i_j\left(x^k\right)\dot{x}^j, \quad i = 1 \ldots 6N, \quad j = 1 \ldots M \tag{2.6}$$

$$\dot{x}^j = B^j_k\left(x^l\right)v^k, \quad j = 1 \ldots M, \quad k = 1 \ldots 6N \tag{2.7}$$

Here $A_k^{\ i}\, B_j^{\ k} = \delta_j^{\ i}$ and $B_k^{\ i}\, A_j^{\ k}\, x^j = x^i$. We use the Einstein summation rule, i.e. summation over pairwise like upper and lower indices is always assumed. To describe the conformation of a constrained dynamical system, we introduce a set of M' variables $\tilde{x}^\alpha$ that may be subject to s' constraints, such that $M' = f + s'$, where f is the number of degrees of freedom. We assume that the positions and orientations of the constituents can be written as functions of the generalized coordinates,

$$x^i = x^i\left(\tilde{x}^1, \ldots, \tilde{x}^{M'}\right) \tag{2.8}$$

Differentiating the coordinates x^i with respect to time yields

$$\dot{x}^i = \frac{\partial x^i}{\partial \tilde{x}^\alpha}\dot{\tilde{x}}^\alpha \tag{2.9}$$

where Greek indices label generalized coordinates. In analogy to (2.6) and (2.7) we assume linear relations between the $\dot{\tilde{x}}^\alpha$ and the generalized velocities $\tilde{v}^\alpha$ ($\alpha = 1 \ldots f$):

$$\tilde{v}^\alpha = \tilde{A}^\alpha_\beta\left(x^\gamma\right)\dot{\tilde{x}}^\beta, \quad \alpha = 1 \ldots f, \quad \beta = 1 \ldots M' \tag{2.10}$$

$$\dot{\tilde{x}}^\beta = \tilde{B}^\beta_\gamma\left(x^\delta\right)\tilde{v}^\gamma, \quad \beta = 1 \ldots M', \quad \gamma = 1 \ldots f \tag{2.11}$$

where $\tilde{A}^\alpha_\gamma \tilde{B}^\gamma_\beta = \delta^\alpha_\beta$ and $\tilde{B}^\alpha_\gamma \tilde{A}^\gamma_\beta \dot{\tilde{x}}^\beta = \dot{\tilde{x}}^\alpha$. We note that $s' = 0$, $\tilde{A}^\alpha_\gamma = \delta^\alpha_\gamma$, and $\tilde{B}^\gamma_\beta = \delta^\gamma_\beta$ for the choice $\tilde{v}^\alpha = \dot{\tilde{x}}^\alpha$. Combining relation (2.9) between the $\dot{x}^i$ and the $\dot{\tilde{x}}^\alpha$ with (2.6) and

(2.11) leads us to the following linear relation between the Cartesian velocities v^i and the generalized velocities $\tilde{v}^\alpha$:

$$v^i = A^i_j \frac{\partial x^j}{\partial \tilde{x}_\beta} \tilde{B}^\beta_\alpha \tilde{v}^\alpha \equiv C^i_\alpha \tilde{v}^\alpha, \quad i = 1..6N, \quad \alpha = 1..f \tag{2.12}$$

In contrast to the time derivatives of the coordinates, the velocities always correspond to the actual degrees of freedom. We note that in general the matrix $\mathbf{C} = \left(\mathbf{C}^i_\alpha\right)$ is not the Jacobian of a coordinate transformation. This is not only because $\mathbf{C}$ is rectangular and therefore not invertible, but also since the velocities may include angular velocities, which are non-integrable differential forms of the corresponding angular coordinates. An exception is rotation about a fixed axis.

A well known example for linear velocity constraints is the motion of a rigid body. The translational and angular velocities of the constituents are then given by

$$\mathbf{v}_i = \tilde{\mathbf{v}} + \tilde{\boldsymbol{\omega}} \wedge \mathbf{r}_i \quad , \quad \boldsymbol{\omega}_i = \tilde{\boldsymbol{\omega}} \tag{2.13}$$

where $\tilde{\mathbf{v}}$ is the translational velocity of some reference point, and $\tilde{\boldsymbol{\omega}}$ is the angular velocity of the rotational motion. The positions $\mathbf{r}_i$ refer to the reference point and $\wedge$ denotes a vector product. A generalization of the rigid-body velocity constraints to the case of topologically linked rigid bodies can be used to describe chain molecules [1]. An example will be given in the application section

Projector on the constrained Cartesian velocities. The linear velocity constraints (2.12) can be expressed in matrix form as

$$\mathbf{v}_c = \mathbf{C}\tilde{\mathbf{v}} \tag{2.14}$$

The vector $\mathbf{v}_c$ contains the components of the constrained Cartesian velocities, whereas $\tilde{\mathbf{v}}$ comprises the reduced set of generalized velocities, $\tilde{v}^1 \ldots \tilde{v}^f$. The subscript c in $\mathbf{v}_c$ indicates the presence of constraints. The components of the $6N \times f$ matrix $\mathbf{C}$ are defined by (2.12). Using the generalized inverse of $\mathbf{C}$, one can construct the projector $\wp$ on the space of constrained velocities. Multiplying Eq. (2.12) from the left by $\mathbf{C}\mathbf{C}^+$, we obtain $\mathbf{C}\mathbf{C}^+\mathbf{v}_c = \mathbf{C}\mathbf{C}^+\mathbf{C}\tilde{\mathbf{v}} = \mathbf{C}\tilde{\mathbf{v}} = \mathbf{v}_c$, i.e.

$$\mathbf{v}_c = \wp \mathbf{v}_c \quad , \quad \wp = \mathbf{C}\mathbf{C}^+ \tag{2.15}$$

The explicit form for $\mathbf{C}^+$ can be found from relation (2.5). Assuming that $\mathbf{C}$ has full column rank, i.e. the number of its columns corresponds to the number of degrees of freedom, one can write $\mathbf{C} = \mathbf{F}\mathbf{G}$, with $\mathbf{F} = \mathbf{C}$ and $\mathbf{G} = 1$. Therefore

$$\mathbf{C}^+ = \left(\mathbf{C}^T\mathbf{C}\right)^{-1}\mathbf{C}^T \tag{2.16}$$

and the projector $\wp$ reads

$$\wp = \mathbf{C}\left(\mathbf{C}^T\mathbf{C}\right)^{-1}\mathbf{C}^T \tag{2.17}$$

We see from Eq. (2.16) that $\mathbf{C}^+\mathbf{C}$ is equal to the unit matrix in f dimensions, where f is the number of degrees of freedom:

$$\mathbf{C}^+\mathbf{C} = \mathbf{1}_f \tag{2.18}$$

This relation can be used to express the generalized velocities in terms of the constrained Cartesian velocities. Multiplying (2.14) from the left by $\mathbf{C}^+$ yields

$$\tilde{\mathbf{v}} = \mathbf{C}^+\mathbf{v}_c = \left(\mathbf{C}^T\mathbf{C}\right)^{-1}\mathbf{C}^T\mathbf{v}_c \tag{2.19}$$

which shows that $\mathbf{C}^+$ can be regarded as the inverse transformation matrix with respect to $\mathbf{C}$.

Friction and mobility with constraints

Constraint forces and torques. In analogy to the velocity vector $\mathbf{v}$ of the unconstrained system, we define the vector $\mathbf{f} \doteq \left(\mathbf{F}_1, \mathbf{T}_1, \ldots, \mathbf{F}_N, \mathbf{T}_N\right)$ containing the forces and torques acting on the particles. The equation of motion for Stokesian Dynamics reads

$$\boldsymbol{\zeta}\mathbf{v} = \mathbf{f} \tag{2.20}$$

where $\boldsymbol{\zeta}$ is the friction matrix and $\mathbf{f}$ is the vector of given forces and torques. The solution of (2.20) with respect to the unknown translational and angular velocities, $\mathbf{v}$, can be written formally as

$$\mathbf{v} = \boldsymbol{\mu}\mathbf{f} \quad , \quad \boldsymbol{\mu} = \boldsymbol{\zeta}^{-1} \tag{2.21}$$

where $\boldsymbol{\mu}$ is the mobility matrix.

We consider now the case of constrained motion where the velocities are subject to linear constraints. As shown above, this situation may be expressed in the form $\mathbf{v}_c = \wp\mathbf{v}_c$, where $\wp$ is a projector onto the subspace of the constrained velocities. In the following $\wp'$ denotes the projector which is orthogonal to $\wp$, i.e. $\wp' = \mathbf{1} - \wp$. In the presence of constraints, Eq. 2.20 contains an additional force term comprising constraint forces and constraint torques which keep the dynamics of the system in accordance with the imposed constraints:

$$\boldsymbol{\zeta}\mathbf{v}_c = \mathbf{f} + \mathbf{z} \quad , \quad \mathbf{v}_c = \wp\mathbf{v}_c \quad , \quad \mathbf{z} = \wp\mathbf{z} \tag{2.22}$$

The condition $\mathbf{z} = \wp'\mathbf{z}$ means that the constraint forces do not perform work. From a mathematical point of view, the vector $\mathbf{z}$ must be introduced to ensure the existence of a solution for $\mathbf{v}_c$. It should be noted that $\mathbf{z}$ is unknown as well and the condition $\mathbf{z} = \wp'\mathbf{z}$ ensures that both $\mathbf{v}_c$ and $\mathbf{z}$ can be obtained from the same set of linear equations, $\boldsymbol{\zeta}\mathbf{v}_c = \mathbf{f} + \mathbf{z}$. Systems of linear equations like (2.22) have a unique solution. To our knowledge such systems have first been studied by Bott and Duffin in the context of electrical networks [29]. Here we use generalized inverse matrices to express the solution of (2.22). At the time when Bott and Duffin developed the theory of electrical networks, the powerful concept of generalized inverse matrices was not yet developed.

Solving for the constrained velocities. To solve Eq. 2.22, we multiply from the left by $\wp$ and make use of $\wp\mathbf{z} = 0$. With $\mathbf{v}_c = \wp\mathbf{v}_c$, the resulting equation can be cast in the form

$$\wp\boldsymbol{\zeta}\wp\mathbf{v}_c = \wp\mathbf{f} \tag{2.23}$$

For the following considerations we define the *constrained friction matrix* $\boldsymbol{\zeta}_c$ as

$$\boldsymbol{\zeta}_c \doteq \wp\boldsymbol{\zeta}\wp \tag{2.24}$$

We will now show that (2.23) has a unique solution which can be written as

$$\mathbf{v}_c = \boldsymbol{\mu}_c\mathbf{f} \tag{2.25}$$

where the *constrained mobility matrix* $\boldsymbol{\mu}_c$ is related to $\boldsymbol{\zeta}_c$ by

$$\boldsymbol{\mu}_c \doteq \boldsymbol{\zeta}_c^+ \tag{2.26}$$

A solution of (2.23) exists if the consistency condition $\boldsymbol{\zeta}_c\boldsymbol{\zeta}_c^+\wp\mathbf{f} = \wp\mathbf{f}$ is fulfilled. This is always the case as we will see now. Using (2.17) we write $\boldsymbol{\zeta}_c \doteq \wp\boldsymbol{\zeta}\wp$ explicitly as

$$\boldsymbol{\zeta}_c = \underbrace{\mathbf{C}\left(\mathbf{C}^T\mathbf{C}\right)^{-1}\left(\mathbf{C}^T\boldsymbol{\zeta}\mathbf{C}\right)^{-1}}_{\mathbf{F}}\underbrace{\mathbf{C}^T}_{\mathbf{G}} \tag{2.27}$$

The pseudoinverse $\boldsymbol{\zeta}_c^+$ is obtained from relation (2.5), using a factorization $\boldsymbol{\zeta}_c = \mathbf{FG}$ as indicated above. The result is

$$\boldsymbol{\zeta}_c^+ = \mathbf{C}\left(\mathbf{C}^T\boldsymbol{\zeta}\mathbf{C}\right)^{-1}\mathbf{C}^T \tag{2.28}$$

As a prerequisite we must require that $\det(\mathbf{C}^T\boldsymbol{\zeta}\mathbf{C}) \neq 0$. Since the unconstrained friction matrix, $\boldsymbol{\zeta}$, is non-singular and all column vectors in $\mathbf{C}$ are linearly independent, this is always true. From (2.27) and (2.28) we find the relations

$$\boldsymbol{\zeta}_c^+\boldsymbol{\zeta}_c = \boldsymbol{\zeta}_c\boldsymbol{\zeta}_c^+ = \wp \quad , \quad \wp\boldsymbol{\zeta}_c^+ = \boldsymbol{\zeta}_c^+\wp = \boldsymbol{\zeta}_c^+ \tag{2.29}$$

for the generalized inverse of $\boldsymbol{\zeta}_c$. It follows immediately that $\boldsymbol{\zeta}_c\boldsymbol{\zeta}_c^+\wp\mathbf{f} = \wp\mathbf{f}$, showing that the consistency condition is fulfilled. The general solution for $\mathbf{v}_c$ then reads $\mathbf{v}_c = \boldsymbol{\zeta}_c^+\wp\mathbf{f} + (\mathbf{1} - \boldsymbol{\zeta}_c^+\boldsymbol{\zeta}_c)\mathbf{h} = \boldsymbol{\zeta}_c^+\mathbf{f} + \wp'\mathbf{h}$, where $\mathbf{h}$ is an arbitrary vector. Since we require that $\wp\mathbf{v}_c = \mathbf{v}_c$, it follows that $\mathbf{h} = 0$, i.e

$$\mathbf{v}_c = \boldsymbol{\zeta}_c^+\mathbf{f} \equiv \boldsymbol{\mu}_c\mathbf{f} \tag{2.30}$$

This shows that the constrained mobility matrix is indeed the generalized inverse of the constrained friction matrix, as postulated in (2.26). It remains to show that the constraint forces fulfil the condition $\wp'\mathbf{z} = \mathbf{z}$. We write

$$\mathbf{z} = \boldsymbol{\zeta}\mathbf{v}_c - \mathbf{f} = \left(\boldsymbol{\zeta}\boldsymbol{\mu}_c - 1\right)\mathbf{f} \tag{2.31}$$

and multiply from the left by $\wp$. This yields $\wp\mathbf{z} = (\wp\boldsymbol{\zeta}\boldsymbol{\mu}_c - \wp)\mathbf{f}$. Since $\boldsymbol{\mu}_c = \wp\boldsymbol{\mu}_c$, the product $\wp\boldsymbol{\zeta}\boldsymbol{\mu}_c$ can be replaced by $\wp\boldsymbol{\zeta}\wp\boldsymbol{\mu}_c = \boldsymbol{\zeta}\boldsymbol{\mu}_c = \wp$. Therefore $\wp\mathbf{z} = (\wp - \wp)\mathbf{f} = 0$, which is equivalent to $\wp'\mathbf{z} = \mathbf{z}$.

Explicit expressions for reduced friction and mobility matrices. Expressions for the friction and mobility matrices in reduced space are obtained by writing $\mathbf{v}_c - \boldsymbol{\mu}_c\mathbf{f} = 0 = \mathbf{C}\tilde{\mathbf{v}} - \boldsymbol{\mu}_c\mathbf{f}$ and inserting expression (2.28) for $\boldsymbol{\mu}_c = \boldsymbol{\zeta}_c^+$:

$$\mathbf{C}\left[\tilde{\mathbf{v}} - \left(\mathbf{C}^T\boldsymbol{\zeta}\mathbf{C}\right)^{-1}\mathbf{C}^T\mathbf{f}\right] = 0 \tag{2.32}$$

Since $\mathbf{C}$ has full column rank, the vector in square brackets must be the null vector. This can be written as

$$\tilde{\mathbf{v}} = \tilde{\boldsymbol{\mu}}\tilde{\mathbf{f}} \Leftrightarrow \tilde{\boldsymbol{\zeta}}\tilde{\mathbf{v}} = \tilde{\mathbf{f}} \tag{2.33}$$

and defines the reduced mobility matrix $\tilde{\boldsymbol{\mu}}$, the reduced friction matrix $\tilde{\boldsymbol{\zeta}}$, and the reduced force vector $\tilde{\mathbf{f}}$:

$$\tilde{\boldsymbol{\mu}} = \tilde{\boldsymbol{\zeta}}^{-1} \quad , \quad \tilde{\boldsymbol{\zeta}} = \mathbf{C}^T\boldsymbol{\zeta}\mathbf{C} \quad , \quad \tilde{\mathbf{f}} = \mathbf{C}^T\mathbf{f} \tag{2.34}$$

A minimum principle. One can easily show that the equations of motion for constrained Stokesian Dynamics can be derived by minimizing

$$g(\mathbf{v}) = \tfrac{1}{2}\mathbf{v}\cdot\boldsymbol{\zeta}\mathbf{v} - \mathbf{v}\cdot\mathbf{f} \tag{2.35}$$

with respect to **v**. In the absence of constraints, the condition $\partial g(\mathbf{v})/\partial\mathbf{v} = 0$ immediately yields the equations of motion (2.20); setting $\mathbf{v} = \wp\mathbf{v}$ yields the constrained equations of motion (2.23) in Cartesian coordinates, and setting $\mathbf{v} = \mathbf{C}\tilde{\mathbf{v}}$ yields the equations of motion (2.33) if one minimizes with respect to $\tilde{\mathbf{v}}$. The principle (2.35) can be considered the equivalent of Gauß' principle of least constraint in classical mechanics [30], replacing the accelerations by velocities and the diagonal mass matrix by the friction matrix. We note that the form of $g(\mathbf{v})$ is not trivial, although it seems plausible. Consider the alternative quadratic form $g'(\mathbf{v}) = \frac{1}{2}(\boldsymbol{\zeta}\mathbf{v} - \mathbf{f})^2$. Both quadratic forms give the same equations of motion for unconstrained systems but *different* equations of motion for constrained systems.

Curvilinear space

To establish a connection to Kirkwood's theory of polymer solutions [2], we will show how the relations between reduced friction and mobility matrices and their respective Cartesian counterparts can be described formally in terms of coordinate transformations between $6N$ constrained Cartesian velocities and f reduced velocities. In this framework our approach appears as an extension of Kirkwood's theory, which deals with polymers consisting of point-like beads. The correct transformation rules for the reduced friction matrix and the reduced mobility tensor are automatically obtained. In this context we briefly comment on a mistake in the Kirkwood theory which has been reported in the book by Yamakawa [4].

Basis vectors. We start by introducing a set of basis vectors $\{\mathbf{e}_1,\ldots,\mathbf{e}_{6N}\}$ spanning the $6N$-dimensional Euclidian space, and a set of basis vectors $\{\mathbf{b}_1,\ldots,\mathbf{b}_f\}$ spanning the reduced space of constrained velocities. The constrained velocities may then be expressed in either of the two basis sets:

$$\mathbf{v}_c = \mathrm{v}^i_{(c)}\mathbf{e}_i = \tilde{\mathrm{v}}^\alpha\mathbf{b}_\alpha \tag{2.36}$$

We use Latin indices to enumerate basis vectors and coordinates in Euclidian space and Greek indices to enumerate the corresponding quantities in reduced space. Inserting expression (2.14) for the linear velocity constraints into (2.36) shows that the basis vectors $\mathbf{b}_\alpha$ are the columns of **C**. Moreover the transformation rules

$$\mathrm{v}^i_{(c)} = C^i_\alpha\tilde{v}^\alpha \quad , \quad \mathbf{b}_\alpha = C^i_\alpha\mathbf{e}_i \tag{2.37}$$

can be read off. In addition to the basis vectors, we introduce the metric tensor whose components in reduced space read

$$\tilde{g}_{\alpha\beta} = \mathbf{b}_\alpha\cdot\mathbf{b}_\beta = \sum_i C^i_\alpha C^i_\beta \tag{2.38}$$

whereas $g_{ij} = \mathbf{e}_i\cdot\mathbf{e}_j = \delta_{ij}$ in cartesian coordinates. In general the basis vectors $\mathbf{b}_\alpha$ do not form an orthonormal basis. One can, however, define dual basis vectors, $\mathbf{b}^\alpha$, which are orthonormal to the $\mathbf{b}^\alpha$, i.e. $\mathbf{b}_\alpha\cdot\mathbf{b}^\beta = \delta^\beta_\alpha$. In terms of the metric tensor they can be expressed as

$$\mathbf{b}^\alpha = \tilde{g}^{\alpha\beta}\mathbf{b}_\beta \quad , \quad \left(\tilde{g}^{\alpha\beta}\right) = \left(\tilde{g}_{\alpha\beta}\right)^{-1} \tag{2.39}$$

Here $\left(\tilde{g}^{\alpha\beta}\right)$ denotes the matrix formed by the components of the metric tensor and $\left(\tilde{g}_{\alpha\beta}\right)^{-1}$ is the corresponding inverse matrix. We note that vector and tensor components which refer to the basis vectors $\mathbf{b}_\alpha$ are called contravariant components, and those which refer to the $\mathbf{b}^\alpha$ are called covariant components. Since $\mathbf{e}^i = \mathbf{e}_i$, co- and contravariant components in Euclidian space are the same. Consider the co- and contravariant components of the constrained velocities in reduced space, defined by $\mathbf{v}_c = \tilde{\mathrm{v}}^\alpha\mathbf{b}_\alpha = \tilde{\mathrm{v}}_\alpha\mathbf{b}^\alpha$. Using $\mathbf{b}_\alpha\cdot\mathbf{b}^\beta = \delta^\beta_\alpha$, one obtains the transformation rules

$$\tilde{\mathrm{v}}^\alpha = \mathbf{b}^\alpha\cdot\mathbf{v}_c = \tilde{g}^{\alpha\beta}C^i_\beta\mathrm{v}_{(c)i} = \left(C^+\right)^\alpha_i\mathrm{v}^i_{(c)} \tag{2.40}$$

$$\tilde{\mathrm{v}}_\alpha = \mathbf{b}_\alpha\cdot\mathbf{v}_c = C^i_\alpha\mathrm{v}_{(c)i} \tag{2.41}$$

This is exactly relation (2.19) in tensor notation, since $\mathbf{C}^+ = \left(\mathbf{C}^T\mathbf{C}\right)^{-1}\mathbf{C}^T = \left(\tilde{g}_{\alpha\beta}\right)^{-1}\mathbf{C}^T = \left(\tilde{g}^{\alpha\beta}\right)\mathbf{C}^T$.

Although $v_{(c)i} = v^i_{(c)}$, we distinguish between co- and contravariant Cartesian components to respect the Einstein summation rule. $\mathbf{C}^+$ replaces the normal inverse describing non-singular coordinate transformations between spaces of equal dimension. According to (2.15)) and (2.18) we have

$$C^j_\alpha\left(C^+\right)^\alpha_i = P^j_i \tag{2.42}$$

$$\left(C^+\right)^\beta_i C^i_\alpha = \delta^\beta_\alpha \tag{2.43}$$

Here $P^j_i = P_{ij} = P^{ij}$ are the Cartesian components of the projector $\wp$. Eqs. (2.40) and (2.41) also yield the familiar relations between co- and contravariant components:

$$\tilde{v}_\alpha = \tilde{g}_{\alpha\beta}\tilde{v}^\beta \quad , \quad \tilde{v}^\alpha = \tilde{g}^{\alpha\beta}\tilde{v}_\beta \tag{2.44}$$

Reduced friction and mobility matrix. Now we apply Eq. (2.34) and write the components of the reduced friction matrix and the reduced force vector as

$$\tilde{\zeta}_{\alpha\beta} = C^i_\alpha C^i_\beta \zeta_{ij} = \mathbf{b}_\alpha \cdot \boldsymbol{\zeta}\mathbf{b}_\beta \tag{2.45}$$

$$\tilde{f}_\alpha = C^i_\alpha f_i = \mathbf{b}_\alpha \cdot \mathbf{f} \tag{2.46}$$

which shows that they are covariant tensor components. The components of the reduced mobility matrix are found to be contravariant tensor components:

$$\begin{aligned}\tilde{\mu}^{\alpha\beta} &= \left(C^+\right)^\alpha_i \left(C^+\right)^\beta_j \mu^{ij}_{(c)} = \\ &= \tilde{g}^{\alpha\alpha'}\tilde{g}^{\beta\beta'} C^i_{\alpha'} C^j_{\beta'} \mu_{(c)ij} = \mathbf{b}^\alpha \cdot \boldsymbol{\mu}_{(c)} \mathbf{b}^\beta\end{aligned} \tag{2.47}$$

Note that $\mu_{(c)ij} = \mu^{ij}_{(c)}$, since Cartesian tensor components refer to a Euclidian basis. Relation (2.47) follows from Eqs. (2.28) and (2.34) by writing $\boldsymbol{\mu}_c = \mathbf{C}\tilde{\boldsymbol{\mu}}\mathbf{C}^T$. Multiplying from the left by $\mathbf{C}^+$ and from the right by $(\mathbf{C}^+)^T$ leads to $\mathbf{C}^+\boldsymbol{\mu}_c\left(\mathbf{C}^+\right)^T = \left(\mathbf{C}^+\mathbf{C}\right)\tilde{\boldsymbol{\mu}}\left(\mathbf{C}^+\mathbf{C}\right)^T = \tilde{\boldsymbol{\mu}}$, making use of $\mathbf{C}^+\mathbf{C} = \mathbf{1}$. We emphasize that the contravariant tensor $\tilde{\boldsymbol{\mu}}$ must be derived from its *constrained* Cartesian counterpart, whereas the covariant tensors $\tilde{\boldsymbol{\zeta}}$ and $\tilde{\mathbf{f}}$ are derived from their *unconstrained* Cartesian counterparts. This is not surprising, since the inversion of $\tilde{\boldsymbol{\zeta}}$ cannot be achieved by multiplications with $\mathbf{C}^+$. In this context we note that the Cartesian components of the friction matrix and the force vector in (2.45) and (2.46) may be replaced by the components of the corresponding constrained quantities, $\boldsymbol{\zeta}_c = \wp\boldsymbol{\zeta}\wp$ and $\mathbf{f}_c = \wp\mathbf{f}$, respectively. This follows from Eq. (2.34) and the identity $\wp\mathbf{C} = \mathbf{C}\mathbf{C}^+\mathbf{C} = \mathbf{C}$. We have therefore

$$\tilde{\zeta}_{\alpha\beta} = \mathbf{b}_\alpha \cdot \boldsymbol{\zeta}\,\mathbf{b}_\beta = \mathbf{b}_\alpha \cdot \boldsymbol{\zeta}_{(c)}\mathbf{b}_\beta \tag{2.48}$$

$$\tilde{f}_\alpha = \mathbf{b}_\alpha \cdot \mathbf{f} = \mathbf{b}_\alpha \cdot \mathbf{f}_{(c)} \tag{2.49}$$

$$\tilde{\mu}^{\alpha\beta} = \mathbf{b}^\alpha \cdot \boldsymbol{\mu}_{(c)}\mathbf{b}^\beta \neq \mathbf{b}^\alpha \cdot \boldsymbol{\mu}\mathbf{b}^\beta \tag{2.50}$$

A strict analogy to coordinate transformations between spaces of equal dimension can be established only if all vectors and tensors in Euclidian space are elements of the subspace defined by the constraints. In the original Kirkwood theory [2] the reduced mobility matrix was defined as $\tilde{\mu}^{\alpha\beta} = \mathbf{b}^\alpha \cdot \boldsymbol{\mu}\mathbf{b}^\beta$ with $\boldsymbol{\mu} = \boldsymbol{\zeta}^{-1}$. As reported in Yamakawa's book [4], the mistake has been corrected by Ikeda [31] and by Kirkwood and Erpenbeck [16]. Ikeda derives an expression for the reduced mobility matrix in the Oseen approximation, starting from the correct relation $\tilde{\boldsymbol{\mu}} = \tilde{\boldsymbol{\zeta}}^{-1}$. Kirkwood-Erpenbeck define $\tilde{\boldsymbol{\mu}}$ as the submatrix in chain space of the transformed *unconstrained* mobility matrix, using a quadratic transformation matrix for the full coordinate set describing the chain space and its complement. This is, however, still not the same as $\tilde{\boldsymbol{\mu}}$, no matter how the basis vectors for chain space and its complement are chosen. We note that for point-like constituents the matrix $\mathbf{C}$ is a Jacobian, since for translational degrees of freedom $A^i_j = \delta^i_j$ and $\tilde{B}^\beta_\alpha = \delta^\beta_\alpha$ in Eq. (2.21).

Application

As an application for the computation of hydrodynamic interactions in systems with geometrical constraints, we simulate the Stokesian Dynamics of an initially stretched pentamer moving under the influence of a constant force through a viscous liquid. The system is depicted in Figure 1. It consists of five identical spherical monomers connected to massless rods. The ends of the rods are linked by joints. Each joint allows free rotation, i.e. it has three angular degrees of freedom. In the stretched conformation the distance between the spheres is 3*a*, where *a* is the radius of the monomers, and the joints are positioned halfway between the centers of the spheres. Our model deviates in two aspects from the widely-used bead-rod models:

- The monomers have a *finite size* and therefore three translational and three rotational degrees of freedom.
- The positions of the joints do not coincide with the positions of the monomers. This picture is somewhat more realistic with respect to modelling hinges in macromolecules. We note that our method does not depend on this choice of joints; any other one could be treated as well.

For the calculation of the unconstrained friction matrix, we use an accurate scheme that is applicable even for densely packed spheres [19, 22]. The implementation we use is described in [24].

The assumptions underlying our simulation technique, i.e. clear length scale separation between solute and solvent and negligible contributions from random (Brownian) motion, mean that our monomers must be quite large, representing not small groups of atoms, but whole domains of large macromolecules. This model should not be confused with the

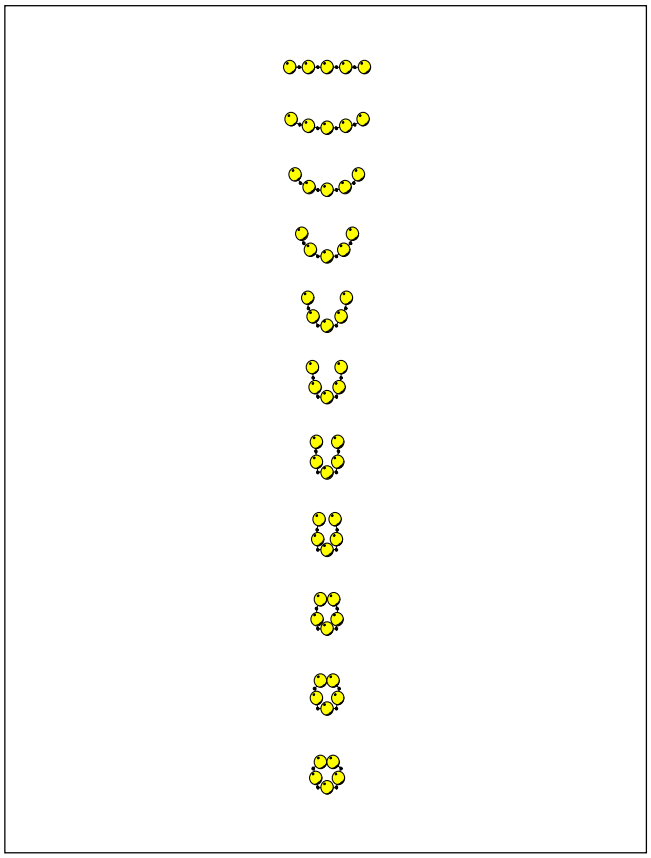

Figure 1. *Sedimentation of a pentamer. The monomers are equally sized spherical particles of radius a and the distance between two spheres in the initial configuration is 3a. The constant gravitational force* **F** *points from top to bottom. The figure shows 11 equidistant frames of a 75000 time step simulation with a time step of* $\Delta t = 0.001$. *The separation between consecutive frames is* $\Delta t_{frame} = 7.5$, *i.e. the whole simulation is shown. Within one time step* Δt *a free sphere would move by* $2/3 \cdot 10^{-3}$ *a.*

modelling of non-spherical structures (such as helices) by closely packed conglomerates of spheres [13].

Linear velocity constraints

Numbering spheres and joints from left to right, we choose the position of the first sphere, $\mathbf{r}_1$, to be the reference point for the translational motion of the chain. We obtain the following expressions for the positions of the joints and the monomers (primed quantities refer to joints):

$$\mathbf{r'}_i = \mathbf{r'}_{i-1} + \mathbf{D}(\mathbf{q}_i)\left(\mathbf{r'}_{0,i} - \mathbf{r'}_{\mathbf{0.i-1}}\right), \quad i = 1\ldots5 \tag{3.1}$$

$$\mathbf{r'}_0 \equiv \mathbf{r}_1 \tag{3.2}$$

$$\mathbf{r}_i = \tfrac{1}{2}\left(\mathbf{r'}_i + \mathbf{r'}_{i-1}\right), \quad i = 2,3,4 \tag{3.3}$$

$$\mathbf{r}_5 \equiv \mathbf{r'}_5 \tag{3.4}$$

We have added the fictitious joints 0 and 5 which coincide with the centers of monomers 1 and 5. The vectors with subscript 0 refer to the initial configuration and the time-dependent vectors $\mathbf{q}_i$ contain the angular parameters describing the rotation of the momomers about their respective anchor points. For practical reasons we use quaternion parameters, i.e. $\mathbf{q} = (q_0, q_1, q_2, q_3)$, where $q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1$ [25, 1]. The rotation matrix $\mathbf{D}(\mathbf{q})$ in terms of quaternion parameters reads [28]

(3.5)

$$\mathbf{D} = \begin{pmatrix} q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2(-q_0 q_3 + q_1 q_2) & 2(q_o q_2 + q_1 q_3) \\ 2(q_0 q_3 + q_1 q_2) & q_0^2 + q_2^2 - q_1^2 - q_3^2 & 2(-q_0 q_1 + q_2 q_3) \\ 2(-q_0 q_2 + q_1 q_3) & 2(q_0 q_1 + q_2 q_3) & q_0^2 + q_3^2 - q_1^2 - q_2^2 \end{pmatrix}$$

By differentiating the positions $\mathbf{r}_i$ with respect to time, one obtains a linear relation between the Cartesian components of the translational velocities $\mathbf{v}_i$ of the monomers and the generalized velocities, which are the translational velocity of the whole chain $\tilde{\mathbf{v}}$ and the angular velocities $\tilde{\boldsymbol{\omega}}_i$ corresponding to the rotations described by $\mathbf{q}_i$. The tilde indicates the generalized velocities, which correspond to the actual degrees of freedom. An expression for the velocities $\mathbf{v}_i$ can be found by writing the time derivative of the rotation matrices $\mathbf{D}(\mathbf{q}_i)$ as $\tilde{\boldsymbol{\Omega}}_i \mathbf{D}(\mathbf{q}_i)$, where the $\tilde{\boldsymbol{\Omega}}_i$ are skew-symmetric matrices containing the components of the angular velocity $\tilde{\boldsymbol{\omega}}_i$ of monomer *i* in the laboratory frame. One obtains the following expressions for the velocities of the joints and the spheres:

$$\mathbf{v'}_i = \mathbf{v'}_{i-1} + \tilde{\boldsymbol{\omega}}_i \wedge \left(\mathbf{r'}_i - \mathbf{r'}_{i-1}\right), \quad i = 1\ldots5 \tag{3.6}$$

$$\mathbf{v'}_0 = \mathbf{v}_1 = \tilde{\mathbf{v}} \tag{3.7}$$

$$\mathbf{v}_i = \mathbf{v'}_{i-1} + \tfrac{1}{2}\tilde{\boldsymbol{\omega}}_i \wedge \left(\mathbf{r'}_i - \mathbf{r'}_{i-1}\right), \quad i = 2,3,4 \tag{3.8}$$

$$\mathbf{v}_5 = \mathbf{v'}_5 \tag{3.9}$$

Clearly, the angular velocities ω_i describing the rotations of the monomers about their centers are the same as those describing the rotations about the joints:

$$\boldsymbol{\omega}_i = \tilde{\boldsymbol{\omega}}_i \tag{3.10}$$

Therefore the relation between the 18 components of $\tilde{\mathbf{v}} = (\tilde{\mathbf{v}}, \tilde{\boldsymbol{\omega}}_1, \ldots, \tilde{\boldsymbol{\omega}}_5)$ and the 30 components of $\mathbf{v} = (\mathbf{v}_1, \boldsymbol{\omega}_1, \ldots, \mathbf{v}_5, \boldsymbol{\omega}_5)$ reads explicitly

$$\begin{pmatrix} \mathbf{v}_1 \\ \boldsymbol{\omega}_1 \\ \mathbf{v}_2 \\ \boldsymbol{\omega}_2 \\ \mathbf{v}_3 \\ \boldsymbol{\omega}_3 \\ \mathbf{v}_4 \\ \boldsymbol{\omega}_4 \\ \mathbf{v}_5 \\ \boldsymbol{\omega}_5 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & -\mathbf{R}'_{01} & -\frac{1}{2}\cdot\mathbf{R}'_{12} & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & -\mathbf{R}'_{01} & -\mathbf{R}'_{12} & -\frac{1}{2}\cdot\mathbf{R}'_{23} & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 1 & -\mathbf{R}'_{01} & -\mathbf{R}'_{12} & -\mathbf{R}'_{23} & -\frac{1}{2}\cdot\mathbf{R}'_{34} & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 1 & -\mathbf{R}'_{01} & -\mathbf{R}'_{12} & -\mathbf{R}'_{23} & -\mathbf{R}'_{34} & -\mathbf{R}'_{45} \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \mathbf{v} \\ \tilde{\boldsymbol{\omega}}_1 \\ \tilde{\boldsymbol{\omega}}_2 \\ \tilde{\boldsymbol{\omega}}_3 \\ \tilde{\boldsymbol{\omega}}_4 \\ \tilde{\boldsymbol{\omega}}_5 \end{pmatrix} \tag{3.11}$$

The submatrices $\mathbf{R}_{ij}$ are the skew-symmetric 3 × 3 matrices

$$\mathbf{R}_{ij} = \begin{pmatrix} 0 & -z_{ij} & y_{ij} \\ z_{ij} & 0 & -x_{ij} \\ -y_{ij} & x_{ij} & 0 \end{pmatrix} \tag{3.12}$$

where x_{ij}, y_{ij}, and z_{ij} are the Cartesian components of $\mathbf{r}_{ij} \doteq \mathbf{r}_j - \mathbf{r}_i$.

Integrating the equations of motion

According to (2.33) and (2.34), the equations of motion can be cast in the form

$$\tilde{\boldsymbol{\zeta}}\tilde{\mathbf{v}} = \tilde{\mathbf{f}} \tag{3.13}$$

where $\tilde{\boldsymbol{\zeta}} = \mathbf{C}^T\boldsymbol{\zeta}\mathbf{C}$ and $\tilde{\mathbf{f}} = \mathbf{C}^T\mathbf{f}$ are the reduced friction matrix and the reduced force vector, respectively. The constraint matrix **C** follows from (3.11) and $\boldsymbol{\zeta}$ is the friction matrix for an unconstrained system of 5 spherical particles. The latter is computed using the approach of Cichocki *et al.* [19, 22, 25, 24]. The external forces and torques in **f** are

$$\mathbf{f} = (\mathbf{F}_1, \mathbf{T}_1, \ldots, \mathbf{F}_5, \mathbf{T}_5) \tag{3.14}$$

$$\mathbf{F}_i = (0,0,-F) \tag{3.15}$$

$$\mathbf{T}_i = (0,0,0) \tag{3.16}$$

We choose the gravitational force to point towards the negative *z*-axis. From a numerical point of view, it is more efficient to solve (3.13) for $\tilde{\mathbf{v}}$ rather than computing $\tilde{\mathbf{v}} = \tilde{\boldsymbol{\zeta}}^{-1}\tilde{\mathbf{f}}$, which would require a full matrix inversion. The equations of motion are solved as follows:

1. For each configuration, $\{\mathbf{r}_1(n),\ldots,\mathbf{r}_5(n)\}$, compute
   (a) the unconstrained friction matrix $\boldsymbol{\zeta}$,
   (b) the constraint matrix **C**,
   (c) the reduced friction matrix $\tilde{\boldsymbol{\zeta}} = \mathbf{C}^T\boldsymbol{\zeta}\mathbf{C}$,
   (d) the reduced force vector $\tilde{\mathbf{f}} = \mathbf{C}^T\mathbf{f}$.
2. Solve $\tilde{\boldsymbol{\zeta}}\tilde{\mathbf{v}} = \tilde{\mathbf{f}}$ for $\tilde{\mathbf{v}} \equiv \tilde{\mathbf{v}}(n)$.
3. Update the reference position $\mathbf{r}_1$ and the quaternion parameters $\mathbf{q}_i$ describing the orientation of the monomers according to the following central difference scheme:
   (a) $\mathbf{r}_1(n+1) = \mathbf{r}_1(n-1) + 2\Delta t\cdot\tilde{\mathbf{v}}(n)$.
   (b) $\mathbf{q}_i(n+1) = \mathbf{q}_i(n-1) + 2\Delta t\cdot\mathbf{B}[\mathbf{q}_i(n)]\tilde{\boldsymbol{\omega}}_i(n)$.
4. Update the positions of monomers 2 to 5 according to (3.1) – (3.4).

In step 3 we use the following singularity-free relation between the components of the angular velocity components and the time derivatives of the quaternion parameters:

$$\dot{q}_\alpha = B_{\alpha j}(q_\beta)\omega_j \tag{3.17}$$

$$\mathbf{B} = \frac{1}{2}\begin{pmatrix} -q_1 & -q_2 & -q_3 \\ q_0 & q_3 & -q_2 \\ -q_3 & q_0 & q_1 \\ q_2 & -q_1 & q_0 \end{pmatrix}$$

This relation has already been employed in molecular dynamics simulations [1, 27, 28].

Results

To simulate the sedimentation of the model pentamer described above, we performed a Stokesian Dynamics simulation of 75000 time steps of length Δt – see video sequence

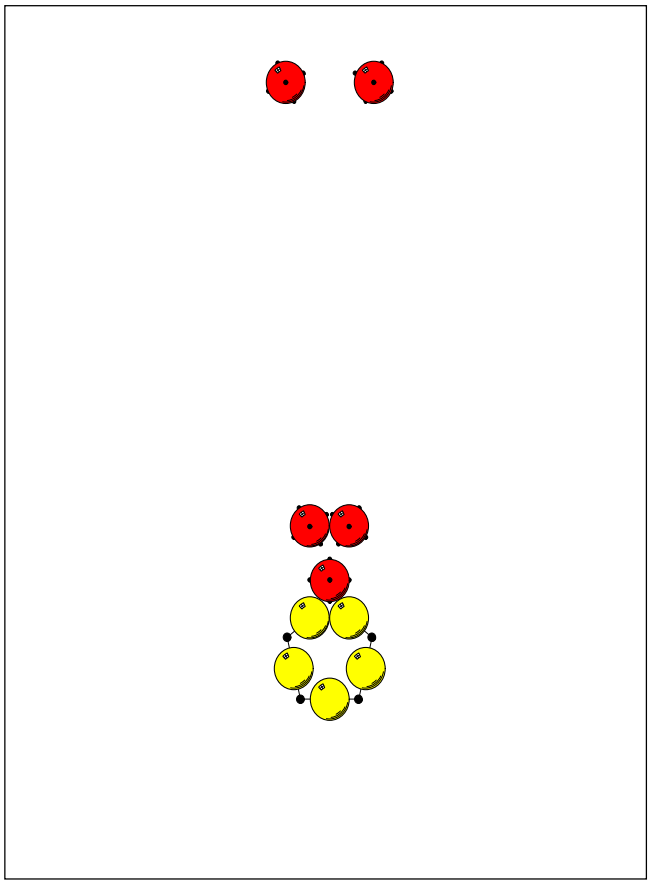

Figure 2. *Comparison of the last configuration of the pentamer simulation (light grey) and the corresponding configuration of five unconnected spherical monomers of equal size (dark grey). The initial configuration for the unconstrained system was the same as for the constrained one. The dots on the unconstrained monomers indicate the presence of rotational motion.*

no. IIa ('Pentamer starting in the stretched conformation'). As in the video sequences in [25] *the center of mass motion is subtracted*. Again, the overall sedimentation of the cluster is shown on the left hand side of the screen. The height of the frame indicates the total falling distance, and the height of the black bar corresponds approximately to the height of the screen. In the simulation we used internal units with force $F = 1$, viscosity $\eta = \frac{1}{4}\pi$, particle radius $a = 1$, and time step $\Delta t = 10^{-3}$. In these units, the displacement of a single sphere in an infinite medium per dimensionless unit time is given by $\Delta r = F/(6/\pi\eta a) = 2/3$. The initial configuration of the pentamer was the stretched configuration shown in Figure 1. The monomers interact only via the background fluid – i.e no explicit interaction forces are considered. The constant driving force points from top to bottom and the time difference between consecutive configurations shown in Figure 1 is $\Delta t_{frame} = 7.5$, corresponding to 7500 time steps. For comparison we performed a second simulation of a system of five unconnected spherical particles of equal size – see video sequence no. IIb ('5 equally sized spheres starting in a linear configuration'). The total falling height indicated by the frame is the same as in the simulation shown in video sequence no. IIa. Apart from removing the constraints, the simulation parameters were the same as for the simulation of the pentamer. Figure 2 shows the superposition of the configurations at the end of the respective runs. The pentamer is drawn in light grey and the five unconnected spheres in dark grey. In the final configuration of the pentamer, monomers 1 and 5 touch each other. It is interesting to look at the heat production of the two systems which is defined as

$$p(\mathbf{v}) = \mathbf{v} \cdot \mathbf{f} \tag{3.18}$$

In our example the external torques are zero and therefore

$$p = \sum_i \mathbf{F}_i \cdot \mathbf{v}_i \tag{3.19}$$

Since the external forces are equal and constant, $\mathbf{F}_i = \mathbf{F}$, p is proportional to the average settling speed. Figure 3 shows the normalized heat production p/p_0 for the pentamer and the five unconnected spheres, where p_0 is the corresponding heat production of five spheres at infinite distance which are driven by the same force, i.e. $p_0 = 5 \cdot F^2/(6\backslash\pi\eta a) = 10/3$ in our internal units. The curve for the pentamer shows that the final configuration is reached at about $t = 60$. This can also be seen in Figure 1, where the configuration corresponding to $t = 60$ is the 9th configuration from top (3rd from bottom). Note that for $t \leq 20$ the constrained and the unconstrained systems settle with approximately the same speed. The configurations in the initial phase (not shown here) are similar. Then the pentamer settles faster, reducing the friction, whereas the unconstrained system starts to lag behind and at about $t = 35$ it starts to form the separate groups (2,3,4) and (1,5) while the friction increases. As in the example we studied in [25], the heat production is neither monotonically increasing nor decreasing.

Conclusions

We have presented a rigorous method to derive the friction and mobility matrices for constrained dynamical systems consisting of rigid constituents. The method is based on the assumption that the constraints can be expressed as linear constraints for the Cartesian velocities, which is true for all situations in which the positions and orientations of the constituents can be expressed as functions of a set of generalized coordinates. We have shown that the constrained friction and mobility matrices are mutually generalized inverses

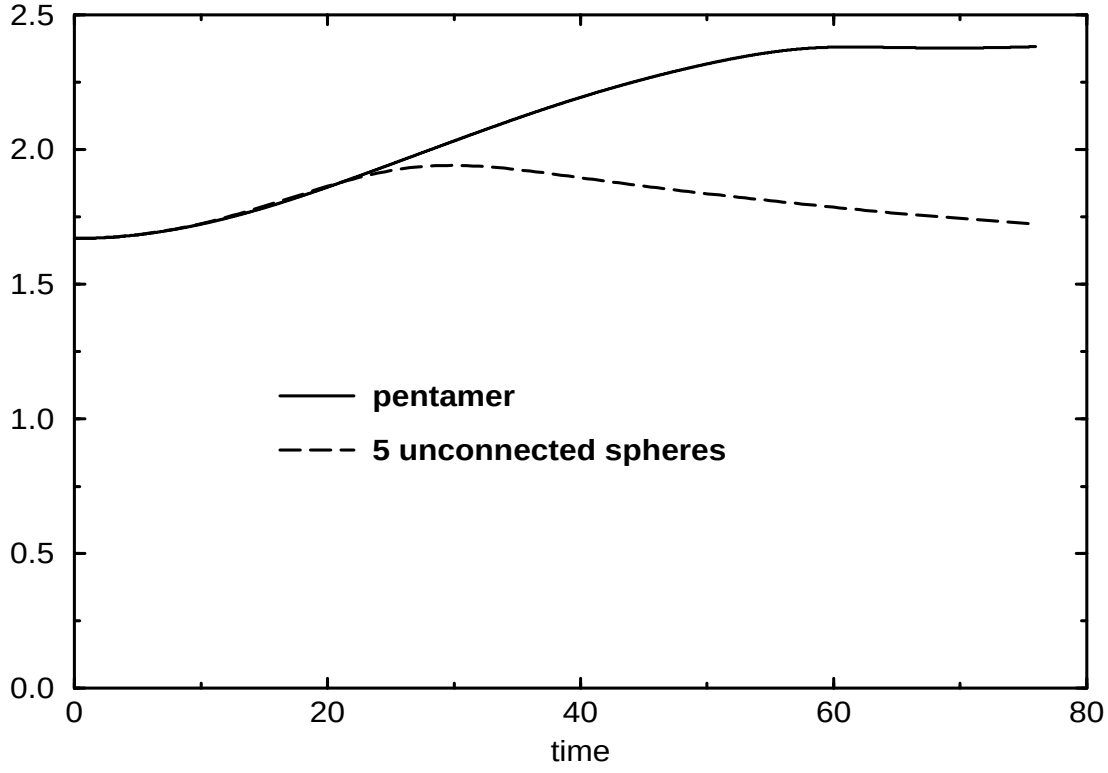

Figure 3. *Normalized heat production, p/p_0, of the pentamer and the corresponding system of five unconnected spherical monomers of equal size. The normalization factor p_0 is the heat production of five single spheres at infinite distance.*

in Cartesian velocity space, $\mu_c = \zeta_c^+$, which translates into the relation $\tilde{\mu} = \tilde{\zeta}^{-1}$ in reduced space. Explicit expressions for all relevant vectors and tensor quantities were given in both Cartesian and reduced space. The equations of motions for Stokesian Dynamics were shown to follow from a minimum principle analogous to Gauß' principle of least constraint in classical mechanics.

We have also shown that vectors and tensors in reduced space and in constrained cartesian space are formally mapped onto each other by coordinate transformations. Although this formal scheme is not of practical importance it shows that our method yields automatically the right transformation rules.

We conclude that complex constrained dynamical systems with hydrodynamic interactions can be described conveniently and correctly in the framework of generalized inverse matrices and linear velocity constraints. An efficient scheme for the computation of the divergence of the mobility matrix still needs to be developed in order to perform Brownian Dynamics simulations.

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