Molecular dynamics simulation methods revised
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The equations of constrained motion of systems subject to holonomic time independent constraints are studied. This is done for systems with unconstrained equations of motion of zeroth, first and second order. Special attention is given to systems of which the equations of constrained motion can be written as a matrix equation. As an example, the instantaneous decay of motion along a polymer chain is investigated.

4.1 Introduction

The equations of motion of a system are differential equations, which give the relationship between the force exerted on the system and the response of the system, in terms of either position, velocity or acceleration. So, in principle, the trajectory of a system, subject to a given force, can be obtained by integrating the equations of motion. However, when the system is subject to constraints, it takes a bit more effort to evaluate the motion of the system. Generally speaking, two different approaches may then be used:

A: The non-constrained equations of motion may be integrated, subject to constraints. A general purpose method may be used, capable of integration subject to algebraic constraints, as for example the NAG routine D02SAF, or an integration method developed for a specific type of problem may be used. An example of the last case is the SHAKE method [1], which is based on solving a set of Lagrange multipliers, and which is used to integrate the equations of motion of a constrained molecular system. In the SHAKE algorithm the equations of motion are not formulated in a closed form. Because it is designed to
integrate without drift, it is conceptually more complex than naive methods.

**B:** New, and fewer coordinates are introduced by switching to generalised coordinates. In principle, the equations of constrained motion may then be expressed in closed form. The new equations of motion are not expressed in Cartesian coordinates, and are of the Euler-Lagrange type or of the Hamilton type, without constraint conditions [2]. In general they are complex, and not easily integrated.

In this chapter we will study the equations of motion of a constrained discrete particle system in a closed form, expressed in Cartesian coordinates. The price paid for this explicit form, and for avoiding the use of generalised coordinates, is that numerical drift may occur during the integration process. Drift is however no problem when only instantaneous properties of the system are investigated, because such properties can be derived from the equations of motion without actual integration.

Usually, with ‘equations of motion’ are meant first or higher order differential equations. In this chapter, with ‘equations of motion’ we will also mean zeroth order differential equations, i.e. Hookelike equations. We will show that for a number of systems the equations of motion of zeroth, first and second order systems, constrained and unconstrained, are of the same form.

Deriving the equations of constrained motion is straightforward. It is done in the next section. In Section 4.6, as an example, we will use the equations of motion to calculate the ensemble averaged instantaneous decay of motion along a random polymer chain. We will also mention some other possible applications of the theory.

### 4.2 Zeroth order equations of motion

We consider a system of $N$ particles, at Cartesian positions $r_1, \ldots, r_N$. We will denote these positions by a single vector $R$, defined as

$$
\begin{pmatrix}
R_1 \\
R_2 \\
\vdots \\
R_{3N}
\end{pmatrix}
= 
\begin{pmatrix}
 r_{1x} \\
r_{1y} \\
\vdots \\
r_{Nz}
\end{pmatrix} .
$$

The system is subject to a conservative potential $V(R)$. We assume that $V(R)$ has a (local) minimum at $(R_0)$, i.e. the second derivative matrix of $V(R)$ is positive
definite at \((\mathbf{R}_0)\). Around \(\mathbf{R}_0\), \(V(\mathbf{R})\) can be expanded into

\[
V(\mathbf{R}) = V(\mathbf{R}_0) + \sum_{i=1}^{3N} \frac{\partial V}{\partial R_i} \Delta R_i + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left( \frac{\partial^2 V}{\partial R_i \partial R_j} \right) \Delta R_i \Delta R_j + \cdots .
\] (4.2)

The first term on the right hand side is the potential energy of the equilibrium position. Because the zero-point of the potential energy may be freely chosen, we choose it to be zero. The second term is also zero because in \(\mathbf{R}_0\) the system is in equilibrium, i.e. \(\frac{\partial V}{\partial R_i} = 0\). We will assume that \(\Delta \mathbf{R}\) is so small that terms in (4.2) beyond the second derivative are negligible, so that

\[
V(\mathbf{R}) = \sum_{i=1}^{3N} \sum_{j=1}^{3N} \frac{1}{2} \left( \frac{\partial^2 V}{\partial R_i \partial R_j} \right) \Delta R_i \Delta R_j = \frac{1}{2} \mathbf{R}'^T \mathbf{K} \mathbf{R}'.
\] (4.3)

This means that the system behaves like a multidimensional linear spring, with a matrix valued spring constant \(\mathbf{K}\) defined as

\[
K_{ij} = \frac{\partial^2 V}{\partial R_i \partial R_j}.
\] (4.4)

When on the particles an external force \(\mathbf{F}\) is exerted, which is defined as

\[
\begin{pmatrix}
F_1 \\
F_2 \\
\vdots \\
F_{3N}
\end{pmatrix}
\equiv
\begin{pmatrix}
f_{1x} \\
f_{1y} \\
\vdots \\
f_{Nz}
\end{pmatrix},
\] (4.5)

the displacement of the particles from the equilibrium position may be written as

\[
\Delta \mathbf{R} = \mathbf{K}^{-1} \mathbf{F}.
\] (4.6)

Although this equation is about displacements, we will call it the equation of (unconstrained) motion. Because no time derivatives of \(\mathbf{R}\) are involved, we will call it a zeroth order equation of motion.

With (4.6) we arrive at the starting point of our investigation. We will constrain the motion of the system by \(\ell\) time independent constraint equations

\[
g_1(\mathbf{R}) = 0, \quad \ldots, \quad g_\ell(\mathbf{R}) = 0
\] (4.7)
and we will derive the equations of motion of the constrained system. We will show that the equation of constrained motion is still of the form (4.6) and we will derive an explicit expression for the new $K$.

The variations in the constraint equations have to be zero, so

$$
\frac{\partial g_h}{\partial R_1} \Delta R_1 + \cdots + \frac{\partial g_h}{\partial R_{3N}} \Delta R_{3N} = 0, \quad 1 \leq h \leq \ell .
$$

(4.8)

This can be written concisely as

$$
B \Delta R = 0 ,
$$

(4.9)

where $B$ is an $\ell \times 3N$ matrix, defined by

$$
B_{ij} \equiv \frac{\partial g_i}{\partial R_j} .
$$

(4.10)

In [3], [4] and [5], by using Lagrange multipliers, respectively by using the principle of least constraint, respectively by using the principle of least action, it is shown that for specific $\lambda_j$'s the constraint force $F^c$ is given by

$$
F^c_i = \sum_{j=1}^{\ell} \lambda_j \frac{\partial g_j}{\partial R_i} .
$$

(4.11)

Defining $A$ as

$$
A \equiv \begin{pmatrix}
\lambda_1 \\
\lambda_2 \\
\vdots \\
\lambda_\ell
\end{pmatrix}
$$

(4.12)

(4.11) may be written as

$$
F^c = B^T A .
$$

(4.13)

In the new equilibrium position the net force on every particle has to be zero again, i.e. the sum of force of the linear springs, the constraints, and the external force has to be zero, so

$$
-K \Delta R + B^T A + F = 0 .
$$

(4.14)

Multiplying this expression with $BK^{-1}$, and using (4.9) gives

$$
BK^{-1} B^T A + BK^{-1} F = 0
$$

(4.15)
so,

\[ A = -(BK^{-1}B^T)^{-1}BK^{-1}\Delta F. \] (4.16)

This equation, together with (4.13) shows that there is a linear relation between the constraint force \( \mathbf{F}^c \) and the exerted force \( \mathbf{F} \). Inserting \( A \) into (4.14) and solving for \( \Delta \mathbf{R} \) gives

\[ \Delta \mathbf{R} = (K^{-1} - K^{-1}B^T(BK^{-1}B^T)^{-1}BK^{-1})\mathbf{F}. \] (4.17)

We can now define a new matrix \( \mathbf{L} \) as

\[ \mathbf{L} \equiv K^{-1} - K^{-1}B^T(BK^{-1}B^T)^{-1}BK^{-1}. \] (4.18)

The constrained motion of the system can thus be written as

\[ \Delta \mathbf{R} = \mathbf{L}\mathbf{F}. \] (4.19)

which is of the same form as (4.6). Note that the rank of \( \mathbf{L} \) is \( 3N - \ell \).

### 4.3 First order equations of motion

We again consider a system of \( N \) particles, with positions given by \( \mathbf{R} \), and velocities given by \( \dot{\mathbf{R}} \). Without further motivation, we assume that the velocity of the particles only depends on the forces, i.e. their motion is governed by a linear friction as

\[ \dot{\mathbf{R}} = \mathbf{D}^{-1}\mathbf{F}, \] (4.20)

where \( \mathbf{D} \) is a \( 3N \times 3N \) matrix, representing the ‘drag’ per unit velocity. An example of such a system is a set of identical spherical particles in a medium with linear viscosity. In that case \( \mathbf{D} \) is a diagonal matrix with identical diagonal elements. However, in later discussions we will only assume that \( \mathbf{D} \) is non-singular.

We will now constrain the motion of the system by \( \ell \) time-independent constraint equations

\[ g_1(\mathbf{R}) = 0, \ldots, g_\ell(\mathbf{R}) = 0. \] (4.21)

In the following we will show that the equation of constrained motion is still of the form (4.20), and we will derive an explicit expression for the new \( \mathbf{D} \).
The time derivatives of the constraint equations have to be zero, so
\[
\frac{\partial g_h}{\partial R_1} \frac{dR_1}{dt} + \cdots + \frac{\partial g_h}{\partial R_{3N}} \frac{dR_{3N}}{dt} = 0, \quad 1 \leq h \leq \ell. \tag{4.22}
\]
This can be written as
\[
B \dot{\mathbf{R}} = 0, \tag{4.23}
\]
where \(B\) is defined in (4.10). Just as in the previous section, the constraint force may be written as
\[
\mathbf{F}^c = B^T \mathbf{A}. \tag{4.24}
\]
During stationary, constrained motion of the system, the sum of the drag force, the constraint force, and the exerted force is zero, so
\[
- \mathbf{D} \dot{\mathbf{R}} + B^T \mathbf{A} + \mathbf{F} = 0. \tag{4.25}
\]
Solving for \(A\) in the same manner as in (4.14) \cdots (4.16) gives
\[
A = -(\mathbf{BD}^{-1} \mathbf{B}^T)^{-1} \mathbf{BD}^{-1} \mathbf{F}. \tag{4.26}
\]
Inserting \(A\) in (4.25) and solving for \(\dot{\mathbf{R}}\) gives
\[
\dot{\mathbf{R}} = (\mathbf{D}^{-1} - \mathbf{D}^{-1} \mathbf{B}^T (\mathbf{BD}^{-1} \mathbf{B}^T)^{-1} \mathbf{BD}^{-1}) \mathbf{F}. \tag{4.27}
\]
We can now define a matrix \(E\) as
\[
\mathbf{E} \equiv \mathbf{D}^{-1} - \mathbf{D}^{-1} \mathbf{B}^T (\mathbf{BD}^{-1} \mathbf{B}^T)^{-1} \mathbf{BD}^{-1}. \tag{4.28}
\]
The constrained motion of the system can thus be written as
\[
\dot{\mathbf{R}} = \mathbf{EF}, \tag{4.29}
\]
which is of the same form as (4.20). Note that the rank of \(E\) is \(3N - \ell\).
4.4 Second order equations of motion

We again consider a system of $N$ particles, with positions given by $\mathbf{R}$, velocities by $\dot{\mathbf{R}}$, and accelerations by $\ddot{\mathbf{R}}$. We will assume that, under the influence of some force $\mathbf{F}$ the behaviour of the system is given by

$$\ddot{\mathbf{R}} = \mathbf{M}^{-1} \mathbf{F}, \quad (4.30)$$

where $\mathbf{M}$ is a $3N \times 3N$ matrix, representing the masses of the particles. For a system of interacting particles in Cartesian coordinates, $\mathbf{M}$ is a diagonal matrix. However, in later discussions we will only assume that $\mathbf{M}$ is non-singular.

We will again constrain the motion of the system by a time independent constraint equations

$$g_1(\mathbf{R}) = 0, \ldots, g_\ell(\mathbf{R}) = 0. \quad (4.31)$$

The second derivatives of the constraint equations have to be zero, so

$$\frac{d^2 g_h}{dt^2} = \sum_{i=1}^{3N} \left( \frac{\partial g_h}{\partial \dot{R}_i} \dot{R}_i + \sum_{j=1}^{3N} \frac{\partial^2 g_h}{\partial R_i \partial R_j} \ddot{R}_i \ddot{R}_j \right) = 0, \quad 1 \leq h \leq \ell. \quad (4.32)$$

Introducing an $\ell$ dimensional vector $\mathbf{H}$, defined as

$$H_h \equiv \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left( \frac{\partial^2 g_h}{\partial R_i \partial R_j} \ddot{R}_i \ddot{R}_j \right), \quad (4.33)$$

we can rewrite (4.32) as

$$\mathbf{B} \ddot{\mathbf{R}} + \mathbf{H} = 0. \quad (4.34)$$

The sum of the acceleration force, the constraint force, and the exerted force has to be zero, so

$$-\mathbf{M} \ddot{\mathbf{R}} + \mathbf{B}^T \mathbf{A} + \mathbf{F} = 0. \quad (4.35)$$

Substitution of $\mathbf{B} \ddot{\mathbf{R}}$ in (4.35) with (4.34) gives

$$\mathbf{H} + (\mathbf{BM}^{-1} \mathbf{B}^T) \mathbf{A} + \mathbf{BM}^{-1} \mathbf{F} = 0. \quad (4.36)$$

Solving this for $\mathbf{A}$ and substituting $\mathbf{A}$ in (4.35) gives

$$\ddot{\mathbf{R}} = -\mathbf{M}^{-1} \mathbf{B}^T (\mathbf{BM}^{-1} \mathbf{B}^T)^{-1} \mathbf{H} +$$

$$+ \left( \mathbf{M}^{-1} - \mathbf{M}^{-1} \mathbf{B}^T (\mathbf{BM}^{-1} \mathbf{B}^T)^{-1} \mathbf{BM}^{-1} \right) \mathbf{F}. \quad (4.37)$$
In this differential equation, the term $-\mathbf{B}^T(\mathbf{BM}^{-1}\mathbf{B}^T)^{-1}\mathbf{H}$ represents the constraint force due to the motion of the system, i.e. the centrifugal force, the Coriolis force, etc. The term $-\mathbf{B}^T(\mathbf{BM}^{-1}\mathbf{B}^T)^{-1}\mathbf{BM}^{-1}\mathbf{F}$ represents the constraint force caused by the exerted force $\mathbf{F}$.

(4.37) is a non-linear differential equation, and there is no general way to transform it into a linear one. However, for some special cases it reduces to a linear differential equation without first derivative.

1. When $\dot{\mathbf{R}} = 0$, obviously, the term $-\mathbf{B}^T(\mathbf{BM}^{-1}\mathbf{B}^T)^{-1}\mathbf{H}$ becomes zero. A matrix $\mathbf{N}$ can be defined as

$$\mathbf{N} \equiv \mathbf{M}^{-1} - \mathbf{M}^{-1}\mathbf{B}^T(\mathbf{BM}^{-1}\mathbf{B}^T)^{-1}\mathbf{BM}^{-1}.$$  \hspace{1cm} (4.38)

The constrained motion of the system (at rest), can then be written as

$$\ddot{\mathbf{R}} = \mathbf{NF},$$  \hspace{1cm} (4.39)

i.e. it is of the same form as the equation of motion of the unconstrained system (4.30).

2. As mentioned before, the term $-\mathbf{B}^T(\mathbf{BM}^{-1}\mathbf{B}^T)^{-1}\mathbf{H}$ represents the constraint force due to the motion of the system. This means that, when the system is rotated (including the particle velocities), this term rotates in the same way. So, for a given configuration with given particle velocities, averaging this term over all spatial orientations, gives zero. This means that the orientation averaged response, for a given configuration, is given by

$$\langle \ddot{\mathbf{R}} \rangle = \left\langle \left(\mathbf{M}^{-1} - \mathbf{M}^{-1}\mathbf{B}^T(\mathbf{BM}^{-1}\mathbf{B}^T)^{-1}\mathbf{BM}^{-1}\right) \right\rangle \mathbf{F},$$  \hspace{1cm} (4.40)

or more concise, $\langle \ddot{\mathbf{R}} \rangle = \langle \mathbf{N} \rangle \mathbf{F}$.

In the literature [6] a method is described to integrate (4.37) by using a non-iterative matrix method, i.e. the impression is given that (4.37) can be transformed in a differential equation of the form (4.39). This method is incorrect for the following reason. To integrate the unconstrained equations of motion, the Verlet algorithm is chosen. In this algorithm it is assumed that the differential equation does not contain first derivatives, which is the case for the unconstrained equations of motion. Subsequently, the integration scheme of this method is adapted to handle the first derivative term in (4.37), i.e., afterwards, at the level of the integration scheme the first derivative is introduced.
4.5 Discussion

In an obvious way the equations of motion of higher order systems can be derived. We will however not do so because, with the theory as presented, we can already study phenomena of realistic systems. But first we make a few remarks about the equations we have derived in the previous paragraphs.

We define a pure $n^{th}$ order differential equation as a differential equation only containing $n^{th}$ order derivatives. As can be seen in the derivations of (4.19) . . . (4.30), a pure zeroth respectively first order equation of unconstrained motion can be transformed into a pure zeroth respectively first order equation of constrained motion. A pure second order equation of unconstrained motion only transforms into a pure second order equation of constrained motion under special conditions.

Because (4.19), (4.29), and (4.39) are of the same form we limit our remarks to (4.39); similar remarks hold for (4.19) and (4.29). A necessary and sufficient condition for the existence of $(BM^{-1}B^T)^{-1}$ in (4.39) is that the rank of $B$ is $\ell$, and the rank of $M$ is $3N$, and $\ell < 3N$. When the rank of $B$ is less than $\ell$ the constraint conditions are overdetermined. In the theory as presented, the only condition on $M$ is that it is non-singular. Of course, for conservative systems in a stable position, $M$ is symmetric and positive definite, but the theory presented also holds for non-symmetrical and indefinite or negative definite $M$. (A matrix $M$ is called positive (resp. negative) definite when $R^TMR > 0$ (resp. $R^TMR < 0$) for every $R$. Usually, systems absorb energy subject to an external force, which is equivalent to saying that $M$ is positive definite.)

As is shown in most textbooks on classical mechanics, holonomic time independent constraints do no work. This means that constraints cannot change a positive definite system without constraints into a negative definite one, and the other way around, or put in a different way, a system with a positive resp. negative definite $M^{-1}$ also has a positive resp. negative definite $N$. An indefinite system without constraints can be made positive definite or negative definite at will by applying constraints.

Every column vector of $M^{-1}$ and $N$ represents the accelerations of the particles of the system in the $x$, resp. $y$, and resp. $z$, direction as a result of a unit force in the $x$, resp. $y$, and resp. $z$, direction on a particular particle. Resulting from this unit force, the energy, the momentum, and the angular momentum of the system change. Because every column represents the behaviour of the whole system under a particular force, the conservation of energy, momentum, and angular momentum shows up as properties within every column. For example, in Appendix C it is shown
that for some systems the sum of the elements of every column in $M^{-1}$ and $N$ is one.

It is a well known property of positive- and negative definite matrices that they can be represented by a symmetric matrix. This means that when $M^{-1}$ is symmetric, $N$ is also symmetric. When $M^{-1}$ is non-singular, its rank is $3N$. However, in $N$, $\ell$ constraint conditions are incorporated, so the rank of $N$ is $3N - \ell$. This means that from the motion of the system it cannot be determined what force was exerted, which is equivalent to saying that $N$ has no inverse.

The derivations in this chapter are very simple compared with the ones in [1], for short RCB. The RCB algorithms include the well known SHAKE algorithm. The derivations of the RCB algorithms are complex because the RCB algorithms are designed so that the constraint condition itself is maintained, while the equations of constrained motion derived from (4.19), (4.29) and (4.37), only maintain the derivatives of the constraint equations. As a result, the RCB algorithms can be used without any drift correction, while the algorithms discussed here sooner or later will suffer from drift. In that respect, our algorithm is inferior to the RCB ones. However, (4.19), (4.29), and (4.37) are explicit expressions as opposed to the RCB expressions, which makes it possible to use them for other purposes than the RCB expressions.

It is interesting to compare our formulation of constraint dynamics with the essential dynamics (E.D.) method [9]. In both E.D. and in our method a matrix $N$ is constructed. The difference between E.D. and our method is that in our method $N$ is calculated using mathematical constraint relations known in advance, while in the E.D. method $N$ is calculated without using mathematical constraint relations, but by analysing the dynamic behaviour of the system over a long time-span. The essence of the E.D. method is that a low dimensional $N$ is constructed, that approximates the observed motion of the system. The rank of $N$ is often chosen to be $\approx 20$. To get a low dimensional $N$ from the observed $N$, small eigenvalues are set to zero. It can be shown that zeroing eigenvalues is equivalent to introducing constraints. So, in the E.D. method, the system is subject to typically $3N - 20$ constraints. The main goal of the E.D. method is to give a good approximation of the observed motion of the system.

### 4.6 Example applications

We will now apply the theory by studying the instantaneous decay of motion along a polymer chain. The polymer chain consists of $N$ identical atoms, linearly connected
by length constraints of length one. Atom \( n, 1 \leq n \leq N - 1 \), is connected to atom \( n + 1 \) by a length constraint \(|\mathbf{r}_n - \mathbf{r}_{n+1}| = 1\). There is no interaction potential between the atoms and the chain is not self avoiding. This means that a random chain may be generated by making a random walk with step size one. We will assume that the polymer is in a medium with linear viscosity, and that without the existence of constraints, the relation between the drag force on the particles and the exerted force is given by (4.20), where \( \mathbf{D}^{-1} \) is the unit matrix. For the constraint relations described above, every row of \( \mathbf{B} \) contains six non-zero elements, each given by (4.10). With known \( \mathbf{D}^{-1} \) and \( \mathbf{B} \), \( \mathbf{E} \) can be calculated according to (4.28).

To get some confidence in the method we will first do some simple calculations, of which the results can be checked by inspection. We will first calculate \( \mathbf{E} \) of two particles coupled by the unit-length constraint. The particle positions are

\[
\mathbf{r}_1 = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}, \quad \mathbf{r}_2 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}.
\]

Calculating \( \mathbf{E} \) with (4.28) gives

\[
\mathbf{E} = \begin{pmatrix}
\frac{1}{2} & 0 & 0 & \frac{1}{2} & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 \\
\frac{1}{2} & 0 & 0 & \frac{1}{2} & 0 & 0 \\
0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 1
\end{pmatrix}.
\]

It can be seen that the properties of this \( \mathbf{E} \) are in accordance with those mentioned in the previous section, i.e. it is symmetric, positive definite, the sum of the elements in every column is one, etc. It can also be seen that motion of the system is correctly represented by (4.42): a unit force in the \( x \) direction on particle 1 results in a velocity of \( \frac{1}{2} \) in the \( x \) direction of particle 1 and 2 (column 1 of \( \mathbf{E} \)). A unit force in the \( y \) direction on particle 1 results in a velocity 1 in the \( y \) direction of particle 1, (column 2 of \( \mathbf{E} \)).

Let us now look at the decay of motion along this very short chain. Obviously, as can be seen in (4.42), the velocity in the \( x \) direction of particle 1 is the same as the velocity in the \( x \) direction of particle 2. So the motion in the \( x \) direction does not decay. This is because the length constraint is oriented in the \( x \) direction. As can be seen in (4.42), in the \( y \) and \( z \) direction the motion of particle 1 and 2 is not coupled.
Let us now calculate analytically the ensemble averaged decay of motion in the $x$ direction, where the averaging is done over all spatial orientations of the vector $\mathbf{r}_1 - \mathbf{r}_2$. Later we will calculate this same quantity by averaging $\mathbf{E}$ over a randomly generated ensemble. We assume that the angle between the vector $\mathbf{r}_{21}$ and the $x$ axes is $\varphi$ (see Figure 4.1), and that on particle 1 a unit force is exerted in the $x$ direction, so, $\mathbf{f}_1 = \hat{x}$, where $\mathbf{r}_{21} = \mathbf{r}_2 - \mathbf{r}_1$. Due to the length constraint, the velocity of both particles in the direction $\mathbf{r}_{21}$ is the same, and is half the component of $\mathbf{f}_1$ in the direction $\mathbf{r}_{21}$, so, is $\frac{1}{2} \cos \varphi$. Therefore, the constraint force on particle 1 is given by

$$ f^c_1 = -\frac{1}{2} \cos \varphi \mathbf{r}_{21}. \quad (4.43) $$

The constraint force on particle 2 is the opposite. The $x$ component of the total force on particle 1 is

$$ (\mathbf{f}^{\text{tot}}_1)_x = (\mathbf{f}_1 + f^c_1)_x = 1 - \frac{1}{2} \cos^2 \varphi. \quad (4.44) $$

Averaging this last expression over all spatial orientations in 3D gives

$$ \langle (\mathbf{f}^{\text{tot}}_1)_x \rangle = \frac{1}{4\pi} \int_0^\pi \left(1 - \frac{1}{2} \cos^2 \varphi\right) 2\pi \sin \varphi \, d\varphi = \frac{5}{6}. \quad (4.45) $$

In the same way $\langle (\mathbf{f}^{\text{tot}}_2)_x \rangle$ can be calculated, giving

$$ \langle (\mathbf{f}^{\text{tot}}_2)_x \rangle = \frac{1}{4\pi} \int_0^\pi \left(\frac{1}{2} \cos^2 \varphi\right) 2\pi \sin \varphi \, d\varphi = \frac{1}{6}. \quad (4.46) $$

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**Figure 4.1** Molecule of two atoms with an angle of $\varphi$ between $\mathbf{r}_{12}$ and the $x$-axis. A force $\mathbf{F}$ is applied to atom 1.
Thus, the ensemble averaged decay of motion is given by
\[
\frac{\langle \mathbf{f}_2 \rangle_x}{\langle \mathbf{f}_1 \rangle_x} = \frac{\langle \dot{\mathbf{r}}_2 \rangle_x}{\langle \dot{\mathbf{r}}_1 \rangle_x} = \frac{1}{\frac{5}{6}} = \frac{6}{5}. \tag{4.47}
\]

This result can also be obtained in a simpler way by noting that there is a linear relationship between the force and the response. For such a system, orientational averaging may be done by taking the average value of the responses of the system, where the system is oriented along the three coordinate axes. When the system is oriented in the \( x \) direction, the response of the system to a unit force in the \( x \) direction, exerted on particle 1, is given by \((\frac{1}{2}, 0, 0, \frac{1}{2}, 0, 0)^T\), (which is the first column of (4.42)). When the system is oriented in the \( y \) resp. \( z \) direction, as can be seen by inspection, the response to the same force is given by \((1, 0, 0, 0, 0, 0)^T\) resp. \((1, 0, 0, 0, 0, 0)^T\). Averaging these three responses gives \((\frac{5}{6}, 0, 0, \frac{1}{6}, 0, 0)^T\). So, the ratio between the averaged velocities in the \( x \) direction of particle 1 and 2 is 0.2, which is the same as found in the previous calculations. By doing the same for unit forces oriented in the other directions and also applied on particle 2, the complete response matrix can be derived. It is given by
\[
\mathbf{E} = \begin{pmatrix}
\frac{5}{6} & 0 & 0 & \frac{1}{6} & 0 & 0 \\
0 & \frac{5}{6} & 0 & 0 & \frac{1}{6} & 0 \\
0 & 0 & \frac{5}{6} & 0 & 0 & \frac{1}{6} \\
\frac{1}{6} & 0 & 0 & \frac{5}{6} & 0 & 0 \\
0 & \frac{1}{6} & 0 & 0 & \frac{5}{6} & 0 \\
0 & 0 & \frac{1}{6} & 0 & 0 & \frac{5}{6}
\end{pmatrix}. \tag{4.48}
\]

As a test of our formalism we generated \(10^5\) randomly oriented configurations, and calculated the average \(\mathbf{E}\) of this ensemble. It was, within expected tolerance, equal to (4.48).

All this gives enough confidence in the method to try it on a polymer chain consisting of 40 atoms, again linearly connected by unit-length constraints, and with the same properties as the previous example. The atoms are numbered 1 \ldots 40 along the chain. We will concentrate on a few questions:

- What is the ensemble averaged velocity of particles in the middle of the chain, resulting from a unit force on that particle.

- How does the motion, forced upon a particle somewhere in the middle of the chain, decay along the chain?
How long should the chain be in order that particles in the middle of the chain behave as if they are virtually in an infinite chain?

What is the average velocity of particle 1 and particle 40 when a unit force is applied to these particles?

For a system consisting of 40 atoms the matrix \( \langle E \rangle \) is \( 120 \times 120 \). Averaging was done over \( 10^5 \) randomly generated configurations, and over the particles \( 10 \leq i \leq 30 \). The average value of the 60 diagonal elements in the middle of the diagonal was found to be 0.666634, i.e.

\[
\frac{1}{60} \sum_{i=30}^{89} \langle N \rangle (i, i) = 0.666634. \tag{4.49}
\]

This answers our first question. (From (4.49) it can be seen that besides averaging in the \( x \) direction, averaging in the \( y \) and \( z \) direction was also done. That is to get better statistics.)

To answer the second question we assume that particles with numbers between 10 and 30 behave as if they are part of a truly infinite chain, so, only these particles will be used to calculate the decay of motion along the chain. This assumption will be justified later. When a particle \( i \), with \( 10 \leq i \leq 30 \), is subject to a unit force in either the \( x \), \( y \), or \( z \) direction, we are interested in the average velocity of particle \( i+1 \), \( i-1 \), \( i+2 \), \( i-2 \), etc. in the \( x \) resp. \( y \) resp. \( z \) direction. In this way we obtained nine average velocities, including the (already found) average velocity of the particle on which the unit force was applied. The result is listed in Table 4.1, and plotted in Figure 4.2.

In Table 4.1 it can be seen that the average velocity of particle \( i+8 \) and \( i-8 \) is \( 0.17507 \times 10^{-5} \). This shows that the motion decays with a factor of 0.2013 per monomer. We think that in a longer simulation the decay factor will prove to be 0.2, i.e. that it will be the same decay as found in the two particle system, described before. This can be explained as follows.

A particle in an infinitely long chain is in the ensemble average surrounded by an isotropic cloud of particles of its chain. So, in the ensemble average, the particle behaves as a particle with isotropic properties. This holds for all particles of the chain. Therefore, an infinitely long chain may be taken as a chain consisting of two particles with isotropic properties, connected by a length constraint. In the first part of this section we showed that for a chain of two particles, connected by a length constraint, the ratio between the velocities is 0.2. This ratio does not depend on the
Table 4.1 Average velocity versus Distance.

<table>
<thead>
<tr>
<th>Dist.</th>
<th>$\langle \hat{R} \rangle$</th>
<th>$- \log \langle \hat{R} \rangle$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.666634</td>
<td>0.1761</td>
</tr>
<tr>
<td>1</td>
<td>0.13282</td>
<td>0.8768</td>
</tr>
<tr>
<td>2</td>
<td>0.26969 \cdot 10^{-1}</td>
<td>1.5692</td>
</tr>
<tr>
<td>3</td>
<td>0.54873 \cdot 10^{-2}</td>
<td>2.2606</td>
</tr>
<tr>
<td>4</td>
<td>0.11025 \cdot 10^{-2}</td>
<td>2.9578</td>
</tr>
<tr>
<td>5</td>
<td>0.22054 \cdot 10^{-3}</td>
<td>3.6565</td>
</tr>
<tr>
<td>6</td>
<td>0.44221 \cdot 10^{-4}</td>
<td>4.3543</td>
</tr>
<tr>
<td>7</td>
<td>0.91876 \cdot 10^{-5}</td>
<td>5.0368</td>
</tr>
<tr>
<td>8</td>
<td>0.17507 \cdot 10^{-5}</td>
<td>5.7567</td>
</tr>
</tbody>
</table>

Figure 4.2 Simulation result showing that the decay of motion along a polymer chain is almost exactly a factor 0.2 per monomer. The least squares fit gives $\langle \hat{R} \rangle = 0.6669(0.2013)^{-Dist}$. 
drag coefficient of the particles; it was only assumed that the drag coefficients of
both particles are isotropic and identical. This explains why motion decays in an
infinitely long chain in the same way as in a two particle system.

Now that we know that in a long chain the decay of motion is 0.2 per monomer,
we can explain why the driven particle has an average velocity of 0.66666. For this,
we use the fact that, for this system, the sum of the elements in every column is one
(see Appendix C). Calling the unknown average velocity of the driven particle \( V \), we
may write the geometric series

\[
V + 2V(0.2) + 2V(0.2)^2 + 2V(0.2)^3 + \cdots = 1,
\]

which results in \( V = 0.6666 \).

We still have to justify the use of the particles 10, 30 to obtain our results, i.e.,
do these particles behave as if they are part of an infinite chain? Over 9 monomers,
motion has decayed with a factor of \((0.2)^9 = 0.5 \times 10^{-6}\), so our assumption is
justified that the particles more than 9 monomers away from the end of the chain are
virtually in an infinite chain.

Summarising, we have derived by simulation, that the average velocity of the
driven particle is 0.6666, and that the motion along the chain decays with a factor of
0.200 ± 0.001 per monomer.

It is interesting to compare the decay of motion along a polymer chain in the
limit of Rouse dynamics, with the results of Binder's theory [7] for polymer melt
morphology dynamics. There it is conjectured that the effect of a force on an atom in
a polymer melt, where the polymer is long, is that atoms within the gyration radius
of the atom on which the force is exerted, all move approximately over the same
distance, i.e. there the decay is much slower.

Let us now look at the end of the chain. Our simulation shows that the average
velocity of the particles 1 and 40 under a unit force is 0.81461, and that due to
that same force the particles 2 and 39 have an average velocity of 0.14794. So, the
average decay of motion from particle 1 to 2, and particle 40 to 39 is a factor of
\((0.14794/0.81461) = 0.18160\). This ratio is lower than 0.2, as found in the middle
of the chain, and does not look like a ‘nice’ number. As far as we can see, this low
ratio is mainly due to the high average velocity of the end particles, not to a low
average velocity of the particles 2 and 39.

We will stop here with analysing the results of our simple numerical experiment
because this is not a chapter about the behaviour of polymers but about a method to
simulate the behaviour of constraint systems in general.
4.7 Conclusion

In this chapter it has been shown how zeroth, first, and second order equations of unconstrained motion may be transformed into zeroth, first, and second order equations of constrained motion. The unconstrained and constrained equation of motion are given in a closed form. For many cases the equations of motion can be written as matrix equations. The equations of motion suffer from numerical drift, so, are not very suited for integration over many timesteps. In spite of these restrictions, many applications can be thought of, all concerning questions about (near) instantaneous behaviour of the system. Because the equations of constrained motion are in a simple closed form, it is possible to use them for ensemble averaging.

As an example, the ensemble averaged, instantaneous decay of motion along a simple polymer chain in the non-inertial viscous regime was studied. This gave results which to our knowledge are new. The most important result we found is that motion decays along this chain with a factor of $0.2/n^3$ per monomer.

Appendix C

In this appendix we will show that for the polymer system as described in Section 4.6 the sum of the elements in every column of $E$ is one. We return to the conventional notation, so, instead of using $R$, the position of particle $i$ is denoted by $r_i$.

We first have to note that for the polymer system the sum of the constraint forces, as exerted on the particles, is zero because only constraints between particles are
involved. In general, the sum of constraint forces is zero when

$$\sum_{j=1}^{l} \lambda_j [\nabla_i g_j] = 0. \quad (C1)$$

That the sum of the constraint forces is zero means that a unit force exerted on the system will be compensated only by the drag forces on the particles. The relation between the drag force and the velocity is given by the unit matrix $D^{-1}$, so for the constrained and unconstrained system the sum of the velocities of the particles equals the exerted force. Because every column of $E$ and $D^{-1}$ represents the response of the system to a unit force, the sum of every column will be one.

**Literature**


