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Brownian motion with stiff bonds and rigid constraints

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Brownian systems with stiff elastic bonds of nearly constant length, such as long chain polymer molecules, behave differently when the stiff bonds are replaced by rigid bonds of exactly constant length, i.e. in statistical mechanics real stiff systems cannot be idealized by theoretical rigid ones. It is shown that a potential force can be applied to the rigidly constrained system in order to make it behave like the limit of a very stiff elastic system. A simple explicit expression for the required potential, suitable for computer simulations of the Brownian motion, is given for general constraints and also in the particular case of a trumbbell or trimer.

1. Introduction

In computer simulations of the dynamics of polymer chains for the purpose of studying their mechanical properties such as the rheology, the bond lengths are usually considered to be nearly constant while the bond angles are free to change. The lengths of the bonds can be held virtually constant by a bond force with a very stiff spring. Stiff springs in Brownian motion, however, result in rapid oscillations in the tight potential well. As discussed by Fixman (1978), these rapid oscillations dominate and obscure the more interesting slower modes in which the chain changes its configuration. To avoid the expensive resolution of these boring rapid oscillations one would like to replace the stiff bonds with rigid constraints (simplification *I*). The constrained system with reduced degrees of freedom can be represented using suitable generalized coordinates, such as the bond angles. The resulting equations of motion are however complicated to derive, and the back calculation of the positions of the monomers an additional task. Instead of introducing the generalized coordinates, one would like to retain in computer simulations the original Cartesian positions of each of the monomers and employ constraining forces (simplification *II*).

Unfortunately simplifications *I* and *II* each introduce different errors in the statistical mechanical description of the Brownian motion of the real stiff polymer chain. In ordinary, non-thermal, mechanics there is no difficulty in replacing stiff bonds by the idealisation of rigid constraints and no difficulty in treating the constraints directly or by generalized coordinates. In statistical mechanics, however, the limit of a very stiff bond is a singular limit and not correctly described by a rigid link. For example the specific heat is proportional to the number of active degrees of freedom, which changes discontinuously when a stiff bond is replaced by a rigid link. Less obviously the Brownian motion of the configuration depends on whether the bonds are modelled as stiff or rigid.

A simple and well known example of this discrepancy between stiff and rigid systems is provided by the trumbbell or trimer consisting of two outer monomers joined by bonds to a central monomer with no restriction on the rotation of the polar angle θ between the two bonds. If the bonds are stiff (with non-zero natural length), then in thermodynamic equilibrium all bond angles are equally probable, so that the probability distribution function for the included angle θ is

$$p_s(\theta) \;=\; \tfrac{1}{2}\sin\theta$$

in three dimensions. If the stiff bonds are replaced by rigid bonds, then the probability distribution becomes non-uniform (Kramers 1946; Hassager 1974; Gottlieb & Bird 1976; Helfand 1979; Rallison 1979; and van Kampen & Lodder 1984):

$$p_r(\theta) \;\propto\; \sin\theta\left[1-\frac{m_1m_3}{(m_1+m_2)(m_3+m_2)}\cos^2\theta\right]^{\frac{1}{2}},$$

where m_1 and m_3 are the masses of the outer two monomers and m_2 is the mass of the central monomer. Computer simulations of trimers using the Langevin equation (Roy 1990) find these two distributions with the different types of bonds, see figure 3(*b*) later. Computer simulations of inertialess diffusion (setting the masses to zero in the Langevin equation) find the uniform distribution p_s for the stiff bonds and, in the case of the rigid bonds, the non-uniform distribution given by setting the masses equal in the expression for p_r, see figure 3(*a*) later.

The question which this paper addresses then is how can simplifications *I* and *II* of computer simulations be modified so as to produce a correct description of the Brownian motion of the changes in configuration of the stiff polymer chain; a description which avoids the expensive resolution of the rapid oscillation in the stiff bond, and which further uses the simple Cartesian description. While this paper is directed to the Brownian motion of a polymer chain, the same issues apply to any Brownian system with internal degrees of freedom.

The above problems of simplifying the computer simulations of stiff polymer chains were discussed clearly and solved by Fixman (1978), although we shall observe later that some of his remarks may have been incorrect. Using a generalized coordinate formulation, he showed for just the case of zero masses that the configurational changes of a stiff system could be modelled by a rigid one to which a corrective pseudo-potential force was applied. In this paper the problem will be tackled directly in the Cartesian coordinates, producing an explicit expression for the corrective potential in terms of the constraints which is easier to apply in computer simulations. We shall also find how the random forces act in the rigid system to produce the different equilibrium probability distribution to that in a stiff system.

The idea of a corrective pseudo-potential force was suggested independently by Rallison (1979), who used a much simpler approach based on Maxwell–Boltzmann thermodynamic equilibrium distributions in the full phase space, i.e. with non-zero masses. Such an approach is of course not applicable to computer simulations of the dynamics of the polymer chains. Rallison further showed how reducing the temperature in a quantum mechanical description would freeze out the vibrational stiff modes, but that this would not recover the rigid system because the zero point energy would vary with configuration. In this paper we assume that the temperature is sufficiently high for quantum mechanical effects to be ignored.

We start by studying the Brownian motion of a polymer chain with rigid links and using Cartesian coordinates. This study will yield the source of the errors in the rigid

Cartesian description. It will be found that the application of a pseudo-potential force will convert the rigid problem to the correct limit of the very stiff problem. The Brownian motion is first studied using a Langevin equation with mass. Then setting the mass to zero, the usual diffusional description used in many computer simulations is investigated. It is necessary to calculate the small nonlinear effect of a steady drift motion. One part of this drift motion is connected with the variation of the diffusivity with configuration, and this part must be incorporated into the simulation in order to model the diffusion process correctly. The other part connected with the variation of the inertia with configuration is the error which needs to be removed. The Langevin equation approach is used because with and without mass it forms the basis of many computer simulations.

2. Governing equations

Consider a polymer chain with N monomers at Cartesian positions $\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N$, with masses $m_1,\ldots,m_N$ and coefficients of friction $\zeta_1,\ldots,\zeta_N$. We will use the $3N$ vector of positions $x_i = (\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)$ with $i = 1,\ldots,3N$ to describe the configuration of the polymer, along with the $3N\times 3N$ diagonal tensor of masses $m_{ij} = \mathrm{diag}(m_1, m_1, m_1, m_2,\ldots,m_N)$ with $i,j = 1,\ldots,3N$ and similar $3N\times 3N$ diagonal tensor ζ_{ij} of the frictional coefficients.

Let there be K rigid constraints (such as keeping the bond lengths constant) of the form $g^a(x_i) = 0$ with $a = 1,\ldots,K$. These constraints are maintained by tensions (Lagrange multipliers) T^a acting in the directions $g^a_i = \partial g^a/\partial x_i$ in the $3N$ configurational space.

The momentum equation of the polymer chain is then the Langevin equation with a thermal random forcing $f(t)$:

$$m_{ij}\ddot{x}_j + \zeta_{ij}\dot{x}_j + T^a g^a_i = f_i(t).$$

Maintaining the constraints in time requires that the velocity is orthogonal to the constraints

$$\dot{x}_i g^a_i = 0$$

and also that there are components of the acceleration parallel to the constraints only when the constraints are curved (centrifugal components)

$$\ddot{x}_i g^a_i + \dot{x}_i\dot{x}_j g^a_{ij} = 0,$$

where $g^a_{ij} = \partial^2 g^a/\partial x_i \partial x_j$ is the curvature of the constraints. In these governing equations, the usual summation convention is applied to the subscripts taking values in the configurational space $1,\ldots,3N$ and also to the superscripts taking values in the constraint space $1,\ldots,K$.

First it is instructive to derive a form of the momentum equation with the tensions eliminated. Solving the momentum equation for the acceleration

$$\ddot{x}_i = m^{-1}_{ij}\left(f_j - \zeta_{jk}\dot{x}_k - T^a g^a_j\right)$$

we can substitute this into the second constraint equation to yield an instantaneous equation for the tensions:

$$\left(g^a_i m^{-1}_{ij} g^b_j\right) T^b = g^a_i m^{-1}_{ij} f_j - g^a_i m^{-1}_{ij}\zeta_{jk}\dot{x}_k + \dot{x}_i\dot{x}_j g^a_{ij}.$$

Solving this linear system of equations in the constraint space for the tensions T^a

and substituting back into the momentum equation, we obtain

$$\ddot{x}_i + \widetilde{m_{ij}^{-1}}\zeta_{jk}\dot{x}_k = \widetilde{m_{ij}^{-1}}f_j - m_{ij}^{-1}g_j^a M^{ab} g_{kl}^b \dot{x}_k \dot{x}_l,$$

where M is a tensor in the constraint space defined by its inverse

$$\left(M^{-1}\right)^{ab} = g_m^a m_{mn}^{-1} g_n^b$$

and where there is a modified inverse mass tensor

$$\widetilde{m_{ij}^{-1}} = m_{ij}^{-1} - m_{ik}^{-1} g_k^a M^{ab} g_l^b m_{lj}^{-1}.$$

This modified inverse mass tensor is orthogonal to the constraints

$$\widetilde{m_{ij}^{-1}} g_j^c = 0 \quad \text{and} \quad g_i^c \widetilde{m_{ij}^{-1}} = 0,$$

i.e. no component of the force f in the direction of the constraints produces any acceleration and further the force produces an acceleration with no components in the directions of the constraints. This orthogonality is achieved by the application of tensions in the momentum equation.

Mathematically $\widetilde{m^{-1}}$ is the inverse in the constrained configurational space of m which has first been projected orthogonal to the constraints. Define the projection operator for a vector onto the constrained configurational space:

$$P_{ij} = \delta_{ij} - g_i^a G^{ab} g_j^b$$

with G a tensor in the constraint space defined by its inverse

$$\left(G^{-1}\right)^{ab} = g_n^a g_n^b.$$

Then the projection for the mass tensor is

$$m_{ij}^{\perp} = P_{ik} m_{kl} P_{jl}.$$

Now we can see that the modified inverse mass tensor $\widetilde{m^{-1}}$ is simply the inverse of $m^{\perp}$ in the constrained configurational space:

$$\widetilde{m_{ij}^{-1}}\, m_{jk}^{\perp} = \left(m_{ij}^{-1} - m_{ir}^{-1} g_r^a M^{ab} g_s^b m_{sj}^{-1}\right)\left(m_{jk} - m_{jl} g_l^c G^{cd} g_k^d\right) = P_{ik}.$$

Note that the modified inverse mass tensor is not the projection of the inverse mass tensor, i.e. $\widetilde{m_{ij}^{-1}} \neq P_{ik} m_{kl}^{-1} P_{lj}$.

In the special case of a polymer chain with monomers of equal mass m,

$$m_{ij}^{\perp} = m P_{ij} \quad \text{and} \quad \widetilde{m_{ij}^{-1}} = \frac{1}{m} P_{ij}.$$

3. Linear theory of the random walk

We recall briefly in this section the classical linear theory of Brownian motion in order to derive expressions for the diffusivity and the magnitude of the random forces in terms of the Cartesian description of the constrained system. Integrating the linearized momentum equation with tensions eliminated, we have

$$\begin{aligned}
\dot{x}_i &= \int_0^t \left[\mathrm{e}^{-\widetilde{m^{-1}}\zeta(t-\tau)}\right]_{ij} \widetilde{m_{jk}^{-1}} f_k(\tau)\,\mathrm{d}\tau \\
x_i &= \int_0^t \left[\left(\widetilde{m^{-1}}\zeta\right)^{-1}\left(1 - \mathrm{e}^{-\widetilde{m^{-1}}\zeta(t-\tau)}\right)\right]_{ij} \widetilde{m_{jk}^{-1}} f_k(\tau)\,\mathrm{d}\tau.
\end{aligned}$$

Here the two terms in square brackets including exponentials are defined in terms of their convergent power series.

Making the white-noise approximation that the thermal random forcing is correlated on timescales too short to be of interest

$$\overline{f_i(\tau_1)f_j(\tau_2)} \;=\; 2kT\,\delta(\tau_1-\tau_2)\,F_{ij}$$

in the velocity correlation function

$$\overline{\dot{x}_i(t)\dot{x}_\alpha(t)} \;=\; \int_0^t \mathrm{d}\tau_1 \int_0^t \mathrm{d}\tau_2 \left[\mathrm{e}^{-\widetilde{m^{-1}\zeta}(t-\tau_1)}\right]_{ij} \widetilde{m^{-1}_{jk}}\; \overline{f_k(\tau_1)f_\gamma(\tau_2)}\; \widetilde{m^{-1}_{\gamma\beta}} \left[e^{-\widetilde{m^{-1}\zeta}(t-\tau_2)}\right]_{\alpha\beta}$$

and taking the limit $t \to \infty$ in order to forget the initial conditions, we obtain

$$\longrightarrow \quad 2kT \int_0^\infty \left[\mathrm{e}^{-\widetilde{m^{-1}\zeta}\tau}\right]_{ij} \widetilde{m^{-1}_{jk}}\; F_{k\gamma}\; \widetilde{m^{-1}_{\gamma\beta}} \left[\mathrm{e}^{-\widetilde{m^{-1}\zeta}\tau}\right]_{\alpha\beta} \mathrm{d}\tau$$

Premultiply this expression by $\widetilde{m^{-1}\zeta}$ so that one can integrate by parts:

$$\widetilde{m^{-1}_{ij}}\zeta_{jk}\overline{\dot{x}_k\dot{x}_\alpha} \;=\; 2kT\widetilde{m^{-1}_{ij}}F_{j\gamma}\widetilde{m^{-1}_{\gamma\alpha}} \;-\; \overline{\dot{x}_i\dot{x}_\gamma}\zeta_{\gamma\beta}\widetilde{m^{-1}_{\beta\alpha}}.$$

Now the equipartition of energy (really a definition of the temperature kT) requires

$$\overline{\dot{x}_i\dot{x}_\alpha} \;=\; kT\,\widetilde{m^{-1}_{i\alpha}}.$$

[Note that the expression of the equipartition of energy gives the total kinetic energy

$$\tfrac{1}{2}m_{ij}\overline{\dot{x}_i\dot{x}_j} \;=\; \tfrac{1}{2}kT\,m_{ij}\widetilde{m^{-1}_{ij}} \;=\; \tfrac{1}{2}kT\,\left(\delta_{ii} \;-\; g_i^a M^{ab} g_l^b m_{li}^{-1}\right) \;=\; \tfrac{1}{2}kT\,(3N \;-\; K),$$

i.e. $\frac{1}{2}kT$ times the number of unconstrained degrees of freedom.] Substituting the value of the variance of the velocities, we have the magnitude of the random forcing F given by

$$\widetilde{m^{-1}_{ij}}F_{j\gamma}\widetilde{m^{-1}_{\gamma\alpha}} \;=\; \widetilde{m^{-1}_{ij}}\zeta_{j\gamma}\widetilde{m^{-1}_{\gamma\alpha}}.$$

Now there can be no components of the random forcing F parallel to the constraints, because they would have no dynamical effect. Hence the solution for F is

$$F_{ij} \;=\; \zeta^{\perp}_{ij},$$

where $\zeta^{\perp}$ is the orthogonal projection

$$\zeta^{\perp}_{ij} \;=\; P_{ik}\zeta_{kl}P_{lj}.$$

Thus we have the standard fluctuation–dissipation result relating the magnitude of the random forces to the friction coefficient in the constrained configurational space. Note that Fixman (1978) assumed that the random forces would be unchanged by the constraints, $F = \zeta$, which we shall see in §5 can produce an error.

The projected form of the magnitude of the random forces provides a simple computer method for generating the required forces. First one generates unconstrained random forces $f^u(t)$ with an $F^u = \zeta$. Then one constrains these random forces with $f_i(t) = P_{ij}f^u_j(t)$. The resulting $f(t)$ have the correct $F = \zeta^{\perp}$.

Finally the diffusivity is defined as the rate of change in time of the variance of the random Brownian walk:

$$\begin{aligned} D_{i\alpha} &= \overline{\dot{x}_i(t) x_\alpha(t)} \\ &\longrightarrow \int_0^\infty \mathrm{d}\tau \left[\mathrm{e}^{-\widetilde{m^{-1}\zeta}\tau} \right]_{ij} \widetilde{m_{jk}^{-1}}\, 2kT\, F_{k\gamma}\, \widetilde{m_{\gamma\beta}^{-1}} \left[\left(\widetilde{m^{-1}\zeta}\right)^{-1} \left(1 - \mathrm{e}^{-\widetilde{m^{-1}\zeta}\tau}\right) \right]_{\alpha\beta} \end{aligned}$$

as $t \to \infty$. While one can manipulate the exponentials to evaluate the integral directly, it is easier to premultiply by $\widetilde{m^{-1}\zeta}$ and then integrate by parts:

$$\begin{aligned} \widetilde{m_{ij}^{-1}}\zeta_{jk}\overline{\dot{x}_k x_\alpha} &= \int_0^\infty \mathrm{d}\tau \left[\mathrm{e}^{-\widetilde{m^{-1}\zeta}\tau} \right]_{ij} \widetilde{m_{jk}^{-1}}\, 2kT\, F_{k\gamma}\, \widetilde{m_{\gamma\beta}^{-1}} \left[\mathrm{e}^{-\widetilde{m^{-1}\zeta}\tau} \right]_{\alpha\beta} \\ &= kT\, \widetilde{m_{i\alpha}^{-1}} \end{aligned}$$

using results from the fluctuation-dissipation calculation. We can solve this for the diffusivity using the orthogonality of the velocity and the displacement to the constraints g_i^a

$$D_{i\alpha} = kT\, \widetilde{\zeta_{i\alpha}^{-1}} = kT \left(\zeta_{i\alpha}^{-1} - \zeta_{ij}^{-1} g_j^a Z^{ab} g_k^b \zeta_{k\alpha}^{-1} \right)$$

with Z a tensor in the constraint space defined by its inverse

$$\left(Z^{-1}\right)^{ab} = g_n^a \zeta_{nm}^{-1} g_m^b.$$

The diffusivity is thus a modified inverse of the friction tensor, one which uses the tensions in the momentum equation to achieve the orthogonality to the constraints. Note that in the above calculation one can use $F = \zeta$ rather than $F = \zeta^\perp$ without affecting the result for the diffusivity.

In the special case of a polymer chain with monomers with equal friction coefficients ζ

$$F_{ij} = \zeta P_{ij} \quad \text{and} \quad D_{i\alpha} = \frac{kT}{\zeta} P_{i\alpha}.$$

4. Drift at second order

Small nonlinearities coming from the curvature of the constraints lead to a small steady drift motion. Part of this drift leads to equilibrium distributions which are erroneously non-uniform. We need to isolate this erroneous drift term in order to design corrective measures.

To examine the second-order drift we expand the motion

$$x(t) = x^{(0)} + x^{(1)}(t) + x^{(2)}(t) + \cdots .$$

in which $x^{(1)}(t)$ represents the linear theory of the Brownian motion about the basic configuration $x^{(0)}$ with $x^{(2)}(t)$ the small nonlinear correction. Nonlinear terms arise when the constraint direction g_i^a is evaluated at the slightly displaced position $x(t)$ instead of the basic position $x^{(0)}$, the small differences being calculated by a Taylor series expansion

$$g_i^a(x) = g_i^a(x^{(0)}) + x_j^{(1)} g_{ij}^a(x^{(0)}) + \cdots .$$

Note that Fixman (1978) asserted that during a short interval the constraining forces may be restricted to lie along their original directions, although in some sense his analysis included changes in direction equivalent to the above expression.

The linear theory generates no mean motion, so we are interested in the non-zero

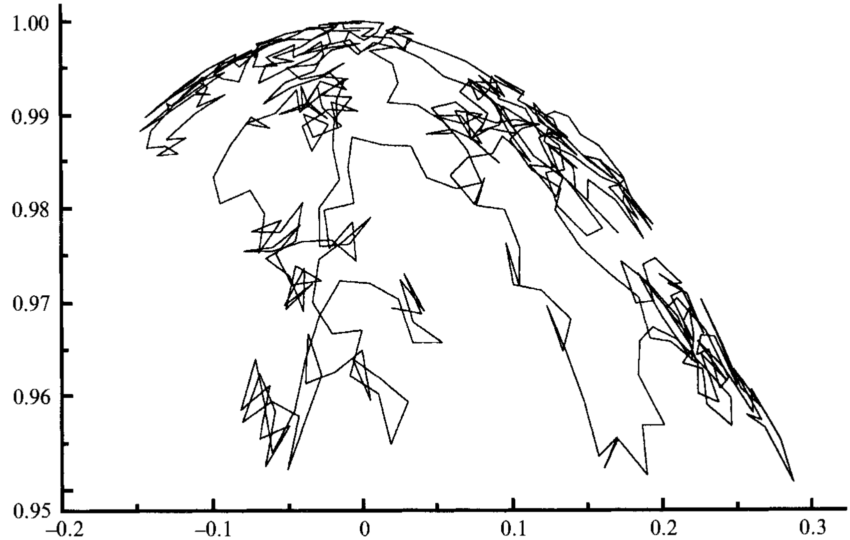

FIGURE 1. A random walk of 500 steps of size 0.02 on a unit sphere starting from the North pole. Note the mean velocity in the axial direction, i.e. normal to the surface at the initial position.

mean drift in $x^{(2)}(t)$. Expanding the governing equations and averaging, we obtain the problem for the second-order mean drift:

$$
\begin{aligned}
m_{ij}\overline{\ddot{x}_j^{(2)}} + \zeta_{ij}\overline{\dot{x}_j^{(2)}} + \overline{T^{a(2)}}g_i^a + \overline{T^{a(1)}x_j^{(1)}}g_{ij}^a &= 0,\\
\overline{\dot{x}_i^{(2)}}g_i^a + \overline{\dot{x}_i^{(1)}x_j^{(1)}}g_{ij}^a &= 0,\\
\overline{\ddot{x}_i^{(2)}}g_i^a + \overline{\ddot{x}_i^{(1)}x_j^{(1)}}g_{ij}^a + \overline{\dot{x}_i^{(1)}\dot{x}_j^{(1)}}g_{ij}^a &= 0.
\end{aligned}
$$

Now in the linear theory for the Brownian motion $x^{(1)}(t)$ the diffusivity $\overline{\dot{x}_i^{(1)}x_j^{(1)}}$ is constant in time and so differentiating we have

$$\overline{\ddot{x}_i^{(1)}x_j^{(1)} + \dot{x}_i^{(1)}\dot{x}_j^{(1)}} = 0.$$

Thus the component of the drift acceleration parallel to the constraints vanishes. On the other hand the component perpendicular to the constraints will vanish once the drift velocity attains its terminal value. Hence all components of the mean second-order acceleration vanish. Note that while the curvature of the constraints leads to small centrifugal accelerations these are cancelled precisely in the Brownian motion by the effects of small changes in the constraint direction, $x^{(1)}g_{ij}^a$.

Thus the nonlinear drift motion $\overline{x_i^{(2)}(t)}$ is a velocity. It has two sources. First there is a geometric effect in which the random walk with $\overline{x^2(t)} \propto t$ on the curved surface $g_{ij}^a \neq 0$ requires a constant velocity in the direction of the normal g_i^a, see figure 1. The second dynamical effect involving the tension–displacement correlation $\overline{T^{a(1)}x_j^{(1)}}$ is more complicated. A tangential velocity $\dot{x}$ produces a frictional force $\zeta_{ij}\dot{x}_j$. This frictional force produces a tangential acceleration $\widetilde{m_{ij}^{-1}}\zeta_{jk}\dot{x}_k$ with the normal components of force being adsorbed by tensions T^a, one part of the tension for the normal components of the frictional force and one part for the normal component of the inertial force. Note that the tension changes sign with the velocity and thus

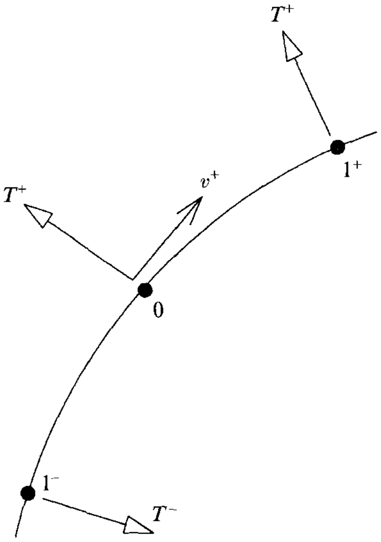

FIGURE 2. A positive random velocity v^+ requires, say, a positive normal tension T^+ in order to constrain the particle as it moves along the surface from 0 to 1^+. Similarly a negative random velocity requires a negative tension T^- as the particle moves from 0 to 1^-. Viewed from 0, the tension T^+ at 1^+ and the tension T^- at 1^- both have a component along the constrained surface from 1^- to 1^+ (with the curvature as drawn).

with the displacement. Now on a curved surface the normal changes direction slightly during a displacement. The correlation of the tension with the small change in normal thus results in a tangential mean force, driving a mean tangential motion, see figure 2.

With the drift acceleration set to zero, the drift momentum equation gives

$$\overline{\dot{x}_i^{(2)}} \quad = \quad -\zeta_{ij}^{-1}\left(\overline{T^{a(2)}}g_j^a \; + \; \overline{T^{a(1)}x_k^{(1)}}g_{jk}^a\right).$$

Substituting this into the velocity constraint condition, we find the instantaneous equation governing the second-order tensions:

$$\left(Z^{-1}\right)^{ab}\,\overline{T^{b(2)}} \quad = \quad -g_i^a\zeta_{ij}^{-1}g_{jk}^b\,\overline{T^{b(1)}x_k^{(1)}} \; + \; \overline{\dot{x}_i^{(1)}x_j^{(1)}}g_{ij}^a\,.$$

To obtain the required correlation between the tension and displacement, we multiply the linear theory equation for the tension $T^{b(1)}$ by the displacement $x_k^{(1)}$ and average (using $\overline{x^{(1)}(t)f(t)} = 0$):

$$\left(M^{-1}\right)^{ab}\,\overline{T^{b(1)}x_k^{(1)}} \quad = \quad -g_i^a m_{ij}^{-1}\zeta_{jl}\overline{\dot{x}_l^{(1)}x_k^{(1)}}\,.$$

Substituting in the expression for the diffusivity $\overline{\dot{x}_l^{(1)}x_k^{(1)}}$ from the linear theory yields

$$\begin{aligned}\left(M^{-1}\right)^{ab}\,\overline{T^{b(1)}x_k^{(1)}} \quad &= \quad -kT\,g_i^a m_{ij}^{-1}\left(\delta_{jk} \; - \; g_j^b Z^{bc}g_l^c\zeta_{lk}^{-1}\right)\\ &= \quad -kT\,\left(g_i^a m_{ik}^{-1} \; - \; \left(M^{-1}\right)^{ab}Z^{bc}g_l^c\zeta_{lk}^{-1}\right).\end{aligned}$$

Hence

$$\overline{T^{a(1)}x_k^{(1)}} \quad = \quad -kT\,\left(M^{ab}g_l^b m_{lk}^{-1} \; - \; Z^{ab}g_l^b\zeta_{lk}^{-1}\right).$$

Thus the tension–displacement correlation has two parts, one from the normal part of the inertial force and one from the normal part of the friction force, as described earlier. These parts will vanish if m and ζ are isotropic in the configuration space, i.e. all the monomers have the same masses and same friction coefficient, because then the tangential velocity will only produce a tangential friction force which will only produce a tangential acceleration with no need for a tension. The tension–displacement correlation can also vanish if m is proportional to ζ, i.e. the mass of a monomer is proportional to its friction coefficient, because again the tangential velocity will only produce a tangential acceleration with no need for a tension. Note that Fixman (1978) asserted that there would be no correlation between the constraints and the displacements, which we find to be true only in special cases.

Substituting into the equation for the second-order mean tensions the above expression for the tension–displacement correlation and also the expression for the diffusivity, we obtain

$$\begin{aligned}\left(Z^{-1}\right)^{ab}\overline{T^{b(2)}} \;=\; kT\Big\{&\left(g_i^a\zeta_{ij}^{-1}g_{jk}^b\right)M^{bc}g_l^c m_{lk}^{-1} \;-\; \left(g_i^a\zeta_{ij}^{-1}g_{jk}^b\right)Z^{bc}g_l^c\zeta_{lk}^{-1}\\ &+\; g_{ij}^a\left(\zeta_{ij}^{-1} \;-\; \zeta_{ik}^{-1}g_k^b Z^{bc}g_l^c\zeta_{lj}^{-1}\right)\Big\}.\end{aligned}$$

Solving we obtain

$$\begin{aligned}\overline{T^{a(2)}} \;=\; kT\Big\{&Z^{ab}\left(g_i^b\zeta_{ij}^{-1}g_{jk}^c\right)M^{cd}g_l^d m_{lk}^{-1} \;+\; Z^{ab}g_{ij}^b\zeta_{ij}^{-1}\\ &-\; Z^{ab}\left(g_i^b\zeta_{ij}^{-1}g_{jk}^c\right)Z^{cd}g_l^d\zeta_{lk}^{-1} \;-\; Z^{ab}\left(g_{ij}^b\zeta_{ik}^{-1}g_k^c\right)Z^{cd}g_l^d\zeta_{lj}^{-1}\Big\}\end{aligned}$$

Using our results for $\overline{T^{a(2)}}$ and $\overline{T^{a(1)}x_k^{(1)}}$ in the expression for the second-order drift velocity, we obtain

$$\begin{aligned}\overline{\dot{x}_i^2} \;=\; kT\Big\{ &-\; \zeta_{ij}^{-1}g_j^a Z^{ab}\left(g_r^b\zeta_{rs}^{-1}g_{sk}^c\right)M^{cd}g_l^d m_{lk}^{-1} \;-\; \zeta_{ij}^{-1}g_j^a Z^{ab}g_{rs}^b\zeta_{rs}^{-1}\\ &+\; \zeta_{ij}^{-1}g_j^a Z^{ab}\left(g_r^b\zeta_{rs}^{-1}g_{sk}^c\right)Z^{cd}g_l^d\zeta_{lk}^{-1} \;+\; \zeta_{ij}^{-1}g_j^a Z^{ab}\left(g_{rk}^b\zeta_{rs}^{-1}g_s^c\right)Z^{cd}g_l^d\zeta_{lk}^{-1}\\ &+\; \zeta_{ij}^{-1}g_{jk}^a M^{ab}g_l^b m_{lk}^{-1} \;-\; \zeta_{ij}^{-1}g_{jk}^a Z^{ab}g_l^b\zeta_{lk}^{-1}\Big\}.\end{aligned}$$

Grouping together those terms which involve the mass M and those which do not, we can simplify this expression:

$$\begin{aligned}\overline{\dot{x}_i^2} \;&=\; kT\left\{\left(\zeta_{ij}^{-1}-\zeta_{ir}^{-1}g_r^a Z^{ab}g_s^b\zeta_{sj}^{-1}\right)g_{jk}^c M^{cd}g_l^d m_{lk}^{-1}-\frac{\partial}{\partial x_k}\left(\zeta_{ij}^{-1}g_j^a Z^{ab}g_l^b\zeta_{lk}^{-1}\right)\right\}\\ &=\; kT\left\{\widetilde{\zeta_{ij}^{-1}}M^{cd}\frac{\partial}{\partial x_j}\left(\tfrac{1}{2}\left(M^{-1}\right)^{cd}\right) \;+\; \frac{\partial}{\partial x_k}\left(\widetilde{\zeta_{ik}^{-1}}\right)\right\}\\ &=\; kT\left\{\widetilde{\zeta_{ij}^{-1}}\frac{\partial}{\partial x_j}\left(\ln\sqrt{\det\left(M^{-1}\right)^{cd}}\right) \;+\; \frac{\partial}{\partial x_k}\left(\widetilde{\zeta_{ik}^{-1}}\right)\right\}.\end{aligned}$$

This provides a concrete form of a result in the general theory cast in terms of generalized coordinates, see for example equation (7.5) of Hinch & Nitsche (1993).

In the special case of a polymer chain with monomers with equal masses and friction coefficients

$$\overline{T^{a(1)}x_k^{(1)}} \;=\; 0, \qquad \overline{T^{a(2)}} \;=\; kTG^{ab}g_{ij}^b P_{ij},$$

and

$$\overline{\dot{x}_i^{(2)}} \;=\; -\frac{kT}{\zeta}g_i^a\left(G^{ab}g_{jj}^b - G^{ab}g_{jk}^b g_j^c g_k^d G^{cd}\right).$$

5. Inertialess diffusion

When one is interested only in the diffusional change of the configuration of the polymer chain and not interested in the inertial–viscous relaxation of the velocity, the mass in the Langevin equation can be set to zero, resulting in governing equations

$$\begin{aligned} \zeta_{ij}\dot{x}_j + T^a g_i^a &= f_i(t), \\ \dot{x}_i g_i^a &= 0. \end{aligned}$$

Solving for the velocity we obtain

$$\dot{x}_i = \zeta_{ij}^{-1}\left(f_j(t) - T^a g_j^a\right).$$

Substituting this into the constraint on the velocity yields an instantaneous equation for the tensions:

$$\left(g_i^a \zeta_{ij}^{-1} g_j^b\right) T^b = g^a \zeta_{ij}^{-1} f_j.$$

Solving for the tensions and substituting back, we obtain

$$\dot{x}_i = \widetilde{\zeta_{ij}^{-1}} f_j$$

so that no component of the random forcing f in the direction of the constraint has any dynamical effect.

In the linear theory of the random walk, one cannot now derive the magnitude of the random forces but instead must set them by the results of the fluctuation–dissipation theorem. With this choice, the diffusivity is given correctly by the inertialess dynamics, as we shall now see. First integrating the momentum equation with the tensions eliminated,

$$x_i(t) = \int_0^t \widetilde{\zeta_{ij}^{-1}} f_j(\tau)\,\mathrm{d}\tau$$

we can evaluate the diffusivity:

$$\overline{\dot{x}_i x_\alpha} = \int_0^t \widetilde{\zeta_{ij}^{-1}}\, \overline{f_j(t) f_\beta(\tau)}\, \widetilde{\zeta_{\alpha\beta}^{-1}}\,\mathrm{d}\tau.$$

Using the fluctuation-dissipation result for the magnitude of the random forces in the constrained system, and also $\int_0^t \delta(t-\tau)\,\mathrm{d}\tau = \frac{1}{2}$, we find

$$\overline{\dot{x}_i x_\alpha} = 2kT\,\tfrac{1}{2}\widetilde{\zeta_{ij}^{-1}}\zeta_{j\beta}^{\perp}\widetilde{\zeta_{\alpha\beta}^{-1}} = kT\,\widetilde{\zeta_{i\alpha}^{-1}}.$$

Note that instead of $\zeta^{\perp}$ we could have used the magnitude of the unconstrained random forces ζ in this calculation without affecting the answer.

Proceeding to the mean drift at second order, we find that in the inertialess dynamics this is governed by the same equations as the drift with inertia, because we found in that case that there was no mean acceleration. The development will therefore be the same except for the calculation of the correlation between the tension and the displacement. When there is no mass the tensions in the linear theory have to cancel the components of the random force and the frictional force in the direction of the constraints, whereas when there is mass they must also cancel components of the inertial force. Multiplying the equation for the inertialess tensions by the displacement and averaging yields

$$\left(g_i^a \zeta_{ij}^{-1} g_j^b\right)\, \overline{T^{b(1)} x_k^{(1)}} = \int_0^t g^a \zeta_{ij}^{-1} \overline{f_j(t) f_l(\tau)} \widetilde{\zeta_{kl}^{-1}}\,\mathrm{d}\tau$$

$$
\begin{aligned}
&= 2kT\,\tfrac{1}{2} g_i^a \zeta_{ij}^{-1} \zeta_{jl}^{\perp} \widetilde{\zeta_{kl}^{-1}} \\
&= kT\, g_i^a \zeta_{ij}^{-1} \left(\zeta_{jl} \widetilde{\zeta_{lk}^{-1}} \; - \; g_j^b G^{bc} g_n^c \zeta_{nl} \widetilde{\zeta_{lk}^{-1}} \right) \\
&= kT \left\{ g_l^a \widetilde{\zeta_{lk}^{-1}} \; - \; \left(Z^{-1}\right)^{ab} G^{bc} \left(g_k^c - \left(G^{-1}\right)^{cd} Z^{de} g_l^e \zeta_{lk}^{-1} \right) \right\} \\
&= -kT \left(Z^{-1}\right)^{ab} \left\{ G^{bc} g_k^c \; - \; Z^{bc} g_l^c \zeta_{lk}^{-1} \right\}.
\end{aligned}
$$

Note here it was *necessary* to use the constrained $\zeta^{\perp}$ for the magnitude of the random forces, because here the unconstrained ζ makes this tension–displacement correlation vanish. Solving the above equation we have

$$
\overline{T^{a(1)} x_k^{(1)}} \; = \; -kT \left\{ G^{ab} g_k^b \; - \; Z^{ab} g_l^b \zeta_{lk}^{-1} \right\}.
$$

In the inertialess dynamics, the tangential velocity produces a tension if the friction coefficient ζ is not isotropic (friction coefficient of all the monomers equal). Thus we see that the above expression for the tension–displacement correlation vanishes when $\zeta \propto \delta$. Noting that the only difference between the inertialess and the inertial calculation of the mean drift is the replacement of M and m by G and δ, we may skip the detailed calculations to assert the result

$$
\overline{\dot{x}_i^2} \; = \; kT \left\{ \widetilde{\zeta_{ij}^{-1}} \frac{\partial}{\partial x_j} \left(\ln \sqrt{\det \left(G^{-1}\right)^{cd}} \right) \; + \; \frac{\partial}{\partial x_k} \left(\widetilde{\zeta_{ik}^{-1}} \right) \right\}.
$$

Again the second term provides a concrete form of a result in the general theory cast in terms of generalized coordinates. The first term involving $\det G^{-1}$ does not have a counterpart in the general theory, and so is an error resulting from using rigid constraints and Cartesian coordinates (simplifications *I* and *II* of the introduction).

The results for the mean tension–displacement correlation, mean tension and mean motion for the special case of a polymer chain which is diffusing with monomers with equal friction coefficients are identical to those given at the end of the previous section 4 for a polymer chain with monomers with equal masses and equal friction coefficients governed by the Langevin equation.

6. The dispersion equation and corrective measures

The probability distribution function for the configuration of the polymer chain $P(x,t)$ satisfies the dispersion equation

$$
\frac{\partial P}{\partial t} + \frac{\partial}{\partial x_i} \left(P\, \overline{x_i^{(2)}} \right) \; = \; \frac{\partial^2}{\partial x_i \partial x_j} \left(P\, \overline{x_i^{(1)} x_j^{(1)}} \right)
$$

which can be derived by integrating over all possible jumps from one configuration to another in a small time δt and by making a Taylor series expansion for small such jumps (Uhlenbeck & Ornstein 1930), taking care with the non-homogeneous drift and diffusivity.

Substituting in the results for the diffusivity and the mean drift, we obtain the more familiar diffusion equation

$$
\frac{\partial P}{\partial t} + \frac{\partial}{\partial x_i} \left(P\, kT \widetilde{\zeta_{ij}^{-1}} \frac{\partial}{\partial x_j} \ln \sqrt{\det} \right) \; = \; \frac{\partial}{\partial x_i} \left(kT \widetilde{\zeta_{ij}^{-1}} \frac{\partial P}{\partial x_j} \right),
$$

where det stands for $\det M^{-1}$ in the first case with mass and for $\det G^{-1}$ in the case of inertialess dynamics. The second term in the mean drift is seen now as essential in this equation to turn the dispersion process into a diffusion process; the diffusion process having a Fickian flux proportional to the gradient of the probability and so no net change with a uniform distribution. In computer simulations, regions with a high diffusivity are depleted by their active random motion (more thrown out than received from the neighbouring less active regions), and so the simulations need the mean drift $\nabla \cdot D$ directed towards the high-diffusivity regions in order to restore a uniform distribution (see e.g. Ermak & McCammon 1978).

In thermodynamic equilibrium, the steady solution is

$$P \propto \sqrt{\det}$$

which will vary non-uniformly over the space of constrained configurations if det varies (Kramers 1946).

Now using stiff bonds, e.g. with a potential energy $g_n^a g_n^a / 2\epsilon$, the probability distribution function will localized to the neighbourhood of the constrained configurations but with no variation around the constrained configurations, i.e. $P \propto 1$. Hence to turn the rigid system into a stiff system one needs to apply the correction of a potential force (Fixman 1978; Rallison 1979)

$$-\frac{\partial}{\partial x_i}\left(kT \ln \sqrt{\det}\right) .$$

This is the main result of this paper.

Previously Rallison (1979) had shown for the case of inertial dynamics that a polymer chain with rigid constraints could be made to behave like one with very stiff constraints by the application of a corrective potential force. His similar potential function $kT(\det)^{\frac{1}{2}}$ involved the determinant of mass in the different space of constrained configurations, which was not simple to relate to a Cartesian description of the polymer chain. The new result for systems with inertia is to express the potential function in terms of a mass in the space of constraints with a simple explicit form in terms of the constraints

$$\det\left(M^{-1}\right)^{ab} = \det\left(g_i^a m_{ij}^{-1} g_j^b\right) .$$

Thus for systems with inertia, simplification I of the introduction can be corrected and a rigid system can be made to behave like one with very stiff constraints.

For the case of inertialess dynamics which was studied by Fixman (1978), a rigid system described by appropriate generalized coordinates (with no explicit constraint condition) can sometimes behave in Brownian motion like a very stiff system if the generalized coordinates are selected so that equilibrium distribution is uniform in those coordinates (see e.g. Grassia, Hinch & Nitsche 1994), i.e. simplification I can be made. The generalized coordinate description has a second-order mean drift of $\nabla \cdot D$, which is required to turn the dispersion process into a diffusion process. When the further simplification II is made of adopting a Cartesian description of the rigid chain, an additional mean drift appears, $\widetilde{\zeta^{-1}} \nabla kT \ln \sqrt{\det G^{-1}}$. This erroneous drift can be suppressed by the application of the corrective pseudo-potential force

$$-\frac{\partial}{\partial x_i} kT \ln \sqrt{\det\left(g_i^a g_i^b\right)}$$

with a simple explicit dependence on the constraints.

7. Details for a trimer

A trimer is a polymer chain with three monomers $N = 3$ linked by two bonds. The constraint functions are

$$g^1 = \tfrac{1}{2}\left(|\boldsymbol{x}_1 - \boldsymbol{x}_2|^2 - l_1^2\right) \quad \text{and} \quad g^2 = \tfrac{1}{2}\left(|\boldsymbol{x}_2 - \boldsymbol{x}_3|^2 - l_2^2\right) .$$

with gradients

$$g_i^1 = (\boldsymbol{x}_1 - \boldsymbol{x}_2, \boldsymbol{x}_2 - \boldsymbol{x}_1, 0) \quad \text{and} \quad g_i^2 = (0, \boldsymbol{x}_2 - \boldsymbol{x}_3, \boldsymbol{x}_3 - \boldsymbol{x}_2).$$

Thus

$$\left(M^{-1}\right)^{11} = l_1^2\left(\frac{1}{m_1} + \frac{1}{m_2}\right), \qquad \left(M^{-1}\right)^{12} = l_1 l_2 \frac{1}{m_2}\cos\theta$$

and

$$\left(M^{-1}\right)^{22} = l_2^2\left(\frac{1}{m_2} + \frac{1}{m_3}\right) .$$

Hence

$$\det\left(M^{-1}\right) = \frac{l_1^2 l_2^2}{m_1 m_2^2 m_3}\left((m_1 + m_2)(m_2 + m_3) - m_1 m_3 \cos^2\theta\right) .$$

(Note that the calculation of the determinant for longer polymer chains only involves a tridiagonal matrix and so is no more complicated.) Now the only dependence of $\det M^{-1}$ on configuration comes through the $\cos\theta$ with

$$\frac{\partial}{\partial x_i}(l_1 l_2 \cos\theta) = (\boldsymbol{x}_3 - \boldsymbol{x}_2, \boldsymbol{x}_2 - \boldsymbol{x}_3 + \boldsymbol{x}_2 - \boldsymbol{x}_1, \boldsymbol{x}_1 - \boldsymbol{x}_2).$$

Thus the pseudo-potential force required to correct the Langevin dynamics of a rigid chain to that of a very stiff chain is

$$\frac{kT m_1 m_3 \cos\theta}{l_1 l_2 (m_1 + m_2)(m_2 + m_3) - m_1 m_3 \cos^2\theta}(\boldsymbol{x}_3 - \boldsymbol{x}_2, \boldsymbol{x}_2 - \boldsymbol{x}_3 + \boldsymbol{x}_2 - \boldsymbol{x}_1, \boldsymbol{x}_1 - \boldsymbol{x}_2).$$

The corrective pseudo-potential force for the case of inertialess diffusion is obtained by setting the masses equal in the above expression.

Figure 3 shows that the application of these corrective forces to computer simulations does convert the behaviour of a rigid trimer to that of a very stiff one. The simulations are of both inertialess diffusion and inertial Brownian motion as described by the Langevin equation. The simulations use the Cartesian coordinates of the monomers and for the rigid trimers constraining tension forces. It is necessary to average the probability distribution of one realization over a long time, $5.1 \times 10^5 \zeta l^2/kT$, in order to achieve the accuracy of 1% required to distinguish between the rigid and stiff behaviours. Further details of the difficulties of computer simulations of Brownian motion of complex systems are being prepared for publication elsewhere (Grassia *et al.* 1994).

The mechanisms which lead to the slight preference of the rigid trimers for the right-angled configuration, $\cos\theta = 0$, are the two mechanisms described in figures 1 and 2. In the geometric effect of figure 1, as the bond between $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$ makes a finite rotation, there is a component of the motion of $\boldsymbol{x}_1$ towards $\boldsymbol{x}_2$ and of $\boldsymbol{x}_2$ towards $\boldsymbol{x}_1$. It is this motion of $\boldsymbol{x}_2$ towards $\boldsymbol{x}_1$, and a similar motion of $\boldsymbol{x}_2$ towards $\boldsymbol{x}_3$, which opens up the included angle of the trimer θ. The induced change in angle is largest for the right-angled configuration $\theta = \pi/2$, vanishing for the straight configuration

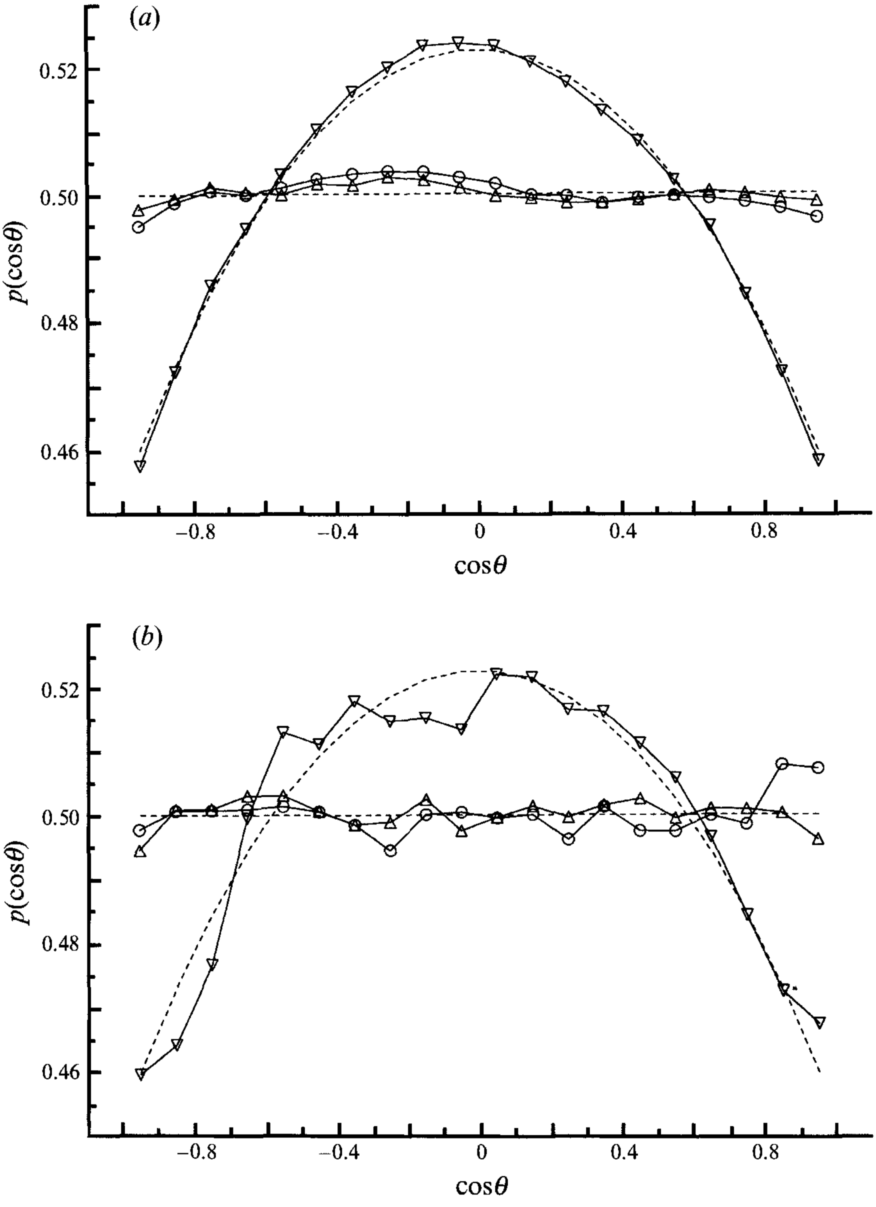

FIGURE 3. The probability distribution for the included angle θ of a trimer from computer simulations, normalized with $m = \zeta = l = kT = 1$, with a time-step 10^{-3}, and with the distribution averaged over a time 5.1×10^5. Figure 3(*a*) is for inertialess diffusion, while figure 3(*b*) is for the Langevin equation with mass. The circles are for stiff springs (spring constant 10^2), the downward-pointing triangles for rigid bonds, and the upward-pointing triangles for rigid bonds with the corrective pseudo-potential force. The dashed curves are the theoretical prediction for stiff and for rigid bonds.

$\theta = \pi$ and the bent-double configuration $\theta = 0$. The second mechanism involves the tension–displacement correlation of figure 2 and it comes into play only when the monomers have different masses and friction coefficients. It is a simple calculation to find the tension in the rigid bonds for the symmetric motion $x_1 = (X + \cos\phi, \sin\phi, 0)$,

$x_2 = (X,0,0)$ and $x_3 = (X + \cos\phi, -\sin\phi, 0)$ with $X = X(t)$ and $\phi = \phi(t)$ and with $m_3 = m_1$ and $\zeta_3 = \zeta_1$:

$$T = -\left(\frac{\zeta_1}{m_1} - \frac{\zeta_2}{m_2}\right)\left(\tfrac{2}{3}\dot{\phi}\sin\phi\cos\phi + \dot{X}\cos\phi\right)\left(\frac{1}{m_1} + \frac{2\cos^2\phi}{m_2}\right)^{-1}$$

Note that the constraining tension is not needed if the monomers have the same masses and friction coefficients, and that for motion which changes the configuration ϕ the tension is largest near $\phi = \pi/4$, i.e. $\theta = \pi/2$.

8. Conclusions

A real polymer with stiff bonds behaves differently in Brownian motion to an idealized one with frozen rigid bonds. Thus some proposed methods of analysis of polymer molecules based on rigid constraints are questionable. As far as configurational changes are concerned, it is possible to make the chain with rigid bonds behave like one with stiff elastic bonds by applying a corrective pseudo-potential force

$$-\frac{\partial}{\partial \boldsymbol{x}_i}\left(kT\ln\sqrt{\det}\right)$$

to the monomer at $\boldsymbol{x}_i$. For inertial dynamics, one must use the determinant of a mass matrix in the space of constraints

$$\det = \det\left(M^{-1}\right)^{ab} = \det\sum_i m_i^{-1}\frac{\partial g^a}{\partial \boldsymbol{x}_i}\cdot\frac{\partial g^b}{\partial \boldsymbol{x}_i}$$

while for inertialess diffusion (when using a Cartesian description of the positions of the monomers with rigid bonds maintained by constraining tensions) one must use the determinant of the simpler matrix

$$\det = \det\left(G^{-1}\right)^{ab} = \det\sum_i \frac{\partial g^a}{\partial \boldsymbol{x}_i}\cdot\frac{\partial g^b}{\partial \boldsymbol{x}_i}.$$

In these expressions m_i is the mass of the monomer at $\boldsymbol{x}_i$, and the rigid constraints are expressed as

$$g^a(\boldsymbol{x}_1, \boldsymbol{x}_2, \ldots, \boldsymbol{x}_N) = 0$$

for $a = 1, \ldots, K$. These corrective potential forces can be easily implemented in computer simulations of the Brownian motion of polymer chains.

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