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Chapter 9.

Brownian Dynamics Simulation

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Classical Brownian Theory for Translational Diffusion

Brownian motion was observed originally as the seemingly unending motion of pollen particles in suspension. Some of the theoretical background has been described in Chapter 2. The most transparent description of Brownian Dynamics is the Langevin equation,¹⁻⁵ which in its simplest form (translational Brownian motion) is

$$m \dot{\mathbf{v}}(t) = -m\beta\mathbf{v}(t) + \mathbf{F}_s(t) \quad (1)$$

where m is the mass of the pollen particle, β a friction coefficient, \mathbf{v} the linear velocity of the pollen particle, and \mathbf{F}_s the random or "stochastic" force on the pollen particle due to the molecules of its surroundings. The latter are much less massive and diffuse much more rapidly than the relatively heavy pollen particle in suspension.

The technique of Brownian dynamics simulation solves the Langevin equation directly, mimicking the random nature of the stochastic force on the right hand side of Eq. (1).⁶⁻¹⁰

The mathematical and physical nature of Eq. (1) is fundamentally different from those of the Newton equation and its deterministic relatives described in Chapter 2. There are inconsistencies in the earliest work leading up to the derivation by Langevin which were first described by Doob.¹¹

Let $X(t)$ be the x coordinate of the Brownian particle at time t . Einstein and Smoluchowski treated¹⁻⁵ $X(t)$ as a random variable and found the distribution of $\{X(t)-X(0)\}$ to be Gaussian with mean zero and variance $\alpha|t|$. This treatment is restricted to configurational space only, not the full configuration/velocity space. The set of random variables $\{X(t)\}$ is more accurately a temporally homogenous differential stochastic process, known as a Wiener process. The sample functions

$X(t)$ of this process are continuous with probability 1. The difference $\{X(s+t) - X(s)\}$ has a standard deviation $\alpha|t|$ and is of the order $|t|^{1/2}$. This implies that $dX(s)/ds$ cannot be finite; i.e. *that the velocity function of the Langevin equation has no time derivative*. However, this directly contravenes the fact that probability hypotheses are imposed on $F_s(t)$, including relations between this random force and $v(t)$ in order to determine the velocity distribution. If such a deterministic relation between force and velocity is assumed, then this implies that the velocity must be differentiable, and in consequence cannot be described by a Langevin equation equivalent to an Einstein or Smoluchowski diffusion equation. The force is indeterminate if the acceleration, the total time derivative of the linear velocity, is not defined. This means that the Einstein and Smoluchowski diffusion equations are equivalent to a Langevin equation with the deterministic acceleration term on the left hand side undefined.

To remedy this fault it is necessary to consider the full configuration/velocity space and the probability of finding the Brownian particle at time t with a given velocity and position given these at the arbitrary initial $t = 0$. This probability density function obeys Eq. (32) of Chapter 2. This leads to a consistent definition of acceleration provided that the Langevin equation is interpreted in terms of Wiener processes as summarized in Ref. 5 for example. Using this interpretation, the stochastic force of Eq. (1) is uncorrelated with the velocity of the Brownian particle, and varies extremely rapidly compared with variations in its position. As in Chapter 2 this implies that in a time interval Δt during which the velocity changes infinitesimally, there is assumed to be no correlation between $F(t)$ and $F(t + \Delta t)$. In the Langevin equation the position vector is a random variable, i.e. one which takes values with a given probability.

All these features must be consistently incorporated in a computer simulation of Brownian dynamics, and the results of such a simulation must also be consistent with known analytical solutions. For example, the velocity auto correlation function (a.c.f.) from Eq. (1) is ¹⁻⁵

$$\langle v(t) \cdot v(0) \rangle = \langle v(0) \cdot v(0) \rangle \exp(-\beta t) \quad (2)$$

an exponential.

Usually, there is another aspect to the computer simulation of Brownian motion designed to render it more useful for the investigation of rheology of suspensions¹²⁻¹⁵ and related complex phenomena. Deterministic non-equilibrium molecular dynamics (n.e.m.d.) computer simulation usually applies to essentially single component molecular fluids, which evolve structurally on the picosecond time scale. They shear thin at shear rates of the order of one THz, which are experimentally unachievable. Shear rates of one Hz are normally used experimentally on macromolecular suspensions of about one micron diameter per particle. The latter may be considered as Brownian particles analogous to pollen grains. In these systems a detailed description of the solvent is not necessary for an adequate rheological appreciation by computer simulation. The important

property is that of the macromolecule or Brownian particle, which can be investigated with Brownian Dynamics computer simulation. This was pioneered by Ermak and McCammon,⁹ and has been used widely since then for the investigation of polymeric suspensions in particular. The extra aspect in these simulations is the presence of another systematic force on the right hand side of Eq. (1), which is the force on one diffusing Brownian particle due to the others in suspension. In general, there are also other aspects due to configuration dependent hydrodynamic terms, but to a good approximation these may be neglected because at high shear rates they become insignificant in comparison with the forces between macromolecules. Their full consideration requires the friction coefficient and random force in Eq. (1) to become both position and time dependent, so that the Langevin equation evolves into a Mori approximation of the Liouville equation.^{1-5,11}

Algorithm

Based on the recent article by Heyes,⁶ a simple algorithm for shear flow in a macromolecular suspension, and for Brownian dynamics in general is described in this Section.

Let \mathbf{r}_n be the position of a particle at timestep n , \mathbf{F}_n be the net force on a particle at timestep n , γ be the shear rate, m the mass of the particle, T the temperature, k_B the Boltzmann constant and h the time step. The algorithm for updating the macromolecular coordinates is derived from that of Dotson⁶ taking the limit of $\beta h \rightarrow \infty$

$$\mathbf{r}_{n+1} = \mathbf{r}_n + \Delta \mathbf{r}_n \quad (3)$$

Considering the Cartesian components of $\Delta \mathbf{r}$

$$\Delta r_{xn} = \frac{(F_{xn} + F_{sxn}(h) + S_{xn}(h))h}{m\beta} + F_{zn}A(h, \beta) + \gamma r_{yn}h \quad (4a)$$

$$\Delta r_{yn} = \frac{(F_{yn} + F_{syn}(h))h}{m\beta} \quad (4b)$$

$$\Delta r_{zn} = \frac{(F_{zn} + F_{szn}(h))h}{m\beta} \quad (4c)$$

where

$$A(h) = \frac{h^2}{2} + \frac{2h}{\beta} - \beta^2 \quad (5)$$

where the random forces \mathbf{F}_{sn} and \mathbf{S}_n are selected from an unbiased normal distribution. For the Cartesian component α

$$\langle F_{s\alpha}^2(h) \rangle = \frac{2mk_B T \beta}{h} \quad (6)$$

and

$$\langle S_\alpha^2(h) \rangle = \left(\frac{2k_B T m \beta}{3h} \right) (\dot{\gamma} h)^2 \quad (7)$$

This formulation is derived from the Langevin equation

$$m \ddot{\mathbf{r}}(t) = \mathbf{F}(t) + \mathbf{F}_s(t) - \beta \mathbf{r}(t) \quad (8)$$

where $\mathbf{F}(t)$ is the deterministic and $\mathbf{F}_s(t)$ the stochastic forces.

If the random force terms are omitted then the dynamics are diffusive or "Stokesian." However, the use of the complete Langevin Eq. 8 enables the limit of zero shear rate to be considered.

Heyes has presented some results⁶ of computations with a repulsive Lennard-Jones potential ϕ_{ij} to represent the excluded volume repulsive interactions, derived from the force of the repulsive part of the Lennard-Jones potential

$$\phi_{LJ}(r) = 4\epsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\} \quad (9)$$

All quantities are written in terms of Lennard-Jones reduced units.⁶ The time step was adjusted so that the maximum displacement due to the random force was 0.01σ . Other parameters in reduced units were $\rho = 1.1$; $T = 1.0$; and $\beta = 2.5 \times 10^4$; equivalent to $10 \mu\text{m}$ silica spheres in water at room temperature. The number of molecules in the periodically repeated Brownian dynamics cell, N , was 108. Shear boundary conditions were employed as described by Heyes⁶ to maintain continuity of velocity profile across the cell boundaries. The decay time for momentum correlation for the Brownian particles is

$$\tau_p = \beta^{-1} = \frac{m}{3\pi\sigma\eta_s}$$

where η_s is the viscosity of the pure suspending medium. The Brownian structural relaxation time is

$$\tau_r = \frac{3\pi\sigma^3\eta_s}{4k_B T}$$

The Peclet Number, P_e , equals $\dot{\gamma}\tau_r/2$. The viscosity of the dispersion is

$$\eta = \eta_s + \sum_i^N \sum_j^N \frac{r_{xij}r_{yij}(d\phi_{ij}/dr)}{2\dot{\gamma}r_{ij}} \quad (10)$$

where $r_{\alpha ij}$ is the α 'th cartesian component of the vector between particles i and j , r_{ij} . The relative viscosity $\eta_r = \eta/\eta_s$ plotted against the Deborah number, the product of the structural relaxation time τ_r and the strain rate $\dot{\gamma}$, from the Brownian dynamics simulation reproduces the experimentally observed behavior as described by Heyes.⁶ Shear thinning is observed at shear rates of the order of the inverse of the structural relaxation time for the fluid, as observed experimentally for simple molecular liquids. It is found that Brownian forces hinder the structural reorganization accompanying shear thinning. A phase change of dispersed particles occurs into a lattice with long range translational order in the plane perpendicular to the streaming direction. The structural changes that take place in the saturation regime of the shear thinning curves are very similar to those observed in deterministic dynamics, the molecules forming into strings along the streaming direction, packing into a distorted trigonal lattice.

Implementation for Flexible Protein Dynamics

This code is easily implemented for the Brownian dynamics of flexible macromolecules by adding a harmonic or anharmonic component to the right hand side of Eq. (8). Two or more of the diffusing Brownian particles are linked together by these spring forces to make one large diffusing flexible macromolecule. This is a rudimentary method of looking at flexibility in diffusing proteins, and can be extended to complex geometries by using Brownian particles of different mass and linking them together by springs according to a given geometry. The linked Brownian particles diffuse as an entity and rotational and translational properties may be investigated at equilibrium and in the presence of shear.

This has the added advantage of avoiding the complexities¹⁻⁵ of rotational Brownian motion in asymmetric tops, where solutions are very complicated and insufficiently worked out analytically.

Rotational Brownian Motion of Non-Spherical Particles

So far we have dealt with translational Brownian motion of the center of mass of a diffusing particle. The theory of rotational Brownian motion is based on the Euler Langevin equations

$$A\dot{\omega}_1 - (A - C)\omega_2\omega_3 = -\zeta_1 A\omega_1 + A\dot{W}_1 \quad (11a)$$

$$B\dot{\omega}_2 - (C - A)\omega_1\omega_3 = -\zeta_2 B\omega_2 + B\dot{W}_2 \quad (11b)$$

$$C\dot{\omega}_3 - (B - A)\omega_2\omega_1 = -\zeta_3 C\omega_3 + C\dot{W}_3 \quad (11c)$$

where A, B and C are the principal moments of inertia of the Brownian particle, and the torques $A\dot{W}_1$ and so on are independent Wiener processes. The angular velocity components ω_1 and so on are defined with respect to a frame of reference (1, 2, 3) fixed in the principal moment of inertia axes of the particle. It is implicitly assumed that the components ζ_1 and so on diagonalize in the same frame. This is a general approximation.

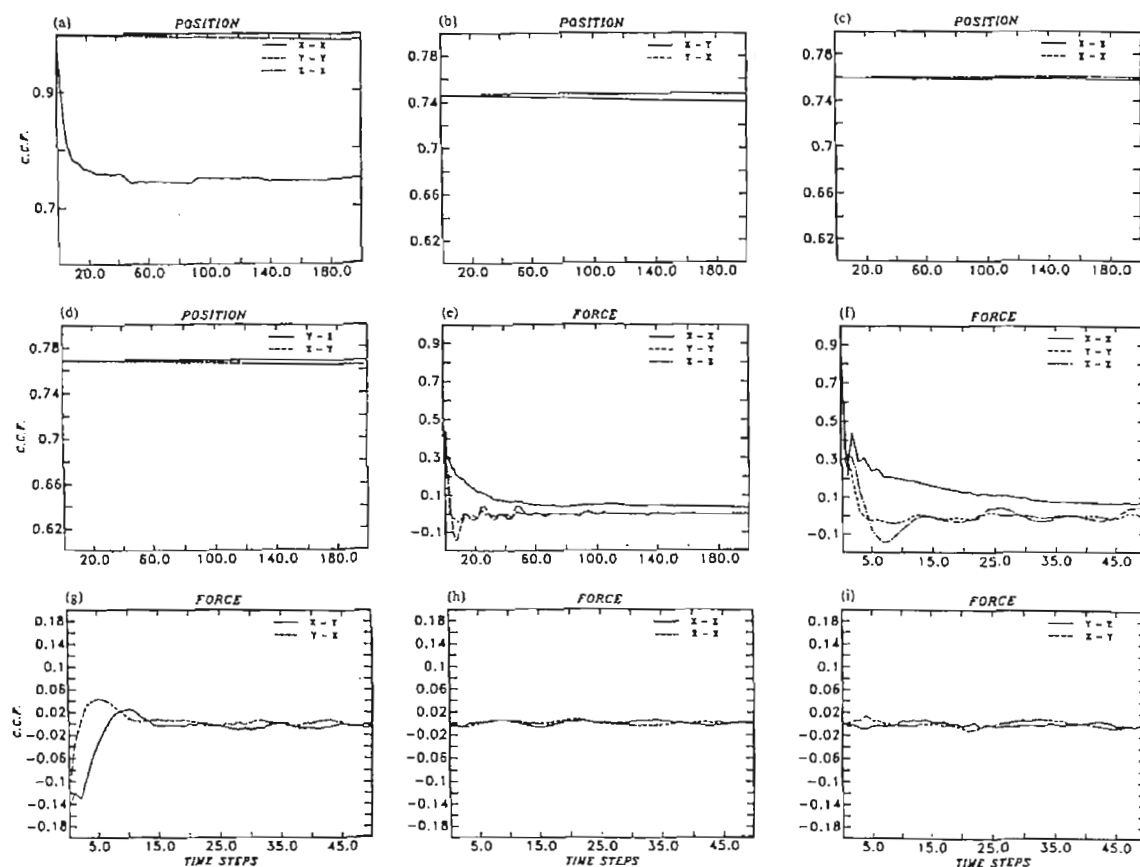


Figure 1. Position correlation function for zero Peclet number (inserts a, b, c, d) and force correlation function for a Peclet of 16.98, diagonal and off-diagonal elements (inserts e, f, g, h, i).

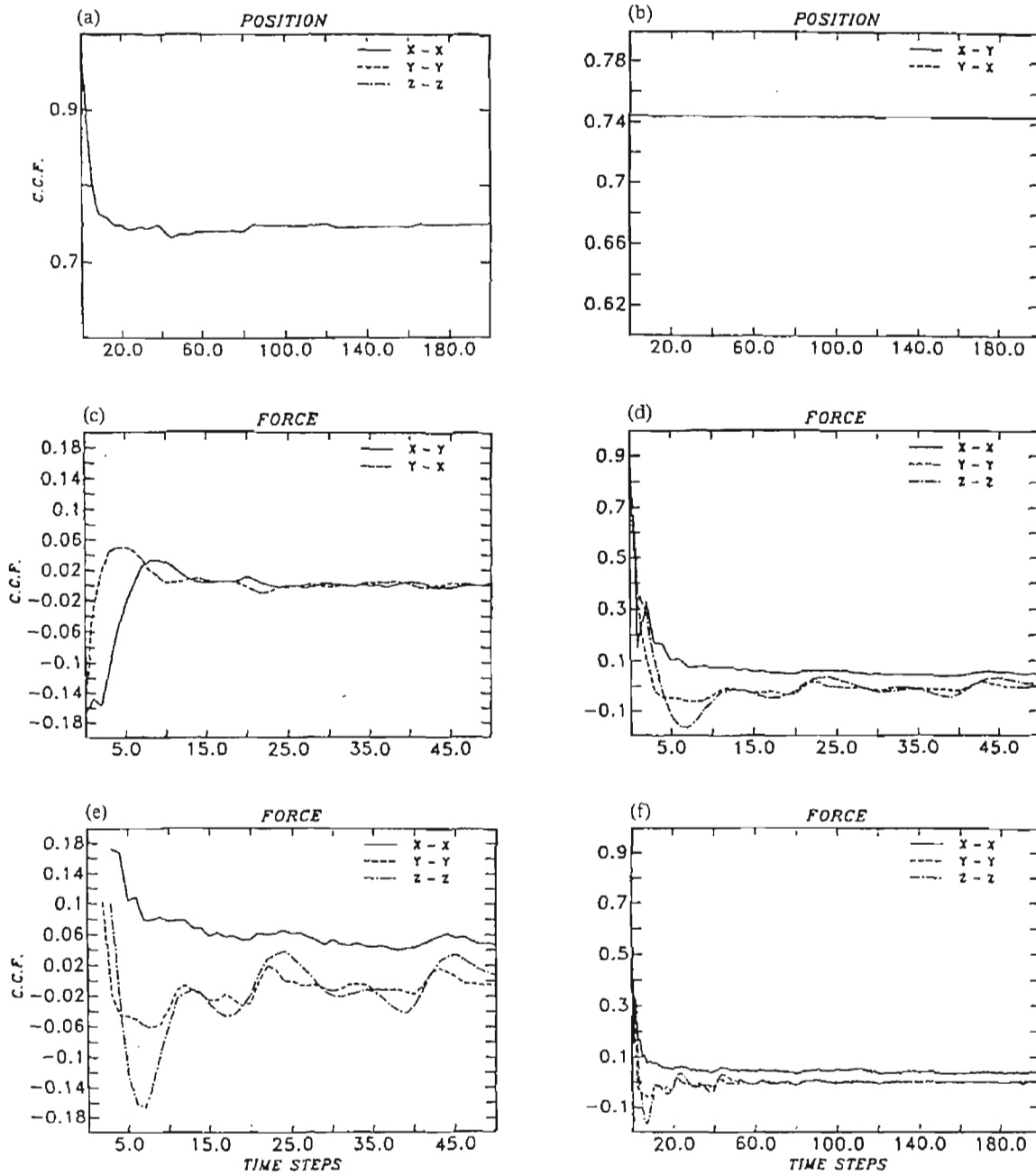


Figure 2. Correlation function for a Peclet number of 16.89: position, (a, b), and force (c, d, e, f).

The solution of Eqs. (11a), (11b) and (11c) requires the Jacobian elliptic functions because they are adaptations of Euler's equations (see chapter 2). There is no exact analytical solution in general and the approximate solutions are complicated. They are expressed in terms of three phenomenological variables, the three friction coefficients. Nonetheless, this is the simplest type Langevin equation that can be written for a rotating Brownian particle that is an inertial asymmetric top. The complexity of the problem is reduced, but not eliminated, for the spherical top, where $A = B = C$.

It is immediately clear therefore, that in the treatment of complex flexible Brownian particles, it is far more straightforward to proceed with Eq. (8) with an extra harmonic term on the right hand side of the form $S_0 \mathbf{r}$ where S_0 is the Hooke's Law spring constant (see Appendix 2A, Eq. (A4)). This can be made anharmonic if necessary, and a term such as this forms flexible bonds between the diffusing Brownian entities, which may be regarded as parts of the overall protein structure or even individual atoms. The diffusion of the complete protein segment may then be mimicked by modelling the bonds with harmonic oscillator terms of this nature, superimposed on the individual atom to atom repulsive and attractive terms derived ab initio. Ultimately, the anharmonic vibrational bonds between atoms could also be derived ab initio.

Description of Results

For no shear applied (zero Peclet number) the results are described in Fig. 1 for the correlation tensor of position and force. Figure 1 (a,b,c,d) shows that there is a constant correlation between the components of the position correlation tensor, introduced by the non-equilibrium molecular dynamics simulation algorithm described already. The force auto correlation functions, Fig. 1 (e,f,g,h,i), are also anisotropic and there is an initial correlation [Fig. 1(g)] between the X and Y components. There is no such correlation, however, between the other components of the force, in marked contrast to the results for the positional correlation tensor.

Results for a Finite Peclet Number

The basic Brownian simulation program contains a facility for applying shear as measured by a finite Peclet number, defined already. Time correlation tensors are given in this section for Peclet numbers 0.00 and 16.89. These results characterize Brownian dynamics under applied shear. The runs were repeated with a Peclet Number of 16.89 and the results are illustrated in Fig. 2. There is a discernible sharpening of the cross correlation function features due to an imposed shear.

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