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Construction of Langevin Forces in the Simulation of Hydrodynamic Interaction[†]

Marshall Fixman

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

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ABSTRACT: In the simulation of Brownian motion with hydrodynamic interaction, the construction of Langevin forces with the proper covariance is by far the slowest operation for large systems if standard, numerically exact methods are used. An approximate method with controlled accuracy is presented that considerably reduces the computation required for the construction of such forces.

1. Introduction

The problem being considered here is the calculation of random numbers y_i that are proportional to the Langevin forces.[1] The y_i have a covariance matrix

$$\langle y_i y_j \rangle = H_{ij} \tag{1.1}$$

where H_{ij} is an element of the (positive-definite) hydrodynamic interaction (HI) or diffusion matrix H. The H_{ij} are function of configuration. There are (at least) two ways of satisfying (1.1). Each starts with a factorization of H

$$H = A^{\mathrm{T}}A \tag{1.2}$$

The properties of A will be discussed below. A^{T} is the transpose of A. If A^{T} is available, the construction

$$y = A^{\mathrm{T}}x \tag{1.3}$$

where

$$\langle x_i x_j \rangle = \delta_{ij} \tag{1.4}$$

is readily verified to satisfy (1.1). y and x are the column matrices composed of y_i and x_i, respectively.

In libraries of mathematical and statistical algorithms, a Choleski factorization[3] of H is commonly used. In this method A is an upper triangular matrix, and of course A^{T} is lower triangular. If H is an $M \times M$ matrix, construction of A takes $M^3/3$ arithmetic operations.[3] In principle A has to be constructed anew for each time step, and the explicit calculation of A is a serious problem for large systems.

It may be that HI is worth including only for large-scale motions of the system, since the physical models and calculations will not be very realistic for local (small-scale) motion. And fortunately the effect of HI on local motion is usually a small correction to the motion induced by potential forces and unperturbed frictional forces due to the solvent. An approximation might then be used in which M is cut down to ca. $3x$ (10 centers of friction) and the standard method followed. Such approximations are not obviously valid, and considerably larger values of M may be necessary, for example, in a theoretical study of the coupling between global and local motion, and the standard method will be very slow. The approximate method to be described allows a much faster calculation and also gives a controlled and uniform accuracy for all motions of the chain. However, it is also possible to impose a nonuniform accuracy that favors large-scale motions, if this is thought to be sufficient. This approach, as opposed to a reduction in the number of forces that perturb solvent motion, requires no tampering with the basic algorithm.

The second approach is to construct S, the square root of H, and take $A = A^{\mathrm{T}} = S$. This approach is not obviously better, because there is no available construction of the square root that is faster than the Choleski factorization of H. Iterative methods have to be used for the calculation of S, and each iteration takes about M^3 steps. Nevertheless, the square root calculation has a major potential advantage for large M. The advantage is that approximation methods can be applied directly to y rather than

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S, and the construction of y to a given order of approximation takes only M^2 steps. It turns out in the polymer application that a sequence of approximations can be devised that converges rather rapidly and at a rate that worsens very slowly with increasing M.

Alternative approaches to the calculation of S are considered in section 2, and the calculation of y is described in section 3. Several remaining practical observations about the calculation are presented in the concluding discussion, section 4.

2. Matrix Square Root

Let H be a positive-definite $M \times M$ matrix with eigenvalues λ_k and eigenvectors $|k\rangle$, $k = 1, ..., M$. The spectral representation is

$$H = \sum_1^M \lambda_k |k\rangle\langle k| \tag{2.1}$$

The λ_k are all finite and positive. Therefore $S = H^{1/2}$ exists and may be represented by

$$S = \sum_1^M \lambda_k^{1/2} |k\rangle\langle k| \tag{2.2}$$

Suppose that the square root of any eigenvalue λ_k is approximated by $s(\lambda_k)$ or by a sequence s_i of such functions. Examples are Newton iteration

$$s_{i+1} = \tfrac{1}{2}(s_i + \lambda/s_i) \tag{2.3}$$

and polynomial approximation

$$s_i = \sum_{l=0}^{N_i} a_l^i T_l(\lambda) \tag{2.4}$$

where $T_l(\lambda)$ is a polynomial in λ, and a_l^i is a numerical coefficient. Iteration 2.3 always converges, and the sum 2.4 may be presumed to converge for some specific range of λ's.

Suppose now that the same functional approximation $s(\lambda)$ or sequence of approximations $s_i(\lambda)$ is used for every λ_k; e.g., (2.3) is started with the same estimate s_0 for every λ_k, or (2.4) has the same a_l^i and polynomial coefficients for every λ_k. Then

$$S_i \equiv \sum_1^M s_i(\lambda_k)|k\rangle\langle k| \tag{2.5}$$

$$= s_i(H) \tag{2.6}$$

defines a sequence of approximations to S that will converge if s_i converges for all λ_k.

A. Newton Iteration. The sequence (2.3) converges to the square root for any initial estimate s_0. Therefore the sequence

$$S_{i+1} = \tfrac{1}{2}(S_i + S_i^{-1}H) \tag{2.7}$$

initiated with $S_0 = s_0 1$, where 1 is the unit matrix, converges. All S_i are ratios of polynomials in H, as may be verified by induction (see The Appendix). Therefore S_i commutes with H as it should.

The rate of convergence of (2.3), for $s_0 = 1$, is the same for λ and $1/\lambda$. The value of i required for a relative accuracy of 0.0001, vs. λ, is found by observation to be $(\lambda,i) = (2,3), (10,4), (100,5)$, so the iteration converges rather well. The iteration 2.7 will converge most rapidly if H is scaled so that the minimum and maximum eigenvalues, λ_0 and λ_M respectively, obey $\lambda_0 = 1/\lambda_M$. This raises the question of estimating the numerical range of the eigenvalues of H, a matter discussed below. The problem is not an important one in the application of (2.7) because of the rapid convergence.

Table I
Minimum and Maximum Eigenvalues of the Averaged Diffusion Matrix H and Ratio of Eigenvalues vs. Bead Diameter and Number of Beads

	28 beads			56 beads		
diameter	min	max	ratio	min	max	ratio
0.25	0.795	2.94	3.7	0.795	3.95	5.0
0.5	0.613	4.82	7.9	0.613	6.84	11
1.0	0.360	8.23	23	0.359	12.23	34

The evaluation of $S_i^{-1}H$ is the slow step in one iteration of (2.7) and takes about M^3 arithmetic operations. What is actually needed in the polymer simulation problem is S_ix, where x is an arbitrary column matrix, and one would like to turn the iterative process into a sequence of matrix operations on x, each of which requires only $O(M^2)$ steps. One possibility is to evaluate the polynomials $N_i(H)$ and $D_i(H)$ (i.e., evaluate the coefficients in the polynomials) that occur in

$$S_i = N_i(H)/D_i(H) \tag{2.8}$$

This construction is considered in the Appendix. Completion of the solution comes down to a solution of some variant of

$$D_iy = N_ix \tag{2.9}$$

The right-hand side of eq 2.9 is easy to evaluate because N_i is a polynomial in H, and the successive multiplications by H each take M^2 steps. However, the solution for y can only be obtained in $O(M^2)$ steps by another iterative process, and it is not clear that this would have any advantages over the direct polynomial approximation considered below.

B. Polynomial Approximation. Equation 2.4 generates the following approximations to the square root of H

$$S_i = \sum_{l=0}^{N_i} a_l^i T_l(H) \tag{2.10}$$

The $T_l(H)$ are polynomials in the matrix H and have eigenvalues $T_l(\lambda_k)$. It seems convenient to choose the T_l as shifted Chebyshev polynomials[3] C_l

$$T_l(H) = C_l(G) \tag{2.11}$$

$$G \equiv h_a H + h_b \tag{2.12}$$

where h_a and h_b are chosen so that the eigenvalues G_k of G range over $-1 < G_k < 1$. Then the eigenvalues of C_l also have magnitude less than unity. The maximum possible error that results from truncating the series (2.4) or (2.10) can be estimated[3] by summing the magnitudes of the discarded coefficients a_l^i over i. The coefficients of the Chebyshev polynomials that occur in the expansion of the square root function are readily obtained by standard methods.[3]

The accuracy of the polynomial approximations depends on the range of the function to be fit and hence on the ratio λ_M/λ_0. This ratio can be calculated for preaveraged HI by explicit construction of the maximum and minimum eigenvalues. Results obtained in this way are shown in Table I, where the unit of length is the root mean square bond distance for the Gaussian chain and Rotne–Prager[4] HI is used. Much more rapid methods can be used to obtain approximate estimates of λ_M and λ_0, which suffice for the purpose. These methods are discussed in section 4.

Estimates of the maximum orders of Chebyshev polynomials that have to be retained in the square root approximation in order to obtain a relative error less than

Table II
Maximum Order of Chebyshev Polynomials Required for the Indicated Maximum Error vs. the Ratio λ_M/λ_0

ratio	0.01 error	0.001 error
10	4	6–7
20	5–6	8–9
30	6–7	10–11
40	7	11–12
50	7–8	13

0.01 and 0.001 are tabulated in Table II vs. the ratio λ_M/λ_0. The relative errors shown in Table II are defined as the ratio norm(S_i–S)/norm(S). The norm of a matrix is here defined to be the sum of the absolute values of the elements.

The ratio λ_M/λ_0 increases asymptotically as $M^{0.5}$ for a chain polymer with M beads, and the maximum polynomial order required for a given accuracy increases roughly as (ratio)$^{0.5}$. Consequently the total number of arithmetic operations required by the polynomial method for the construction of S goes as $M^{3.25}$. The polynomial method is therefore inferior to Newton iteration in the construction of S, and the construction of S is in turn inferior to triangular factorization. However, this judgement will be reversed for the problem of constructing the y_i. This problem is considered in the next section.

3. Vector Polynomial Approximation

We use eq 2.10 for the matrix approximation and suppose that the coefficients are evaluated from an infinite series expansion of the square root function in Chebyshev polynomials. (Mathematical library routines that pass a finite sum of such polynomials through a discrete set of points give a_l that converge very rapidly to the values for the infinite expansion.) Equation 2.10 for the expansion of S_i in unshifted polynomials is written in terms of the shifted polynomials C_l as

$$S_L = \sum_0^L a_l C_l(G) \tag{3.1}$$

Appropriate values of L for a given accuracy were discussed in section 2. Now

$$y_l \equiv S_L x = \sum_0^L a_l x_l \tag{3.2}$$

where

$$x_l \equiv C_l(G)x \tag{3.3}$$

The recursion relation for Chebyshev polynomials $C_l(G)$ on the interval $-1 < G < 1$ is[3]

$$C_{l+1} = 2GC_l - C_{l-1}; \qquad C_0 = 1,\ C_1 = G \tag{3.4}$$

The x_l may be calculated from eq 3.3 and 3.4 as

$$x_{l+1} = 2Gx_l - x_{l-1} \tag{3.5}$$

or

$$x_{l+1} = 2h_a H x_l + 2h_b x_l - x_{l-1} \tag{3.6}$$

h_a and h_b are the constants introduced in eq 2.12.

Practical Observations. Equation 2.12 and the requirement that the eigenvalues of G lie in $-1 < G < 1$ give the following equations for the determination of h_a and h_b:

$$h_a\lambda_M + h_b = 1 \tag{3.7}$$

$$h_a\lambda_0 + h_b = -1 \tag{3.8}$$

λ_M and λ_0 in these equations are supported to be the maximum and minimum eigenvalues of H, respectively, for the given configuration. In practice we have taken them to be 10–20% larger (λ_M) or smaller (λ_0) than the eigenvalues of $\langle H\rangle$, as this accommodated the observed range of fluctuation.

4. Discussion

In the construction of the y_i, each matrix multiplicaion takes O(M^2) steps and the overall computation time goes as $M^{2.25}$, presuming that the same accuracy is wanted for every M. The accuracy seems appreciably better than obtained with the previous method[5] for the same amount of computational effort. The errors are smaller by a factor of 5–10, and the approximation is not subject to the occasional blowups that occurred for large bead diameters (diameter = 1). In practice the inclusion of hydrodynamic interaction in chain polymer simulations with full nonbonded interactions approximately doubles the computation time for moderate chain lengths, in the range 10–50 beads. This is a typical figure for the implicit algorithm.[2] Explicit Brownian algorithms, which use a very small time step but do not incur the overhead of Jacobian calculations, would suffer a larger penalty by the inclusion of hydrodynamic interaction.

If H could be approximated by a positive-definite band matrix, representing HI between beads close together on the backbone, a Choleski factorization into A^TA would give an A of the same bandwidth, and this A can be computed in O(M) operations.[3] However, this restricted interaction is not likely to be physically adequate, and simply chopping up H into a band matrix and a remainder is prone to generating pieces that are not positive-definite.

If an approximation favoring the accuracy of either global or local motions is wanted, this can be achieved be overestimating λ_0 or underestimating λ_M, respectively. Estimates of λ_M and λ_0 with errors in the vicinity of 10%, which is sufficient accuracy for the polynomial construction, can be obtained rather quickly from H rather than $\langle H\rangle$ by a process that does not require a diagonalization or averaging of H. The fastest diffusion is obtained for a cooperative translation of the chain, and a good estimate of λ_M is obtained from the matrix sum $\langle M|H|M\rangle$, where $|M\rangle$ is a (normalized) approximate eigenvector with constant elements. Likewise $\langle 0|H|0\rangle$, with $|0\rangle$ an approximate eigenvector with elements that alternative in sign from one bead to the next, is a good estimate of λ_0.

Appendix on Newton Iteration

We amplify the remark that successive iterations for the square root of H are rational fractions that commute with H. Equations 2.7 and 2.8 are

$$S_{i+1} = \tfrac{1}{2}(S_i + S_i^{-1}H) \tag{A1}$$

$$S_i = N_i/D_i \tag{A2}$$

Then

$$\frac{N_{i+1}}{D_{i+1}} = \frac{1}{2}\left(\frac{N_i}{D_i} + H\frac{D_i}{N_i}\right) = \frac{\tfrac{1}{2}(N_i^2 + HD_i^2)}{N_iD_i} \tag{A3}$$

Take

$$N_{i+1} = \tfrac{1}{2}(N_i^2 + HD_i^2) \tag{A4}$$

and

$$D_{i+1} = N_iD_i \tag{A5}$$

If the estimates are started with $N_0 = D_0 = 1$ (unit matrix), then

$$N_1 = \tfrac{1}{2}(1 + H)$$

$$D_1 = 1 \tag{A6}$$

$$N_2 = \tfrac{1}{2}[\tfrac{1}{4}(1 + H)^2 + H]$$

$$D_2 = \tfrac{1}{2}(1 + H) \tag{A7}$$

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and so forth.

References and Notes

(1) The Langevin forces strictly defined have a covariance matrix proportional to a friction matrix H^{-1}, but the y_i are the random numbers required in a polymer simulation. See ref 2.

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Mechanical Properties of Thermoreversible Atactic Polystyrene Gels

B. Koltisko,[†] A. Keller,[‡] M. Litt,[†] E. Baer,[†] and A. Hiltner*[†]

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106, and Department of Physics, Bristol University, Bristol, England BS8 1TL.
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ABSTRACT: Gels of atactic polystyrene (aPS) in carbon disulfide were formed in the temperature range from 0 to −100 °C. The shear modulus was measured as a function of temperature, concentration, and molecular weight, and a master curve of the data was constructed. The modulus vs. temperature behavior of the aPS gels resembles that of un-cross-linked polymers in the rubbery plateau regime. It is proposed that physical associations act as cross-links and impart elastic properties to the gel network. A molecular weight between associations of 2700 was obtained by using rubber elasticity theory and a simple chain end correction factor for aPS gels of 200 g/L concentration in the plateau region. This defines the minimum molecular weight required for gel formation at this concentration. A more refined statistical approach that accounts for the polymer not included in the network gave a value of 5000. The molecular weight of the chain segment between associations increased as the temperature approached T_{gel} in a manner that was independent of molecular weight.

Introduction

Thermoreversible gels of atactic polystyrene (aPS) can be formed with a variety of solvents.[1] In contrast to thermoreversible gelation of crystallizable polymers, where the crystals themselves act as junctions leading to a network, the subject of a recent review by Keller,[2] none of the current theories concerned with the nature of physical associations involved in network foundation can account for the observed gelation of aPS. Unlike gels of isotactic polystyrene (iPS) and other crystallizable polymers, aPS forms equilibrium gels with equivalent and time-independent gel formation and gel "melting" temperatures.[1,3] The reported heats of formation of 6–26 kJ/mol for aPS gels are significantly lower than 113 kJ/mol observed for iPS gels.[1] Chain entanglements are not required for gel formation since gels can be formed from aPS of molecular weight well below the entanglement molecular weight of polystyrene,[1] although entanglements do appear to increase the stability of aPS gels.[4] Chain overlap is required for gelation, as inferred from the critical gelation concentration for each molecular weight.[1] The shear moduli, approximately 1 kPa, of aPS gels close to T_{gel} are comparable to the moduli of gels formed from crystallizable polymers.[5]

Several authors have discussed the gelation mechanism of aPS solutions. Wellinghoff and co-workers[3] suggested that gels are formed through a microphase segregation process in which finely dispersed polymer domains act as network junction points. "Melting" of the network occurs when the temperature exceeds the T_g of the domains. Tan and co-workers[1] suggested that T_{gel} is not related to T_g since T_{gel} values are in a range 100 °C above the predicted T_g. Two possible gelation mechanisms, chain stiffening and physical associations between chain segments, were hypothesized in this work. Boyer and co-workers[4] related T_{gel} to the fusion flow temperature observed in polymer melts, a $T > T_g$ phenomenon caused by melting of physical associations. These studies give a detailed characterization of the sol–gel transition and have raised interesting questions as to the mechanism by which a stable network of a noncrystallizable polymer can form in solution. In this study of the gel state, the effects of temperature, concentration, and molecular weight on the gel modulus are assessed. The results are compared with the predictions of conventional elastic behavior.

Experimental Section

Narrow disperse aPS ($\overline{M_w}/\overline{M_n} < 1.2$) samples ranging in molecular weight from 2000 to 900 000 were obtained from Pressure Chemical Co. Carbon disulfide (CS_2) was reagent grade and distilled over phosphorous pentoxide prior to use. The freezing point of CS_2 was measured at −110 °C. The concentration of the aPS solutions is given in grams of polymer per liter of solution.

Simple shear tests were performed on gels as a function of temperature, molecular weight, and concentration. Solutions were introduced into a coaxial cylinder instrument shown schematically in Figure 1, and gels were formed in situ by lowering the temperature of the apparatus. Stress–strain measurements were conducted by attaching the inner cylinder to the crosshead of a standard Instron tensile testing device. The outer glass cylinder, a glass vial, remained stationary, while the inner cylinder, a glass rod, was displaced in the vertical direction. A strain rate of 50% per minute was used.

Single-point measurements of the shear modulus were performed by attaching the center cylinder to a modified analytical balance. Loads (0.001–60 g) were applied and deflections approximately of 0.05 mm were measured with a precision of 0.003 mm. Deflections were measured at an elapsed time of 10 s. For this coaxial geometry, the shear modulus, G, is given by

$$G = P \ln (r''/r')/2\pi L x \qquad (1)$$

where P is the load, x is the deflection, L is the depth of the rod in the gel, and r' and r'' are the inner and outer cylinder radii, respectively.[6] The value of $\ln r''/r'$ was 1.64, and L was 17 mm. The temperature of the gel was varied from +25 to −100 °C (±1

[†] Case Western Reserve University.

[‡] Bristol University.

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