Inclusion of Hydrodynamic Interaction in Polymer Dynamical Simulations†

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ABSTRACT: Methods are developed for the inclusion of hydrodynamic interaction in the simulation of chain polymer dynamics. These methods are applied to the calculation of the sedimentation constant and intrinsic viscosity of Gaussian chains. Due to the limited number of trajectories, results for the intrinsic viscosity are indefinite but are consistent with analytical estimates that fluctuating hydrodynamic interaction (HI) causes a decrease in the intrinsic viscosity, relative to results with preaveraged HI, in the range of 5–10%. The decrease in sedimentation or diffusion constant due to fluctuating HI is found to be about 1%.

I. Introduction

The purposes of this work are first to devise a practical scheme for the inclusion of hydrodynamic interaction (HI) in the computer simulation of polymer motion and second to apply that scheme to the calculation of the diffusion constant and intrinsic viscosity of Gaussian chains. These purposes have not been entirely achieved. Further improvements of the algorithm are desirable, and additional simulations are essential, to reduce statistical uncertainty. The method nevertheless seems sufficiently promising to offer in this preliminary form.

The steady-state transport coefficients of long chains reflect only long-range HI. An accurate treatment of short-range HI is required in the quantitative study of fast local motions or in the study of any motion of short chains. We have not attempted this. (One might well wish to attempt such calculations; a literal application of the Navier–Stokes equation with slip boundary conditions has shown good predictive powers.[1] However, the HI of even two spheres at close range is a nontrivial problem.) Here we stick to the traditional model of point centers of friction. The friction constant is presumed proportional to the solvent viscosity, but the proportionality constant is a parameter. In the long-chain limit the friction constant drops out of the steady-state transport coefficients.

This work was inspired mainly by the appealing algorithms developed by Zimm for the sedimentation constant and intrinsic viscosity calculation.[2] These algorithms were based on the assumption that a polymer chain would move as a rigid body in certain uniaxial flows and gave the transport coefficients from a Monte Carlo sampling over the equilibrium phase space. This has to be contrasted with the slower dynamical simulations developed here. However, as we have reported elsewhere,[3] an analytical exploration of the rigid-body assumption leads to expressions for the transport properties that violate appropriate symmetry conditions, and the assumption has to be regarded as approximate. Here we attempt to gauge the error through direct dynamical simulation.

To the best of our knowledge a simulation of polymer chain motion that includes HI has not been achieved.[4] There does not seem to be much question about which basic Langevin or stochastic equations should be used. For systems with[5] or without[6] constraints the stochastic equations equivalent to the usual diffusion equation for chain motion have been recorded. We summarize the unconstrained equations in section II. The major problem is a purely technical one: the square root of the hydrodynamic interaction matrix occurs in the stochastic difference equations; it depends on configuration and must be evaluated anew at every step along a trajectory. An iterative process that partly finesses and partly solves this problem to arbitrary accuracy is developed in section II. The computation time for a single step is proportional to the square of the chain length.

The focus of this work is on the validity of preaveraging the HI matrix. Very few studies of chain polymer dynamics have attempted to avoid this approximation. Indeed, except for papers that make implicit or explicit assumptions about molecular symmetry,[2] we know of only two related calculations.[7,8] These dealt with the intrinsic viscosity and used perturbation theory together with a truncated representation of the diffusion operator. As is discussed in more detail in section V, our simulations are consistent with the intrinsic viscosity calculations but are far from sufficient to give a quantitative confirmation. We can give strong support to perturbative work on fluctuating HI, especially that concerned with long-range HI. Our results also indicate that short-range HI could be treated perturbatively; trajectories computed with and without fluctuating HI lie close together. But this may be an artifact arising from our smoothing of the Oseen interaction at short distances to avoid singularities. Further study of the effect of HI on fast local processes is required.

Our approach has been to study the trajectories for the same sequence of random solvent forces with and without preaveraged HI. In this aspect we mimic Zimm's strategy[2] for minimizing the effects of finite sample size. The results achieved for the diffusion constant are useful largely because the effects of fluctuating HI can be confined to a small part of the diffusion constant. This small part is obtained from a time correlation function developed in section III. On the other hand, all of the intrinsic viscosity has to be obtained from a correlation function, and the results are less precise. (A first-order perturbation treatment of fluctuating HI in intrinsic viscosity theory would have allowed a fairly easy evaluation from the simulations. However, we did not think of this in time. A purely analytical evaluation of the first-order corrections would be extremely tedious if complete.)

Aside from the development of methods which may be useful in other contexts, our major result is that the effect of HI fluctuations on the sedimentation constant of a Gaussian chain does not exceed a few percent. (Indeed, the evidence points to about a 1% correction.) This means that the simple and explicit Kirkwood formula[9] for the sedimentation constant in terms of the average HI matrix is not in error by more than about 3% (the explicit formula fails by 1.67% even with preaveraged HI).

II. Equations of Motion

A. Summary. The appropriate Langevin equations for an unconstrained chain polymer have been given by

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Zwanzig[6] and were reviewed by Fixman.[5] The equations are summarized here with some slight changes from earlier notation.[5] Conventions for upper/lower subscripts are dropped because Cartesian coordinates suffice for the unconstrained system. Superior bars will here designate equilibrium averages rather than Cartesian coordinates. The chain has M bonds and $N = M + 1$ beads which obey the following equations in the coordinate phase space. The sum convention is used.

$$dx_i/dt = V_i^0 + H_{ij}(E_j + W_j + L_j) \tag{2.1}$$

or

$$d\mathbf{R}_i/dt = \mathbf{V}_i^0 + \boldsymbol{H}_{ij}\cdot(\mathbf{E}_j + \mathbf{W}_j + \mathbf{L}_j) \tag{2.2}$$

Equations for tensors or their coordinates will be used as convenient, usually with only boldface type to signify the former. In eq 2 .1 the indices range over $i, j = 0, 1, 2, ..., 3M$ and in eq 2.2 over $i, j = 0, 1, 2, ..., M$. E_j is an external potential force, W_j is an intramolecular potential force, and L_j is the random force. H_{ij} is the hydrodynamic interaction tensor, and V_i^0 is the unperturbed solvent velocity field evaluated at the position of molecule i. The following units are used: length, b; energy, k_BT; time, $\beta b^2/k_BT$. b is a reference bond length (a root mean square for the Gaussian chain) and β is a reference friction constant for the drag on one bead.

For uniform chains H_{ij} is given by

$$H_{ij} = \boldsymbol{H}_{ij}(\mathbf{R}_{ij}) \tag{2.3}$$

where

$$\boldsymbol{H}_{ij}(\mathbf{R}) \equiv \delta_{ij}\boldsymbol{1} + (\beta/8\pi\eta_0 b)(1 - \delta_{ij})(\boldsymbol{1} + \mathbf{ee})f(R) \tag{2.4}$$

where $\boldsymbol{1}$ is the 3×3 unit matrix, η_0 is the solvent viscosity, $\mathbf{e} = \mathbf{R}/R$, and $f(R) = 1/R$ in the Stokes–Oseen approximation. In this work the function $f(R)$ will be modified to remove the singularity at $R = 0$.

The displacement of a bead position during a finite time increment is given to first order in s by

$$\Delta x_i = [V_i^0 + H_{ij}(E_j + W_j)]s + (\partial H_{ij}/\partial x_j)s + H_{ij}M_j \tag{2.5}$$

where

$$M_j \equiv \int_0^s L_j(t + s_1)\, ds_1 \tag{2.6}$$

and s is the time increment. The quantities V_i^0, H_{ij}, E_j, and W_j, are all functions of coordinates and refer to values at the beginning of the time interval.

Equation 2.5 gives the correct first and second moments, $\langle \Delta x_i \rangle$ and $\langle \Delta x_i \Delta x_j \rangle$, respectively, to first order in s, i.e., the moments that result in a conventional diffusion equation, if the Langevin forces are assigned the following statistical properties:

$$\langle M_i \rangle = 0$$
$$\langle M_i M_j \rangle = 2(H^{-1})_{ij}s \tag{2.7}$$

The angle brackets designate an average over the Langevin forces, which constitute the sole random process in the equations of motion. The symbol $\langle\ \rangle_e$ will represent the same average for a system in equilibrium, i.e., with the external forces E_j and the velocity field V^0 suppressed.

In practice the random forces M_i must be generated from independent pseudorandom numbers supplied by the computer. We have used random numbers

$$\langle Q_i \rangle = 0$$
$$\langle Q_i Q_j \rangle = \delta_{ij}/3 \tag{2.8}$$

These were uniformly distributed in an interval. The random forces have a Gaussian distribution, but it was necesssary to choose such a small time interval s that only the first and second moments affect the distribution of trajectories. The normalization in (2.8) was chosen for convenience. It follows that the forces M_i may be constructed from

$$M_i = (6s)^{1/2}(S^{-1})_{ij}Q_j \tag{2.9}$$

where the symmetric matrix S is given by

$$S \equiv H^{1/2} \tag{2.10}$$

Consequently eq 2.5 may be written in the form

$$\Delta x_i = [V_i^0 + H_{ij}(E_j + W_j)]s + (\partial H_{ij}/\partial x_j)s + (6s)^{1/2}Y_i$$
$$Y_i \equiv S_{ij}Q_j \tag{2.11}$$

We retain the nonequilibrium perturbations E_j and V_i^0 only for some work in the next section. The terms were suppressed during simulations.

B. Square Root of HI Matrix. Construction of the square root of H is a major technical difficulty. A spectral decomposition is the textbook route to irrational functions of matrices, but this would require evaluation of the eigenvalues and eigenvectors of H at the beginning of each time interval. This seems impractical except for the shortest chains. For this reason we adapted an interative procedure.[10] The $n + 1$ estimate of S is determined from the nth estimate according to

$$S_{n+1} = S_n + \lambda_n(H - S_n^2) \tag{2.12}$$

where λ_n is a sequence of constants (after some experimentation, we chose $\lambda_1 = 0.5$, $\lambda_2 = 0.4$, and $\lambda_n = 0.35$ for $n > 2$). This iteration was applied first to the square root of $\bar{H}\boldsymbol{1} = \langle \boldsymbol{H} \rangle_e$, to obtain an initial approximation to S. We started with $S_1 = 0$ and obtained convergence to the imposed accuracy in about six to eight iterations. Convergence was judged from the changes in S induced by one iteration. If the norm of the difference matrix was less than 0.001 times the norm of S, the iteration was ended. For the norm we used the root-mean-square value of all elements of S.

The procedure just outlined requires $O(N^3)$ arithmetic operations. This is not especially painful for the square root of $\bar{H}$, since $\bar{H}$ does not fluctuate. However, calculation of the square root of the fluctuating matrix H would require, in comparison, $O(27N^3)$ operations at the start of each time increment in the simulation, and this still seemed impossible. Fortunately it turned out to be unnecessary. Equation 2.11 requires only a single vector formed from S, namely, $Y_i = S_{ij}Q_j$, and this can be made in $O(9N^2)$ operations by the following somewhat abstract procedure.

Let Q be the vector of random numbers described by eq 2.8 and

$$Y_n = S_nQ \tag{2.13}$$

the nth estimate of the force vector required in eq 2.11. The first estimate is defined by

$$Y_1 = \langle H \rangle_e^{1/2}Q \tag{2.14}$$

The square root of $\langle H \rangle_e$ is computed once, at the beginning of the run, by the method previously described. Equation 2.12 gives

$$Y_{n+1} = Y_n + \lambda_n(HQ - S_nY_n) \tag{2.15}$$

This equation does not in itself provide a satisfactory basis for iteration because S_n occurs on the right-hand side and is not explicitly known. We can, however, avoid an explicit

use of S_n through the introduction of an operator O_n on $3N$-dimensional vectors such as Y_n. Indeed, O_n will turn out to be equivalent to matrix multiplication by S_n, but O_n is generated as a sequence of nested subroutines rather than as an array of numbers S_n. The latter is never constructed.

With f and g arbitrary $3N$-dimensional vectors, let

$$g = O_{n+1}f \equiv O_nf + \lambda_n[Hf - O_n(O_nf)] \tag{2.16}$$

In order to perform its function, the operator or subroutine O_{n+1} makes two calls on subroutine O_n, first with the known f as input to O_n and then with the known vector O_nf as input. O_n likewise makes two calls on O_{n-1}. These nested or recursive operations terminate at $n = 1$, with the definition

$$O_1f \equiv S_1f \equiv \langle H\rangle_e^{1/2}f \tag{2.17}$$

It is apparent from eq 2.16 that

$$O_2f \equiv S_2f$$

and by induction from eq 2.16 that

$$O_nf \equiv S_nf \tag{2.18}$$

The following use was made of these nested subroutines. Given Y_n, eq 2.15 and 2.18 give Y_{n+1}:

$$Y_{n+1} = Y_n + \lambda_n(HQ - O_nY_n) \tag{2.19}$$

Thus there is only one call to O_n in the iteration from Y_n to Y_{n+1}. However, O_n makes two calls to O_{n-1}, and so on. So it is obvious that the number of arithmetic operations required to reach Y_n from Y_1 is growing exponentially with n. For the modified iteration scheme the number of operations is proportional to $9N^22^n$, and for the original scheme where the square root of H is computed, to $27N^3n$. Either scheme would be much faster than a spectral decomposition of H, unless a large n is required.

Clearly the modified algorithm is highly advantageous only if small values of n are used. As it turned out, the imposed accuracy was usually achieved with $n = 2$ or 3; larger values occasionally occurred. Accuracy was judged, as for the square root of the average H, by the root mean square of elements of $Y_{n+1} - Y_n$ divided by the root mean square of Y_n. This ratio was required to be less than 0.1 or 0.05; a few trials indicated corresponding differences only in the fourth "significant figure" of correlation functions. This insensitivity suggests a lack of correlation between the errors of Y_n and those properties of the trajectories that were actually computed.

C. Modified Hydrodynamic Interaction. In the equation of motion (2.11) we require $\partial H_{ij}/\partial x_j$, or $\nabla_j\cdot\boldsymbol{H}_{ij}$, since H is symmetric. We need consider only $i \neq j$:

$$\nabla_j\cdot\boldsymbol{H}_{ij} = (\beta/8\pi\eta_0 b)\nabla_R\cdot\boldsymbol{T}(\mathbf{R}) \tag{2.20}$$

where $\mathbf{R} = \mathbf{R}_j - \mathbf{R}_i$ and

$$\boldsymbol{T}(\mathbf{R}) \equiv (\boldsymbol{1} + \mathbf{RR}/R^2)f(R) \tag{2.21}$$

The divergence works out to be

$$\nabla_R\cdot\boldsymbol{T}(\mathbf{R}) = 2(\mathbf{R}/R)(f' + R^{-1}f) \tag{2.22}$$

We used

$$f(R) \equiv R/(R^2 + \alpha^2) \tag{2.23}$$

to eliminate the singularity, with α a parameter chosen variously to be 0.5 or 1 in units of b. The strength of hydrodynamic interaction was measured by h^*

$$h^* \equiv \beta/(6^{1/2}\pi^{3/2}\eta_0 b) \tag{2.24}$$

(which is a factor $2^{1/2}$ larger than Osaki's[11] h^*). The result is

$$\nabla_j\cdot\boldsymbol{H}_{ij} = (3\pi/2)^{1/2}\alpha^2h^*(1 - \delta_{ij})\mathbf{R}_{ij}[R_{ij}(R_{ij}^2 + \alpha^2)^2]^{-1} \tag{2.25}$$

$$\boldsymbol{H}_{ij} = \boldsymbol{1}\delta_{ij} + (1 - \delta_{ij})(3\pi/32)^{1/2}h^*(\boldsymbol{1} + \mathbf{R}_{ij}\mathbf{R}_{ij}/R_{ij}^2)f(R_{ij}) \tag{2.26}$$

III. Time Correlation Functions

In this section we construct the time correlation functions for the correction to the Kirkwood diffusion formula and for the intrinsic viscosity. The latter is given by a well-known stress correlation formula, but we include its derivation for completeness and because few additional lines are required. The first part of the argument parallels the (approximate) analytical discussion of Horta and Fixman.[12]

The diffusion equation for the distribution function $\Psi(\mathbf{R},t)$ of chain coordinates, equivalent to the Langevin equation (2.1), is given by

$$\partial\Psi/\partial t = -\nabla_i\cdot(\mathbf{V}_i\Psi) \tag{3.1}$$

where

$$\mathbf{V}_i = \mathbf{V}_i^0 + \boldsymbol{H}_{ij}\cdot\mathbf{F}_j \tag{3.2}$$

and the frictional force $\mathbf{F}_j$ is given by

$$\mathbf{F}_j = \mathbf{E}_j + \mathbf{W}_j - k_BT\nabla_j \ln \Psi \tag{3.3}$$

We will suppose that either the external force $\mathbf{E}$ or the velocity field $\mathbf{V}^0$ is present, but not both.

The mean increment of stress due to the addition of one polymer molecule in unit volume is given by

$$\sigma = -\sum\langle\mathbf{R}_i\mathbf{W}_i\rangle \tag{3.4}$$

Only the traceless part of σ is intended to be retained; the trace is a contribution to the pressure or osmotic pressure and is discarded. With that understanding, $\mathbf{W}_i$ may be replaced by $\mathbf{F}_i$.[13] We will assume that Ψ is independent of the polymer center of mass and that averages are taken over internal coordinates only.

The average velocity is given by eq 2.2 and 2.3 with $\mathbf{V}^0 = 0$.

$$\langle\mathbf{V}_i\rangle = \int \boldsymbol{H}_{ij}\cdot(\mathbf{E}_j + \mathbf{W}_j - k_BT\nabla_j \ln \Psi)\Psi\, d\{\mathbf{R}\} \tag{3.5}$$

To first order in the external field we have, after an integration by parts and use of the symmetry of H

$$\langle\mathbf{V}_i\rangle = \langle\boldsymbol{H}_{ij}\rangle_e\cdot\mathbf{E}_j + \langle\boldsymbol{H}_{ij}\cdot\mathbf{W}_j + k_BT\nabla_j\cdot\boldsymbol{H}_{ij}\rangle \tag{3.6}$$

The first term on the right-hand side gives the Kirkwood formula, and the second term provides the correction. We note that $\nabla_j\cdot\boldsymbol{H}_{ij}$ vanishes if the Stokes–Oseen tensor is used for H (as a consequence of the incompressibility of the solvent). Our modification of H precludes that simplification at this stage. However, when a sum over i is taken to obtain the center-of-mass velocity $\mathbf{V}_c$, the divergence term will vanish from the expression for $\mathbf{V}_c$ because $\boldsymbol{H}_{ij}$ remains a function of $\mathbf{R}_{ij}$. The divergence of the modified H cannot be deleted from the Langevin equation.

For an evaluation of the averages in eq 3.4 and 3.6, we require the distribution function to first order in the external perturbations. Equations 3.1 to 3.3 give

$$\partial\Psi/\partial t + \mathcal{L}\Psi = -\nabla_i\cdot[\mathbf{V}_i^0 + \boldsymbol{H}_{ij}\cdot\mathbf{E}_j]\Psi \tag{3.7}$$

where

$$\mathcal{L}\Psi = \nabla_i\cdot[\boldsymbol{H}_{ij}\cdot(\mathbf{W}_j\Psi - k_BT\nabla_j\Psi)] \tag{3.8}$$

The linearized steady-state solution is

$$\Psi = \Psi_e - \mathcal{L}^{-1}\nabla_i\cdot[\mathbf{V}_i^0 + \boldsymbol{H}_{ij}\cdot\mathbf{E}_j]\Psi_e \tag{3.9}$$

Contact with a correlation function formalism is made through

$$\mathcal{L}^{-1} = \int_0^\infty e^{-\mathcal{L}t}\,dt \tag{3.10}$$

The last two equations, together with the symmetry of H and the facts that $\Psi_e \propto \exp(-W/k_BT)$ and $\nabla_j\mathbf{V}_i^0 = 0$, give

$$\Psi = \Psi_e - \int_0^\infty e^{-\mathcal{L}t}[(\mathbf{W}_i/k_BT)\cdot(\mathbf{V}_i^0 + \boldsymbol{H}_{ij}\cdot\mathbf{E}_j) + (\nabla_i\cdot\boldsymbol{H}_{ij})\cdot\mathbf{E}_j]\Psi_e\,dt \tag{3.11}$$

We consider an external force for which $\mathbf{E}_i = \mathbf{E}_0$, the same for each bead. This makes the divergence of H drop out of eq 3.11.

We compute the average of the center-of-mass velocity $\mathbf{V}_c$ from eq 3.11, after suppression of the external velocity field $\mathbf{V}^0$, to be

$$\mathbf{V}_c = \sum\langle\mathbf{V}_i\rangle/N = (D_0 - D_1)\mathbf{E}_0 \tag{3.12}$$

where

$$D_0 = (3N)^{-1}\sum_i\sum_j \text{tr}\,\langle\boldsymbol{H}_{ij}\rangle_e \tag{3.13}$$

$$3Nk_BTD_1 = \int_0^\infty C_A(t)\,dt = \int_0^\infty \langle\mathbf{A}(t)\cdot\mathbf{A}(0)\rangle_e\,dt \tag{3.14}$$

and

$$\mathbf{A} \equiv \sum_i\sum_j \boldsymbol{H}_{ij}\cdot\mathbf{W}_j \tag{3.15}$$

We have used $\mathbf{A}(t)\Psi_e = \exp(-\mathcal{L}t)\mathbf{A}(0)\Psi_e$.

Likewise, the mean value of the stress tensor is computed from eq 3.4 and 3.11, with suppression of the external force $\mathbf{E}_j$.

$$k_BT\eta_0[\eta] = \int_0^\infty C_S(t)\,dt = \int_0^\infty \langle S(t)S(0)\rangle_e\,dt \tag{3.16}$$

where

$$S \equiv \sum_i W_i^x R_i^y \tag{3.17}$$

Equation 3.16 is a well-known result. The intrinsic viscosity in this form has concentration units of polymer molecules/volume, rather than the conventional grams/volume. In the actual calculations, eq 3.16 was replaced by its average over orientations of the reference frame.[14] Such an average has already been used implicitly in eq 3.14.

IV. Preaveraged Hydrodynamic Interaction

In this section we evaluate the correlation functions $C_A(t)$ and $C_S(t)$ for the Zimm model, i.e., with H replaced by $\langle H\rangle_e$. A Gaussian distribution of relative bead distances gives

$$\langle\boldsymbol{H}_{ij}\rangle_e = I[\delta_{ij} + (1 - \delta_{ij})h^*|i - j|^{-1/2}(1 - xe^xE_1(x))] = I\bar{H}_{ij} \tag{4.1}$$

where

$$x \equiv 1.5\alpha^2/|i - j| \qquad E_1(x) \equiv \int_x^\infty y^{-1}e^{-y}\,dy \tag{4.2}$$

With the preaveraged H, a conditional average of eq 2.2 or 2.11 for a given initial configuration shows that

$$d\mathbf{R}_i/dt = \bar{H}_{ij}\mathbf{W}_j \tag{4.3}$$

A transformation of this equation to bond vector coordinates[15]

$$\mathbf{b}_i \equiv \mathbf{R}_i - \mathbf{R}_{i-1} = A_{ij}^T\mathbf{R}_j \qquad 1 \le i \le M \qquad 0 \le j \le M$$
$$A_{ji}^T \equiv A_{ij} = \delta_{ij} - \delta_{i,j-1} \qquad 0 \le i \le M \quad 1 \le j \le M \tag{4.4}$$

is advantageous because the mean center of mass is invariant according to eq 4.3. Moreover, a Gaussian chain has

$$\mathbf{W}_i = -\partial W/\partial\mathbf{R}_i = -A_{ij}(\partial W/\partial\mathbf{b}_j) = -3A_{ij}\mathbf{b}_j \tag{4.5}$$

It follows that

$$d\mathbf{b}_i/dt = -3B_{ij}\mathbf{b}_j \tag{4.6}$$

where B is the $M \times M$ matrix

$$B \equiv A^T\bar{H}A \tag{4.7}$$

and

$$\mathbf{b}(t) = \exp(-3Bt)\mathbf{b}(0) \tag{4.8}$$

Calculation of the stress correlation function is based on eq 3.16, 3.17, and 4.8 and the supplemental observation that orthogonal projections of the chain vectors relax independently:

$$C_S^{PA}(t) = \sum_i[\exp(-6Bt)]_{ii} = \text{tr}\,\exp(-6Bt) \tag{4.9}$$

Equations 3.14 and 3.15 similarly give

$$C_A^{PA}(t) = 9\sum_i\sum_j[E\,\exp(-3Bt)E^T]_{ij} \tag{4.10}$$

where

$$E = \bar{H}A \tag{4.11}$$

The actual calculations followed eq 4.9 and 4.10 quite literally, with $\exp(-3Bt)$ evaluated as a power of $\exp(-3Bs)$ and integral values of t/s. Since s was chosen to be small, $\exp(-3Bs)$ could be obtained from a power series expansion. (Probably we should have diagonalized B; matrix multiplication seemed easier at the time.)

Integration of C_A^P according to eq 3.14 and 4.10 gives

$$D_1^P = N^{-1}\sum_0^M\sum_0^M(EB^{-1}E^T)_{ij} \tag{4.12}$$

Equations 3.16 and 4.9 give

$$\eta_0[\eta]^P = (\text{tr}\,B^{-1})/6 \tag{4.13}$$

We have been especially interested in corrections to the Kirkwood formula foor the diffusion or sedimentation constant of long chains. A crude estimate of the limit of D_1^P/D_0 was given by Horta and Fixman[12] using a Rouse mode representation of the diffusion operator. This gave 0.014 for the ratio. An exact calculation, summarized in the Appendix, gives

$$\lim_{N\to\infty} D_1^P/D_0 = 1 - \frac{3\pi\Gamma(\frac{1}{2})}{8(2^{1/2})[\Gamma(\frac{3}{4})]^2} = 0.01673 \tag{4.14}$$

This is equivalent to the result ascribed to Auer and Gardner by Zimm.[2] (We redid the analysis to check the old result and our formula of D_1.) Equation 4.14 is, of course, based on preaveraged HI. The corresponding correction for fluctuating HI, D_1/D_0, will be inferred from

$$D_1/D_0 = (D_1/D_1^P) \times 0.01673 \tag{4.15}$$

Figures 1–3 illustrate the several correlation functions calculated analytically with preaveraged HI. We have also shown the correlation function $C_L^P(t)$ for the end-to-end vector $\mathbf{L}(t)$:

$$C_L(t) \equiv \langle\mathbf{L}(0)\cdot\mathbf{L}(t)\rangle_e \tag{4.16}$$

$$C_L^P(t) = \sum_1^M\sum_1^M(e^{-3Bt})_{ij} \tag{4.17}$$

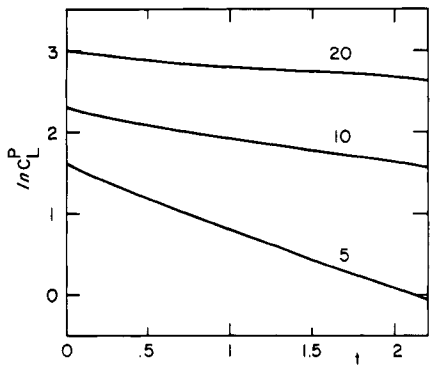

Figure 1. Logarithm of the correlation function C_L^P for the end-to-end vector vs. time for chains of 5, 10, and 20 bonds. Preaveraged hydrodynamic interaction with strength parameter $h^* = 0.5$ and smoothing parameter $\alpha = 0.5$.

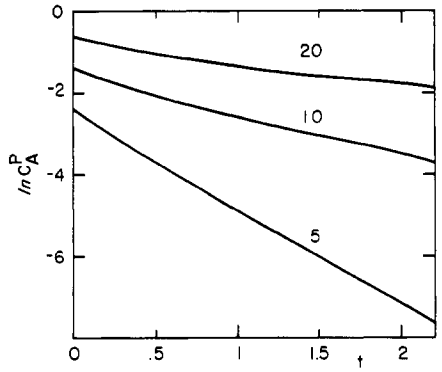

Figure 2. Diffusion vector correlation function C_A^P vs. time. Other conditions as in Figure 1.

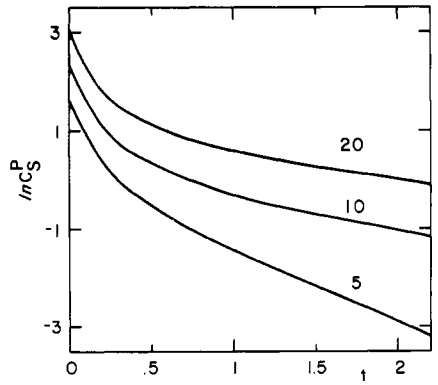

Figure 3. Stress correlation function C_S^P vs. time. Other conditions as in Figure 1.

The simulation results for preaveraged HI will not be displayed directly because the focus of the calculation was on such ratios as C_A/C_A^P. However, the simulation results with preaveraged HI all agreed with the analytical results to within, and usually well within, the statistical errors of the former. Those errors were estimated to lie in the range 2–10% for $t = 0$ and to increase with t in roughly inverse proportion to the correlation functions.

To provide some feeling for the magnitude of corrections D_1 to the Kirkwood formula D_0 for the diffusion constant, we have listed values for the 5-, 10-, and 20-bond chains in Table I.

V. Results

A. Expected Time Dependence. The HI matrix is required to be positive definite, and it follows that the diffusion operator will also have this property (if the equilibrium distribution function, an eigenfunction with zero eigenvalue, is excluded). Consequently we expect that any correlation function has a representation

$$C(t) = \sum a_k \exp(-\nu_k|t|) \tag{5.1}$$

with positive eigenvalues ν_k. A steady-state transport property will be obtained from the integral

$$\int_0^\infty C(t)\,dt = \sum a_k/\nu_k \tag{5.2}$$

For large N and small k the Rouse or Rouse–Zimm eigenvalues vary with N as $(k/N)^2$ or $(k/N)^{1.5}$, respectively.[9] Therefore the steady-state transport property is dominated by the slowest modes. We expect this to remain true with fluctuating HI, and so the long-time behavior of the correlation functions is required if inferences are to be drawn about the transport properties of long chains.

For very long times the asymptotic behavior of correlation functions computed with fluctuating and with preaveraged HI should have the ratio

$$C/C^P \sim (a/a^P) \exp[-(\nu - \nu^P)t] \tag{5.3}$$

and a plot of ln (C/C^P) against t should approach a straight line. The eigenvalues without subscripts refer to the slowest modes of the chain. Moreover, this line must have a nonnegative slope for vector correlation functions. This follows from a variational principle $\nu < \nu^P$ for eigenfunctions of a given spatial symmetry. (A similar remark could be made about tensor eigenfunctions, but the preaveraged HI matrix would have to be slightly modified along the lines discussed by Pyun and Fixman.[16])

B. Parameters. The list of parameters that had to be specified at the start of any simulation was rather extensive: the number of beads N, the number of trajectories, the time interval s, the total duration of a trajectory, the permitted error in the square root of the HI matrix, the smoothing parameter α in the modified HI matrix, and the smoothing parameter x_m. The last parameter, x_m, was introduced as follows: H_{ij} was replaced by $\langle H_{ij}\rangle_e$ for $|i-j| \le x_m$. The HI strength parameter was always taken to be $h^* = 0.5$. According to eq 2.24, this represents a bead radius $a = 0.362b$ if a Stokes value is used for the bead friction constant.

The computation time did not seem inordinate. For $N = 21$ a single time increment along a trajectory required about half a second of computer time on a computer that required about 1.5×10^{-5} s for a floating-point operation. Computer time increases as N^2 for trajectories of fixed duration. The longest relaxation times presumably increase as $N^{3/2}$, as in the Rouse–Zimm model, and one might wish to increase the durations accordingly, depending on the problem under study. However, our ratios C/C^P had settled down to apparent constancy with respect to t at

Table I
Values for the Diffusion Constant Given by the Kirkwood Formula (D_0) and the Correction (D_1) to It in the Preaveraged Hydrodynamic Interaction Approximation as a Function of the Number of Bonds M and the Short Distance Smoothing Parameter α [a]

α	M	D_0	D_1/D_0
1	5	1.79	0.00015
1	10	2.49	0.00116
1	20	3.67	0.00427
0.5	5	2.25	0.00263
0.5	10	3.17	0.00625
0.5	20	4.63	0.0109
	∞		0.0167

[a] The HI strength parameter $h^* = 0.5$. The ratio D_1/D_0 for the infinite chain is independent of α and h^*.

rather short times, on the order of 0.6 ± 0.2 in reduced units, with no clear dependence on N. Consequently, we did not increase the duration of trajectories with increasing N.

The short-time behavior of the correlation functions is naturally important in a quantitative calculation of transport coefficients of short chains. But that behavior may be strongly influenced by the values of the smoothing parameters α and/or x_m, in addition to the more fundamental physical limitations of the model. So we do not report any numerical integrations for the transport coefficients.

Because our main interest was the effect of fluctuations in hydrodynamic interaction on the two transport coefficients, we compared the correlation functions computed with and without the use of preaveraged HI, but for the same initial configurations and same Langevin forces. This procedure, an adaptation of Zimm's,[2] reduces the effect of sample fluctuations.

For the results to be reported, we chose $\alpha = 0.5$ or 1. Larger α's reduce HI of nearby beads and accelerate the convergence of the iteration scheme for square roots. However, the chains we deal with are short (the root-mean-square end-to-end distance of a 20-bond chain is only 4.47), and large α's lead to relatively long-range forces because of the $\nabla_j \cdot \boldsymbol{H}_{ij}$ terms in the equation of motion. A serious practical difficulty also results from the fact that C_A/C_A^P for small times increases rapidly with increasing α (mainly due to decreasing C_A^P). This makes the long-time behavior of the ratio very noisy.

Other parameters were time increment $s = 0.01$, duration of a trajectory equal to about 3, in reduced units, and number of trajectories equal to $1600/M$, where M is the number of bonds. Correlation functions were calculated to about $t = 2$, typically, but the stastical uncertainty increases with t, in part because the correlation functions decrease and in part because the number of samples decreases.

C. Results. It is apparent from the correlation functions with preaveraged HI, as shown in Figures 1–3, that the relative contribution of slow and fast relaxation is greatest for the end-to-end vector, least for the stress, and intermediate for C_A^P. It is therefore not surprising, in retrospect, that the results are clearest for relaxation of the end-to-end vector and least clear for stress relaxation. Indeed, only for the 20-bond chain could we obtain stress correlations for which the long-time behavior seemed resonably independent of smoothing parameters.

We begin with the correlation function $C_L(t)$ for the end-to-end vector $\mathbf{L}(t)$. The effect of fluctuating HI on this correlation function was negligible within statistical error. More precisely, the ratio C_L/C_L^P was unity for $t < 2$, the largest value calculated, to within the statistical error of the ratio, about 0.01 for small t to 0.03 for large t. The uncertainty in the individual correlation functions was 5–10 times larger. Two inferences can reasonably be drawn from this result. First, the long-wavelength vector modes of the chain are very slightly affected by fluctuating HI. Second, the rotational diffusion constant will be affected very little by fluctuating HI because the slow relaxation of $\mathbf{L}$ is predominantly achieved by rotational diffusion.

The ratios C_A/C_A^P are shown in Figure 4 for chains with 5, 10, and 20 bonds. The values of this ratio at short times are highly dependent on the smoothing parameters α and x_m. Remarkably, however, almost all of that short-time dependence arises in the values of the fluctuating quantity $\mathbf{A}$ and not in the trajectories themselves. When we computed C_A from trajectories generated with preaveraged HI,

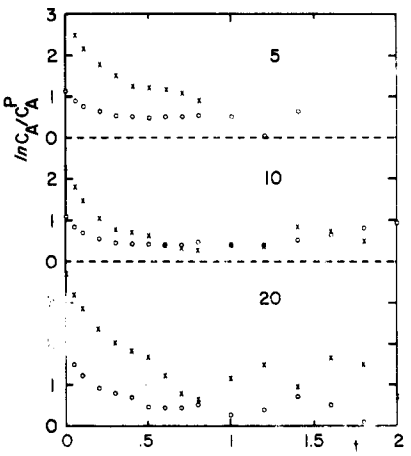

Figure 4. Logarithm of the ratio C_A/C_A^P vs. time for chains of 5, 10, and 20 bonds. $h^* = 0.5$ and smoothing parameters α and x_m varied. Five bonds: (×) $\alpha = 1$, $x_m = 3$; (○) $\alpha = 0.5$, $x_m = 3$. Ten bonds: (×) $\alpha = 0.5$, $x_m = 3$; (○) $\alpha = 0.5$, $x_m = 6$. Twenty bonds: (×) $\alpha = 1$, $x_m = 5$; (○) $\alpha = 0.5$, $x_m = 10$.

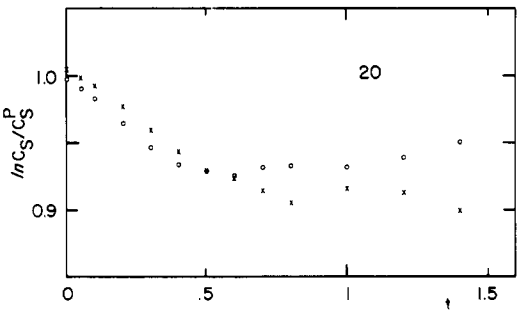

Figure 5. Logarithm of the ratio C_S/C_S^P vs. time for 20-bond chain. Conditions duplicate those for the 20-bond chain of Figure 4.

but with $\mathbf{A}$ evaluated from the fluctuating HI matrix, the short-time behavior of C_A ($t < 0.3$) was not affected within the statistical error of about 4%. This relative insensitivity of the trajectories (at least in this one respect) to fluctuations in HI might well persist to longer times. The results are quite suggestive that perturbative theories and pertubative simulations of fluctuating HI are worth further study.

At long times the ratio C_A/C_A^P shown in Figure 4 seems to approach a constant value. Admittedly the data are not very precise. For $M = 5$ bonds the sequence of points has been truncated because the ratio dropped below unity and simultaneously showed highly erratic time dependence. Ratios for $\alpha = 0.5$ were much smoother functions of time and showed much smaller sample variance than ratios for $\alpha = 1$. The former data indicate that C_A/C_A^P approaches a ratio of about 1.5 at large times, independent of chain length. This limiting value is reached at fairly short times, $t < 0.6$, where the statistical uncertainty is still reasonably small, 10–20%.

We conclude, therefore that the ratio D_1/D_0 for long chains does not exceed the value 0.0167 obtained with preaveraged HI by more than 50%. Thus D_1/D_0 is estimated to be under 3%.

The stress correlation function undergoes the largest decay of the three correlation functions that were studied, and therefore the results for it were the least significant. Systematic behavior at moderate values of t was not achieved until we reached the 20-bond chain. Results are shown in Figure 5. If the long-time results are indeed representative, one would predict that fluctuating HI lowers the intrinsic viscosity of long chains by 7–9%.

However, our results are few and rough, and we do not see the positive slope at large times predicted by the eigenvalue calculations of Bixon and Zwanzig[8] (they calculated $\nu = 0.5\nu^P$ on the basis of a truncated representation of the diffusion operator given by Pyun and Fixman[7]). So firm conclusions must be deferred.

All the simulation results must be regarded as preliminary, as is evident from the figures. The methods also could no doubt be improved. For example, scaling the HI matrix is a possible device to improve the convergence properties of the square root algorithm. On a more fundamental level, alternative methods of smoothing the HI matrix should be explored. For example, the short-wavelength Rouse–Zimm modes could be preaveraged or, alternatively, decoupled from the long-wavelength modes. How this can be done with minimum loss of precision remains to be seen, but it seems very probable that the detailed local dynamics is irrelevant to the gross motions studied here. Some study of its elimination is therefore worthwhile.

Acknowledgment. We are grateful to W. H. Stockmayer and B. H. Zimm for many discussions of the subject treated here.

Note Added in Proof. The recent acquisition of computational facilities allowed the study of a greater range of parameters and chain lengths. Some slight improvements in the algorithm and the HI tensor[19,20] were also made, but the calculations were basically as described here.

The new results cast doubt on the interpretation of data in this paper. This interpretation was based on several premises, namely: (1) Only the long-time behavior of the correlation functions is relevant to the calculation of $[\eta]$ or D_1 for long chains. (2) The long-time, long-chain behavior will not depend on local dynamical properties such as the friction constant. (3) The notoriously slow convergence of hydrodynamic properties to long-chain limits could be compensated by a comparison of correlation functions for fluctuating HI with correlation functions for preaveraged HI. These premises, and a desire to save computing time, motivated the smoothing of HI for beads close together along the backbone, or close in space for a particular configuration. Unfortunately, the new data do not substantiate the premises. Even the first premise, which we consider more trustworthy than computer simulations on short chains, seems somewhat dubious for D_1. It is safe enough for $[\eta]$, since the amplitude of $C_S(0)$ is limited by purely conformational rather than dynamic properties. The third premise has a somewhat practical nature, and we need only remark that it is not borne out in practice.

It seems unlikely that the simulations have major systematic errors, because the transport coefficients D_1 and $[\eta]$ satisfy several bounds computed independently. Wilemski and Tanaka[21] have shown that Zimm's algorithm[2] provides an upper bound to $[\eta]$, and we have shown the same to be true of his algorithm for D_1.[22] We have also devised lower bounds,[22] rather similar in form and derivation to the Peierls theorem of quantum statistics[23] (numerical application has been made only to $[\eta]$). The dynamical simulations satisfy both bounds.

We hope to report on the new simulation and analytical results in the near future.

Appendix

The analytic correction to the Kirkwood formula is derived here for large N under the conditions of preaveraged HI. A summary of formulas from the main text is presented for reference. The Kirkwood formula is simply our eq 3.13 for D_0. The correction to it is given by eq 4.12 for D_1^P.

$$D_0 = N^{-1}\sum_0^M\sum_0^M \bar{H}_{ij} \tag{A1}$$

$$D_1^P = N^{-1}\sum_0^M\sum_0^M (EB^{-1}E^T)_{ij} \tag{A2}$$

where eq 4.4, 4.7, and 4.11 give

$$E \equiv \bar{H}A \tag{A3}$$

$$B \equiv A^T\bar{H}A \tag{A4}$$

$$A_{ij} \equiv \delta_{ij} - \delta_{i,j-1} \qquad 0 \le i \le M \qquad 1 \le j \le M \tag{A5}$$

Elements of the averaged HI matrix are given in eq 4.1, but here we need only the asymptotic form because we go to the limit of long chains.

$$\bar{H}_{ij} \sim h^*|i-j|^{-1/2} \tag{A6}$$

We now define the column array P_i by

$$P_i \equiv \sum_0^M \bar{H}_{ij} \tag{A7}$$

Equation A1 gives

$$ND_0 = \sum_0^M P_i \tag{A8}$$

With the column array G defined by

$$G = AB^{-1}A^TP \tag{A9}$$

eq A2 gives

$$ND_1^P = \sum_0^M P_iG_i \tag{A10}$$

The A matrix on the right-hand side of (A9) suffices to give

$$\sum_0^M G_i = 0 \tag{A11}$$

Multiplication of eq A9 from the left by $A^T\bar{H}$ gives, with eq A4

$$A^T\bar{H}G = A^TP \tag{A12}$$

The purpose of all this jugglery has been to put the equations in a form suitable for conversion to continuous indices and thereby to obtain an integral equation for the basic unknown G_i. Let

$$\begin{aligned} i &= (N/2)(1+x) \qquad -1 \le x \le 1 \\ j &= (N/2)(1+y) \qquad -1 \le y \le 1 \end{aligned} \tag{A13}$$

Conversion of eq A9 to continuous variables and evaluation of the integral gives

$$P_i = h^*(N/2)^{1/2}w(x) \tag{A14}$$

where

$$w(x) \equiv 2[(1+x)^{1/2} + (1-x)^{1/2}] \tag{A15}$$

Replacement of the elements G_i in (A10) by the function $g(x)$ gives, with eq A14 and A8

$$D_1^P/D_0 = \int_{-1}^1 w(x)g(x)\,dx \Big/ \int_{-1}^1 w(x)\,dx \tag{A16}$$

or

$$D_1^P/D_0 = [3/16(2^{1/2})]\int_{-1}^1 w(x)g(x)\,dx \tag{A17}$$

In the matrix equation for G, eq A12, the matrix A^T is simply a difference operator which goes in the continuous

limit to d/dx. Conversion of the remaining part of the matrix equation to continuous variables and integration over x gives

$$\int_{-1}^{1}|x - y|^{-1/2}g(y)\,dy = w(x) + K \qquad \text{(A18)}$$

where K is an integration constant. K has to be chosen so that $g(x)$ satisfies the continuous version of eq A11, i.e.

$$\int_{-1}^{1}g(x)\,dx = 0 \qquad \text{(A19)}$$

A last transformation appreciably simplifies the integral equation. Let

$$g(x) = 1 + Kf(x) \qquad \text{(A20)}$$

Equation A18 becomes

$$\int_{-1}^{1}|x - y|^{-1/2}f(x)\,dx = 1 \qquad \text{(A21)}$$

while (A19) gives

$$K = -2/\int_{-1}^{1}f(x)\,dx \qquad \text{(A22)}$$

Equation A17 reduces to

$$D_1^P/D_0 = 1 + [3K/8(2^{1/2})] \qquad \text{(A23)}$$

The solution of eq A21 has been obtained by two independent approaches. The method of Latta[17] is relatively elementary to work through. The integral transforms of the Gegenbauer polynomials presented by Auer and Gardner[18] are not so elementary to derive, but it is perhaps more straightforward to use their formulas. With either method one derives

$$f(x) = [\pi(2^{1/2})]^{-1}(1 - x^2)^{-1/4} \qquad \text{(A24)}$$

With eq A22 to A24 it is a matter of manipulating Γ functions to derive the result given in eq 4.14.

We have verified the observation of Stockmayer that our result for the diffusion constant with preaveraged HI is identical with that based on the Kirkwood–Riseman equation; see Yamakawa,[9] p 272. The analytical formula of Zimm[2] contains a typographical error; the corresponding numerical result is in agreement with ours.

References and Notes

(1) Hynes, J. T. *Annu. Rev. Phys. Chem.* **1977**, *28*, 301–21.
(2) Zimm, B. H. *Macromolecules* **1980**, *13*, 592.
(3) Fixman, M. *Macromolecules*, preceding paper in this issue.
(4) We wish to acknowledge a stimulating workshop on the subject "Hydrodynamic Interactions in Stochastic Dynamics", organized by H. J. C. Berendsen. At the time of the workshop, Oct 1979, hydrodynamic interactions seem not to have been included in polymer simulations. However, dimers and trimers have been studied (Ermak, D. L.; McCammon, J. A. *J. Chem. Phys.* **1978**, *69*, 1352–60), and David Ceperley has studied decamers (private communication). These workers used matrix decomposition of the HI matrix, e.g., Cholesky factorization. Such methods are slow compared to the iterative technique, taking computation time $O(N^3)$, but are exact.
(5) Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1527–37.
(6) Zwanzig, R. *Adv. Chem. Phys.* **1969**, *15*, 325–31.
(7) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1966**, *44*, 2107–15.
(8) Bixon, M.; Zwanzig, R. *J. Chem. Phys.* **1978**, *68*, 1890–5.
(9) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(10) Bellman, R. "Introduction to Matrix Algebra"; McGraw-Hill: New York, 1960; p 177, problem 5.
(11) Osaki, K. *Adv. Polym. Sci.* **1973**, *12*, 1–64.
(12) Horta, A.; Fixman, M. *J. Am. Chem. Soc.* **1968**, *90*, 3048–55. See also Dubois-Violette, E.; de Gennes, P. G. *Physica* **1967**, *3*, 181–98 for related results.
(13) Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3831–7.
(14) Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1538–45.
(15) Lodge, A. S.; Wu, Y. *Rheol. Acta* **1971**, *10*, 539–53.
(16) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3838–44.
(17) Cochran, J. A. "The Analysis of Linear Integral Equations"; McGraw-Hill: New York, 1972; p 301.
(18) Auer, P. L.; Gardner, C. S. *J. Chem. Phys.* **1955**, *23*, 1545–6.
(19) Rotne, J.; Prager, S. *J. Chem. Phys.* **1969**, *50*, 4831–7.
(20) Fixman, M. "Variational Theorem for the Generalized Diffusion Tensor", preprint submitted to *J. Chem. Phys.*
(21) Wilemski, G.; Tanaka, G. *Macromolecules* **1981**, *14*, 1531.
(22) Fixman, M. "Variational Bounds for Polymer Transport Coefficients", in preparation.
(23) Feynman, R. P. "Statistical Mechanics"; W. A. Benjamin: Reading, Mass., 1972, p 67.

Theoretical Study of Transfer Reactions in Ionic Polymerizations Involving Two Propagating Species

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ABSTRACT: The influence of a transfer agent on the molecular weight distribution of ionic polymerizations in which two active species intervene has been theoretically analyzed. A kinetic scheme that assumes instantaneous initiation as well as instantaneous reinitiation after transfer is used to obtain several mathematical expressions for the number- and weight-average molecular weights. In the same way, the effect of the rate constant of the different active species on the molecular weight averages is also discussed.

Introduction

Living polymers can be prepared only when both termination and transfer reactions are absent. When this is true and the initiation step is instantaneous, a single type of ionic species contributes to the growing chains, so that in most cases the resulting polymer has a narrow Poisson distribution of chain lengths.[1] In ionic polymerization, broadening of the distribution may occur because of different factors, such as slow initiation, spontaneous transfer, and transfer to monomer. The influence of most of these factors on the molecular weight distribution has been theoretically studied in the past.[2–15] Very recently, the

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