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# Bead-Spring Model of a Polymer Chain: A Transient Solution

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With the Rouse–Zimm differential equation of the spring-bead model, the distribution function of $N+1$ beads $\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, t)$ [here $\mathbf{x}$ denotes $(x_0, x_1, \ldots, x_N)$, and similarly for $\mathbf{y}$ and $\mathbf{z}$] is explicitly solved with the two different initial conditions: the Gaussian and delta distribution functions. We find that although the mean end-to-end distances obtained from the two initial conditions are the same, the expressions of the mean square end-to-end distances are different. We also obtain the expression for the mean and mean square end-to-end distances analytically from the Langevin equation with the delta initial distribution function. With this analytic expression, we show that the statistical quantities obtained from the Monte Carlo calculation are consistent with those obtained from the Rouse–Zimm differential equation if a suitable length is chosen for the time increment.

**KEY WORDS:** Rouse–Zimm differential equation; Langevin equation; mean end-to-end distance; distribution function of $N+1$ beads; "free-draining"; Brownian motion; initial conditions; Monte Carlo study; bead-spring statistical macromolecule.

## 1. INTRODUCTION

With the Langevin equation of motion for the bead-spring statistical macromolecule, Simon and Zimm[1] used a high-speed digital computer to simulate the unwinding of DNA. In order to verify that the computer treatment gave

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a correct representation of the analytical equation, simulation of tensile relaxation for a series of polymers was carried out by these workers. The agreement between the computer simulation of the Langevin equation and the analytical solution via the Rouse–Zimm treatment of polymer dynamics was very good for the quantities they compared. However, the initial conditions of the two treatments were different in that the $N + 1$ beads of the machine calculation were initially distributed along the $x$ axis by the delta function, while the beads of the Rouse–Zimm treatment were initially distributed by the Gaussian function. In Section 2, we propose a method of simulating the initial position of beads by the Gaussian distribution function. In Section 3, we first obtain the expression for the mean and mean square end-to-end distances analytically from the Langevin equation with the delta initial distribution function. Second, with these analytic expressions, we show that the mean end-to-end distance obtained from the computer simulation of Simon and Zimm should agree with that of the Rouse–Zimm approach if a suitable length is chosen for the time increment $\Delta t$. Third, since Simon and Zimm obtained the mean square end-to-end distance via the Rouse–Zimm treatment with the Gaussian initial distribution function, we show that this mean square end-to-end distance should be different from that of Simon and Zimm's computer result. In Section 4, the distribution function of $N + 1$ beads $\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, t)$ [here, $\mathbf{x}$ denotes $(x_0, x_1, \ldots, x_N)$, and similarly for $\mathbf{y}$ and $\mathbf{z}$] is explicitly solved with the two different initial conditions. Earlier, Zimm[2] solved $\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, t)$ of a linear tensile relaxation for the steady-state case. The Langevin equation can be applied in studying unwinding of a DNA-like helix.[1,3] In this case, however, it is not possible to obtain a solution of the Langevin equation analytically, and only the Monte Carlo work is available. In Section 5, we show that the analytic expression obtained in Section 3 is very useful in estimating the time increment $\Delta t$ that should be used for the Monte Carlo study. The statistical quantities obtained from the Monte Carlo simulation with too large $\Delta t$ would not represent the correct quantities that can be obtained from the Rouse–Zimm equation.

## 2. COMPUTER SIMULATION OF THE MOTION OF BEADS WITH THE LANGEVIN EQUATION

The motion of a chain of beads connected by ideal springs diffusing through a medium has been treated by Rouse[4] and Zimm[2]. In the "free-draining" case, the equation of motion of $N + 1$ beads can be represented by the following equation:

$$\rho(\dot{u}_i - \dot{u}_i') = -D[\partial(\ln \Psi)/\partial u_i] - (kT/b_u^2)(-u_{i-1} + 2u_i - u_{i+1}),$$
$$u_{-1} = u_0, \quad u_{N+1} = u_N \qquad (1)$$

where $u$ represents either the $x$, $y$, or $z$ coordinate, $kT$ is Boltzmann's constant times the absolute temperature, $\rho$ is a friction constant, and $b_u^2$ is the mean square distance between the successive beads in the $u$ direction and is simply equal to $b_u^2 = b^2/s$ for all $u$'s in a homogeneous $s$-dimensional system. In Eq. (1), $\dot{u}_i'$ is the $x$-, $y$-, or $z$-directional velocity that the fluid would have at position $i$ if the beads were absent. The first and second terms on the right-hand side of the equation represent the Brownian motion term and the spring force term, respectively. The distribution function of $N + 1$ beads $\Psi$ in Eq. (1) is to be determined from the equation of continuity:

$$\partial\Psi/\partial t = \sum_{i=0}^{N} \sum_{u=x,y,z} \sum \partial \dot{u}_i \Psi/\partial u_i \tag{2}$$

The Monte Carlo work can be performed by decoupling Eqs. (1) and (2). The term $-[D\,\partial(\ln \Psi)/\partial u_i]\,\Delta t$ in Eq. (1) can be replaced by $B_{ui}(\Delta t, t)$, which is defined as the net Brownian displacement of molecule $i$ within a time interval $\Delta t$. Thus, for $\dot{u}_i' = 0$, Eq. (1) may be rewritten in a difference form as

$$u_i(t + \Delta t) = u_i(t) + B_{ui}(\Delta t, t) - \sigma\,\Delta t[-u_{i-1}(t) + 2u_i(t) - u_{i+1}(t)] \tag{3}$$

where $\sigma$ is defined as $kTs/b^2\rho$. This is the well-known Langevin equation. In the above equation.

$$B_{ui}(\Delta t, t) = \sum_{j=1}^{n} \Delta U_i(j, t) \tag{4}$$

where $\Delta U_i(j, t)$ is the distance traveled by the $i$th bead due to the Brownian motion in the $j$ th impact, and $n$ is the number of impacts during an interval $\Delta t$. We assume that $\Delta U_i(j, t)$ results from a uniform random displacement with an amplitude $a$ centered around molecule $i$. Then, $\Delta U_i(j, t)$ can be obtained from a quasirandom number $R_{ui}$, which is uniformly distributed between 0 and 1 and is generally available as one of the computer library routines. Thus, $\Delta U_i$ is related to $R_{ui}$ by

$$\Delta U_i = a(1 - 2R_{ui}) \tag{5}$$

where the amplitude $a$ is further related to the other molecular parameters:[1]

$$a = (6D/\nu)^{1/2} = b(6\sigma/s\nu)^{1/2} \tag{6}$$

Simon and Zimm derived a special case of Eq. (4), in that the quantities $n$, $\nu$, and $\Delta t$ were taken to be unity. Equation (4) is the most general form since as

$n$ increases, the distribution of $B_{ui}$ becomes Gaussian according to the central limit theorem. By substituting Eqs. (4)–(6) into Eq. (3), we obtain

$$u_i(t + \Delta t) = u_i(t) - \sigma\Delta t[-u_{i-1}(t) + 2u_i(t) - u_{i+1}(t)] + b(6\sigma/s\nu)^{1/2} \sum_{j=1}^{n} [1 - 2R_{ui}(j, t)] \tag{7}$$

With given initial positions of $N + 1$ beads and for given $\sigma$, $b$, and $\nu$, the Monte Carlo study can be performed with Eq. (7). If we like to simulate the motion of beads which are initially distributed by the delta initial distribution function, we should let the initial position of the beads be

$$x_i(0) = d + hi \tag{8}$$

where $d$ and $h$ are the distances between the origin and zeroth bead and between the successive beads, respectively. The beads may be initially distributed by the Gaussian distribution function. The Gaussian initial distribution of $N + 1$ beads can be determined as follows.[5] First, we pick two random numbers $R_1$ and $R_2$ from a pseudorandom number generator. Second, if $[(-\log R_1 - 1)^2 + 2 \log R_2]$ is positive, we pick two new random numbers. If this quantity is zero or negative, then the position of $i$th bead is taken to be

$$\begin{aligned} x_i(0) &= d + hi \pm (D/\sigma)^{1/2} \log R_1 \\ &= d + hi \pm b_x \log R_1 \end{aligned} \tag{9}$$

where the plus sign is taken if the random number $R_3$ is less than 0.5; otherwise, the minus sign is taken. By determining the initial position of $N + 1$ beads by the above process, the Monte Carlo study on the motion of a chain of beads can be performed.

Simon and Zimm carried out the Monte Carlo study on the tensile relaxation of 31-, 61-, 81-, 121- and 241-bead models with $n = \nu = \Delta t = 1$ and the internally consistent parameters: $\sigma = 0.320$, $b = 10$, and $a = 8$. The $N + 1$ beads were initially distributed according to Eq. (8), where $d = 0$ and $h = b$. In the next section, we will show that the mean square end-to-end distance obtained from Eq. (9) is different from that obtained from Eq. (8).

## 3. ANALYTIC SOLUTION OF THE MEAN AND MEAN SQUARE END-TO-END DISTANCES FROM THE LANGEVIN EQUATION

Zimm[2] and Simon and Zimm[1] obtained the expression for the mean end-to-end distance for a tensile stress applied to the ends of a linear

polymer by multiplying by $x_N - x_0$ on both sides of Eq. (2) and then integrating it:

$$\langle x_N - x_0 \rangle = (f/\rho\sigma) \sum_{k:\text{odd}}^{N} (Q_{Nk} - Q_{0k})^2 e^{-\sigma\lambda_k t}/\lambda_k \tag{10}$$

By the same procedure, Simon[6] obtained the expression for the mean square end-to-end distance as

$$\langle (x_N - x_0)^2 \rangle = \langle (x_N - x_0) \rangle^2 + (D/\sigma) \sum_{k:\text{odd}} (Q_{Nk} - Q_{0k})^2/\lambda_k \tag{11}$$

Simon and Zimm also obtained the mean end-to-end distance by the Monte Carlo calculation with the delta initial distribution of beads, i.e., Eq. (8), and found a beautiful agreement with Eq. (3). In this section, we plan to obtain analytically the mean and mean square end-to-end distances from the Langevin equation and show that the mean square end-to-end distance obtained from the initial condition Eq. (8) will not agree with that of Eq. (11).

The difference equation (3) may be rewritten using a matrix notation

$$\mathbf{u}(t + \Delta t) = \mathbf{u}(t) + \mathbf{B}_u(\Delta t, t) - \sigma \Delta t[\mathbf{A}]\,\mathbf{u}(t) \tag{12}$$

where $\mathbf{B}_u(\Delta t, t)$ is a column vector whose $i$th component is $B_{ui}(t)$. In the above equation, $[\mathbf{A}]$ is a tridiagonal matrix whose components consist of

$$\begin{aligned} A_{00} &= A_{NN} = 1 \\ A_{ii} &= 2 \qquad \text{for} \quad 1 \leqslant i \leqslant N-1 \\ A_{ii-1} &= A_{i-1i} = A_{i+1i} = A_{ii+1} = -1 \end{aligned} \tag{13}$$

It is easier to solve Eq. (12) in the normal coordinates $\xi$, $\eta$, and $\zeta$, with

$$\mathbf{x} = [\mathbf{Q}]\,\xi, \qquad \mathbf{y} = [\mathbf{Q}]\,\eta, \qquad \text{and} \quad \mathbf{z} = [\mathbf{Q}]\,\zeta \tag{14}$$

where $[\mathbf{Q}]$ is a matrix, whose element $Q_{ij}$ is the $i$ th component of the eigenvector $\Phi_j$ of the matrix $[\mathbf{A}]$. With this transformation, Eq. (12) becomes

$$\xi(t + \Delta t) = \xi(t) + [\mathbf{Q}]^T \mathbf{B}_\xi(t) - \sigma[\Lambda]\,\xi(t)\,\Delta t \tag{15}$$

and similarly for $\eta$ and $\zeta$, where $[\Lambda]$ is a diagonal matrix whose diagonal elements consist of the eigenvalues $\lambda_i$, and the superscript $T$ means the transpose of the matrix. The above difference equation has the solution of the following form:

$$\xi_i(t) = \xi_i(0)(1 - \sigma\lambda_i\,\Delta t)^I + \sum_{l=0}^{I-1} \left[ \sum_{k=0}^{N} Q_{ki} B_{\xi k}(\Delta t, l) \right] (1 - \sigma\lambda_i\,\Delta t)^l \tag{16}$$

where $I$ is an integer defined as $[t/\Delta t]$. The explicit forms of $\lambda_i$ and $Q_{ij}$ are given by[7]

$$\lambda_k = 4 \sin^2[k\pi/2(N+1)] \tag{17}$$

and

$$\begin{aligned} Q_{lk} &= [2/(N+1)]^{1/2} \cos[\pi k(l - \tfrac{1}{2}N)/(N+1)], \qquad k \text{ even} \\ &= [2/(N+1)]^{1/2} \sin[\pi k(l - \tfrac{1}{2}N)/(N+1)], \qquad k \text{ odd} \\ Q_{l0} &= 1/(N+1)^{1/2} \end{aligned} \tag{18}$$

In case of a linear tensile relaxation, the end-to-end distance, $L(t, \mathbf{B}_x)$, for a given set of random numbers $\mathbf{B}_x$ can be obtained from Eq. (16) as

$$\begin{aligned} L(t, \mathbf{B}_x) &= x_N(t) - x_0(t) = \sum_{i=0}^{N} (Q_{Ni} - Q_{0i})\, \xi_i(t) \\ &= \sum_{i=0}^{N} (Q_{Ni} - Q_{0i}) \left\{ \xi_i(0)(1 - \sigma\lambda_i \Delta t)^I \right. \\ &\quad \left. + \sum_{l=0}^{I-1} \left[ \sum_{k=0}^{N} Q_{ki} B_{xk}(\Delta t, l) \right] (1 - \sigma\lambda_i \Delta t)^l \right\} \end{aligned} \tag{19}$$

The quantity $\xi_i(0)$ in Eq. (16) can be obtained from the initial distribution of $N+1$ beads as follows. Let $N+1$ beads be initially distributed linearly along the $x$ axis with an equal spacing; i.e., let the initial distribution function of $N+1$ beads be a delta function. With an explicit knowledge on $Q_{lk}$ and $\lambda_k$ given by Eqs. (17) and (18), it is not difficult to verify that

$$\begin{aligned} \xi_i(0) &= \sum_{k=0}^{N} Q_{ki} x_k(0) = \sum_{k=0}^{N} Q_{ki}(d + hk) \\ &= h(Q_{Ni} - Q_{0i})/\lambda_i \end{aligned} \tag{20}$$

where $d$ and $h$ are the distances between the origin and zeroth bead and between the successive beads, respectively. The last equality follows from the property that $\Sigma_k Q_{ki} = 0$ and by evaluating $\Sigma_k k Q_{ki}$ by summation by parts.[8] Let us denote the mean of $L(t, \mathbf{B}_x)$ by $\langle L(t, B_x) \rangle$. Since $B_{xk}$ is a random number taken from a symmetric function according to Eq. (5), the second term of the RHS of Eq. (19) vanishes, and by substituting Eq. (20) into (19), we obtain

$$\langle L(t, B_x) \rangle = h \sum_{i=\text{odd}} (Q_{Ni} - Q_{0i})^2 (1 - \sigma\lambda_i \Delta t)^I / \lambda_i \tag{21}$$

As $\sigma\lambda_i \Delta t \to 0$, Eq. (21) becomes the analytic expression given by Eq. (10). Simon and Zim evaluated $L(t, \mathbf{B}_x)$ by using the Monte Carlo method and compared the mean value of $L(t, B_x)$ with the analytic expression given by

Eq. (10). Thus, it is not at all surprising that they obtained such a good agreement between the analytic result and the machine calculation.

The expression for the mean square end-to-end distance can be obtained by squaring $L(t, B_x)$ and taking the mean. By squaring Eq. (19), we find that the square of the first term of the RHS of the second equality is just $\langle L(t, B_x)\rangle^2$, that the cross-term between the first and second terms vanishes due to the property $\langle B_{xi}(l)\rangle = 0$, and that the square of the second term contains the factor $\langle B_{xi}(l)\, B_{xj}(l')\rangle$. This term can be evaluated from Eqs. (4) and (5):

$$\begin{aligned}\langle B_{xi}(l)\, B_{xi'}(l')\rangle &= \sum_{j'=1}^{n}\sum_{j=1}^{n}\langle \Delta U_i(j, l)\, \Delta U_{i'}(j', l')\rangle \\ &= \sum_{j'=1}^{n}\sum_{j=1}^{n}\int_{-a}^{a}\cdots\int_{-a}^{a}\Delta U_i(j, l)\, \Delta U_{i'}(j', l') \\ &\quad\times\prod_{j=0}^{\infty}\prod_{i=0}^{N}\prod_{l=0}^{N} w_{ijl}[\Delta U_i(j, l)]\, d[\Delta U_i(j, l)] \\ &= (2D/\nu)\sum_{j=1}^{n}\sum_{j'=1}^{n}\delta_{ii'}\delta_{ll'}\delta_{jj'} = 2D(\Delta t)\,\delta_{ii'}\delta_{ll'} \qquad (22)\end{aligned}$$

where $w_{ijl}$ is the probability of occurrence of different values for $\Delta U_i(i, l)$. With Eq. (22) and the property $\Sigma_k Q_{ki}Q_{ki'} = \delta_{ii'}$, the last term of $L^2(t, B_x)$ can be summed by the geometric series. Thus, we obtain

$$\langle L^2(t, B_x)\rangle = \langle L(t, B_x)\rangle^2 + \frac{D}{\sigma}\sum_{i=\text{odd}}\frac{(Q_{Ni}-Q_{0i})^2}{\lambda_i}\left[1-(1-\sigma\lambda_i\,\Delta t)^{2l}\right] \qquad (23)$$

As $\Delta t \to 0$, the above expression becomes

$$\langle L^2(t, B_x)\rangle = \langle L(t, B_x)\rangle^2 + (D/\sigma)\sum_{i=\text{odd}}(Q_{Ni}-Q_{0i})^2\,(1-e^{-2\sigma\lambda_i t})/\lambda_i \qquad (24)$$

This expression does not agree with Eq. (11) of a linear tensile relaxation. It is because the initial conditions for the two cases are different. The initial distribution of $N+1$ beads of the machine calculation of Simon and Zimm is the delta function along the $x$ axis, while that of the analytic approach is the Gaussian distribution function.

In the next section, we obtain the distribution function $\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, t)$ with two different initial distribution functions:

$$\begin{aligned}\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, 0) = \exp\Bigg\{-(3/2b^2)\sum_{j=0}^{N-1}\big[&(x_{j,j+1}-\langle x_{j,j+1}\rangle)^2 \\ &+(y_{j,j-1}-\langle y_{j,j-1}\rangle)^2+(z_{j,j+1}-\langle z_{j,j+1}\rangle)^2\big]\Bigg\} \qquad (25a)\end{aligned}$$

where $x_{j,j+1} = x_j - x_{j+1}$ and $\langle x_{j,j+1} \rangle = h$, $\langle y_{j,j+1} \rangle = \langle z_{j,j+1} \rangle = 0$; and

$$\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, 0) = \delta(x_0 - d)\,\delta(y_0)\,\delta(z_0)\,\delta(x_1 - d - h)\,\delta(y_1)\,\delta(z_1) \times \cdots \delta(x_N - d - Nh)\,\delta(y_N)\,\delta(z_N) \tag{25b}$$

## 4. DISTRIBUTION FUNCTION OF $N+1$ BEADS IN FREE-DRAINING CASE

In order to derive the mean and mean square end-to-end distances for the bead-spring model of Rouse and Zimm, it is not necessary to have an explicit form for $\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, t)$. However, there would be many cases where we need to know the distribution function explicitly. In this section, we solve for $\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, t)$ in Eq. (2) for a linear tensile relaxation. Let us consider the case in which equal and opposite forces of magnitude $f(t)$ are applied to the ends of the chain along the $x$-axis direction. The $f(t)$ is equal to

$$f(t) = f \quad \text{for} \quad t \leqslant 0 \qquad \text{and} \qquad f(t) = 0 \quad \text{for} \quad t > 0 \tag{26}$$

By substituting Eq. (1) into Eq. (2) and with the above initial condition, we find that

$$\partial\Psi/\partial t = \sum_{\mathbf{u}=\mathbf{x},\mathbf{y},\mathbf{z}} \{D(\partial/\partial\mathbf{u}) \cdot (\partial\Psi/\partial\mathbf{u}) + \sigma(\partial/\partial\mathbf{u})^T \cdot [\mathbf{A}]\,\mathbf{u}\Psi\} - [f(t)/\rho](\partial\Psi/\partial\mathbf{u}) \cdot \mathbf{e} \tag{27}$$

where the superscript $T$ means the transpose of the vector, and $\mathbf{e}$ is a column vector with $e_0 = -1$, $e_N = 1$, and $e_i = 0$ for $1 < i < N - 1$. The notation $\mathbf{u}$ (or $\partial/\partial\mathbf{u}$) is defined as a column vector representing either $\mathbf{x}$, $\mathbf{y}$, or $\mathbf{z}$ (or $\partial/\partial\mathbf{x}$, $\partial/\partial\mathbf{y}$, or $\partial/\partial\mathbf{z}$) whose $i$th component is $u_i$ (or $\partial/\partial u_i$). With the transformation discussed in Section 3 [cf. Eq. (14)], Eq. (27) becomes

$$\partial\Psi(\xi, \eta, \zeta, t)/\partial t = \sum_{j=1}^{N} \left\{ \sum_{u_j=\xi_j,\eta_j,\zeta_j} \sum\sum [D(\partial^2\Psi/\partial u_j^2) + \sigma\lambda_j(\partial u_j\Psi/\partial u_j)] - [f(t)/\rho]\,\epsilon_j(\partial\Psi/\partial\xi_j) \right\} \tag{28}$$

where $\epsilon_j$ is equal to the $j$ th component of the vector $[\mathbf{Q}]^T \cdot \mathbf{e}$. In order to solve Eq. (28), let us introduce the function $\hat{\Psi}(\mathbf{k}, \mathbf{p}, \mathbf{q}, t)$, which is the Fourier transform of $\Psi(\xi, \eta, \zeta, t)$:

$$\hat{\Psi}(\mathbf{k}, \mathbf{p}, \mathbf{q}, t) = \int_0^\infty \cdots \int_0^\infty \Psi(\xi, \eta, \zeta, t) \exp[-i(\mathbf{k} \cdot \xi + \mathbf{p} \cdot \eta + \mathbf{q} \cdot \zeta)]\, d\xi\, d\eta\, d\zeta \tag{29}$$

In Eq. (29), the integration runs over $3N + 3$ coordinates. Multiplying Eq. (28) by $\exp[-i(\mathbf{k} \cdot \boldsymbol{\xi} + \mathbf{p} \cdot \boldsymbol{\eta} + \mathbf{q} \cdot \boldsymbol{\zeta})]$ and integrating, we obtain

$$\partial\hat{\Psi}/\partial t = \sum_{j=0}^{N} \sum_{u_j=k_j,p_j,q_j} \sum \sum \sum [-Du_j^2\hat{\Psi} - \sigma u_j\lambda_j(\partial\hat{\Psi}/\partial u_j)] + [if(t)/\rho]\,\epsilon_j k_j\hat{\Psi} \quad (30)$$

For $t \leqslant 0$, we have $\partial\hat{\Psi}/\partial t = 0$ and $f(t) = f$; hence, from Eq. (30), we obtain

$$\hat{\Psi}(\mathbf{k}, \mathbf{p}, \mathbf{q}, t) = \exp\left\{-\sum_{j=1}^{N} [(D/2\sigma\lambda_j)(k_j^2 + p_j^2 + q_j^2) - if(\epsilon_j k_j/\rho\sigma\lambda_j)]\right\}, \quad t \leqslant 0 \quad (31)$$

When $t$ is greater than zero, the last term of Eq. (30) vanishes by Eq. (26), and it can be solved by separation of all the independent variables. That is, $\hat{\Psi}$ is equal to the product over all $j$ of the function $\psi_j$, which consists of the product $K_j(k_j)\,P_j(p_j)\,Q_j(q_j)\,T_j(t)$. By substituting this expression into Eq. (30), we find the particular solutions of the form

$$\psi_j(\alpha_j, \beta_j, \gamma_j) = C_j k_j^{\alpha_j} p_j^{\beta_j} q_j^{\gamma_j} \exp[-\nu_j\sigma\lambda_j t - (D/2\sigma\lambda_j)(k_k^2 + p_j^2 + q_j^2)] \quad (32)$$

where $\nu_j = \alpha_j + \beta_j + \gamma_j$ and $C_j$ can be determined from the initial condition that $\hat{\Psi}$ at $t = 0$ should be continuous. Here, $\psi_j$ is a linear combination of all the particular solutions of $\psi_j(\alpha_j, \beta_j, \gamma_j)$. Hence, $\hat{\Psi}$ may be expressed as

$$\begin{aligned}\hat{\Psi}(\mathbf{k}, \mathbf{p}, \mathbf{q}, t) &= \prod_{j=0}^{N} \psi_j = \prod_{j=0}^{N} \sum_{l,m,n=0}^{\infty} \sum \psi_j(l, m, n) \\ &= \prod_{j=0}^{N} \sum_{l,m,n=0}^{\infty} \sum C_j(l, m, n)\, k_j^l p_j^m q_j^n \\ &\quad \times \exp[-(l + m + n)\,\sigma\lambda_j t - (D/\sigma\lambda_j)(k_j^2 + p_j^2 + q_j^2)] \quad (33)\end{aligned}$$

The term $\exp(if\epsilon_j k_j/\rho\sigma\lambda_j)$ in Eq. (31) should be equal to $C_j(l, m, n)\, k_j^l p_j^m q_j^n$. From this, we find that $m = n = 0$ and $C_j = (1/l!)(if\epsilon_j/\rho\sigma\lambda_j)^l$. The $\hat{\Psi}(\mathbf{k}, \mathbf{p}, \mathbf{q}, t)$ is equal to

$$\hat{\Psi}(\mathbf{k}, \mathbf{p}, \mathbf{q}, t) = \prod_{j=1}^{N} \exp[-(D/2\sigma\lambda_j)(k_j^2 + p_j^2 + q_j^2) + (if\epsilon_j/\rho\sigma\lambda_j)\, k_j e^{-\sigma\lambda_j t}] \quad (34)$$

We note that the normalization condition, $\hat{\Psi}(\mathbf{0}, \mathbf{0}, \mathbf{0}, t) = 1$, is satisfied and from Eq. (34), we may obtain the expression for the $n$th moment $\langle \xi_j^n \rangle$ using the relation

$$\langle \xi_j^n \rangle = i^n [\partial^n\hat{\Psi}/\partial k_j^n]_{\mathbf{k}=\mathbf{p}=\mathbf{q}=0} \quad (35)$$

The $\Psi(\boldsymbol{\xi}, \boldsymbol{\eta}, \boldsymbol{\zeta}, t)$ can be obtained from Eq. (34) by multiplying it by $(1/2\pi)_8^{N+3}$ exp$(i\mathbf{k} \cdot \boldsymbol{\xi} + i\mathbf{p} \cdot \boldsymbol{\eta} + i\mathbf{q} \cdot \boldsymbol{\zeta})$ and integrating from $-\infty$ to $+\infty$.

The integration is a standard one, which can be found from mathematical tables, with the result

$$\Psi(\xi, \eta, \zeta, t) = \left[\prod_{j=1}^{N} (\sigma\lambda_j/2\pi D)^{3/2}\right] \times \exp\{(\xi - \langle\xi\rangle)^T [\Lambda](\xi - \langle\xi\rangle) + \eta^T[\Lambda]\,\eta + \zeta^T[\Lambda]\,\zeta\}$$

$$= \left[\prod_{j=1}^{N} (\sigma\lambda_j/2\pi D)^{3/2}\right] \times \exp\left\{-(\sigma/2D) \sum_{j=1}^{N} \lambda_j[(\xi_j + f\epsilon_j e^{-\sigma\lambda_j t}/\rho\sigma\lambda_j)^2 + \eta_j^2 + \zeta_j^2]\right\} \tag{36}$$

where $\langle\xi\rangle$ is a column vector whose $j$th component is equal to $(-f\epsilon_j/\rho\sigma\lambda_j)$ $\exp(-\sigma\lambda_j t)$. Transforming back to the **x**, **y**, and **z** coordinates, we find from Eq. (36)

$$\Psi(\mathbf{x}, \mathbf{y}, \mathbf{z}, t) = \exp\{-(\sigma/2D)[(\mathbf{x} - \langle\mathbf{x}\rangle)^T [\mathbf{A}](\mathbf{x} - \langle\mathbf{x}\rangle) + \mathbf{y}^T[\mathbf{A}]\,\mathbf{y} + \mathbf{z}^T[\mathbf{A}]\,\mathbf{z}]\}$$

$$= \exp\left\{-(3/2b^2) \sum_{j=0}^{N-1} [(x_{j,j+1} - \langle x_{j,j-1}\rangle)^2 + y_{j,j-1}^2 + z_{j,j+1}^2]\right\} \tag{37}$$

where we define $u_{i,i+1} = u_i - u_{i+1}$. In the above equation, $\langle\mathbf{x}\rangle$ is a column vector whose $i$th component is the mean distance of the $i$th bead at $t$,

$$\langle x_i\rangle = h \sum_{k=\text{odd}} Q_{ik}(Q_{Nk} - Q_{0k})\, e^{\sigma\lambda_k t}/\lambda_k \tag{38}$$

where $h = f/\rho\sigma$. When the external currents $\dot{u}_i$ is zero or in a steady state, Eq. (37) becomes Eq. (18) of Zimm's work.[2] The mean and mean square end-to-end distances can be obtained from Eq. (37) and are given by Eqs. (10) and (11), respectively.

The initial distribution function that we considered above corresponds to the Gaussian distribution function. We can also find the expression for the distribution function whose initial distribution of $N + 1$ beads is given by Eq. (25b). By the similar procedure as we used above, we find that

$$\Psi(\xi, \eta, \zeta, t) = \prod_{j=1}^{N} \frac{\sigma\lambda_j}{2\pi D(1 - e^{-2\sigma\lambda_j t})} \times \exp\left\{-(\sigma/2D) \sum_{j=1}^{N} \frac{\lambda_j}{(1 - e^{-2\sigma\lambda_j t})} [(\xi_j - \langle\xi_j\rangle)^2 + \eta_j^2 + \zeta_j^2]\right\} \tag{39}$$

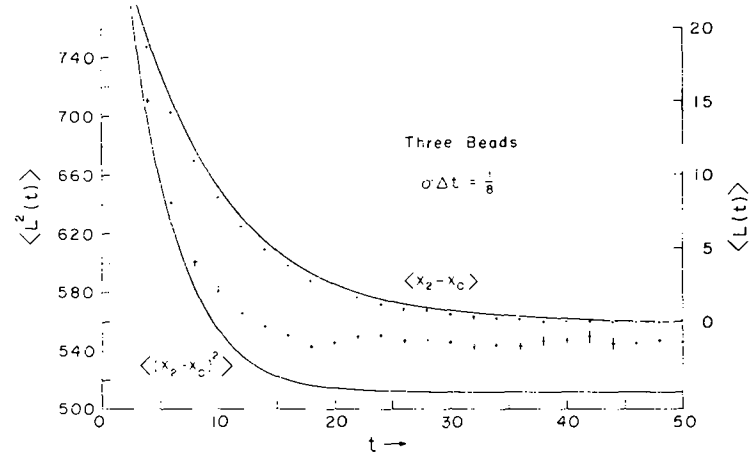


Fig. 1. The mean and mean square end-to-end distances of a linear chain with three beads. The crosses are obtained by the Monte Carlo calculation with Eq. (7), where $\nu = \Delta t = 1$, $\sigma = 0.125$, and $b = 16$. Initially, the beads are distributed by Eq. (8), where $d = -16$ and $h = 16$. The solid lines are obtained from Eqs. (10) and (24). The vertical lines measure the standard deviations, where 50,000 independent runs are taken.

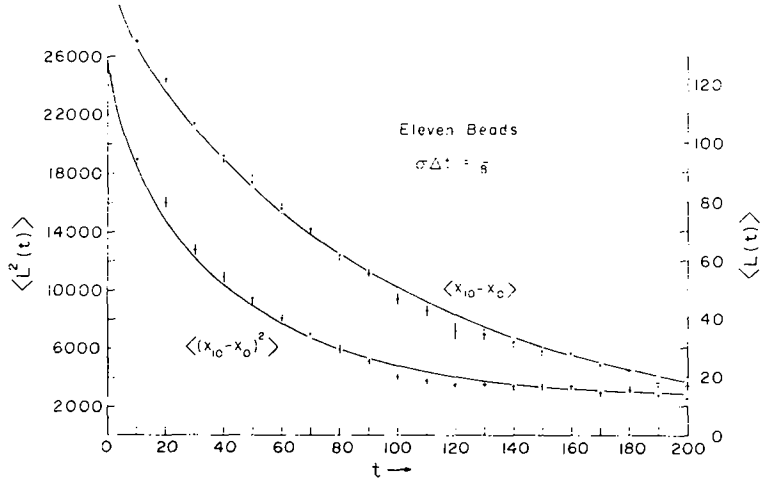


Fig. 2. The mean and mean square end-to-end distances of a linear chain with eleven beads. The crosses are obtained by the Monte Carlo calculation with Eq. (7), where $\nu = \Delta t = 1$, $\sigma = 0.125$, and $b = 16$. Initially, the beads are distributed by Eq. (8), where $d = -5h$ and $h = 16$. The solid lines are obtained from Eqs. (10) and (24). The vertical lines measure the standard deviations, where 400 independent runs are taken.

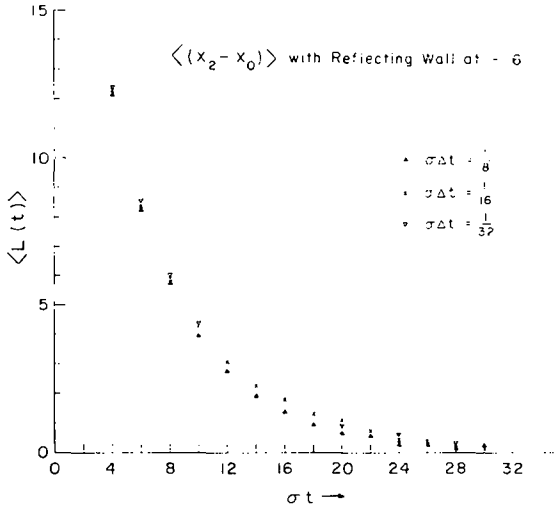


Fig. 3. The mean end-to-end distance of a linear chain with three beads and with the reflecting wall at $x = -16$. Initially, the beads are distributed by Eq. (8), where $d = -16$ and $h = 16$. The parameter in Eq. (7) are taken as $b = 16$ and $n = 1$, and 30,000 independent runs are taken.

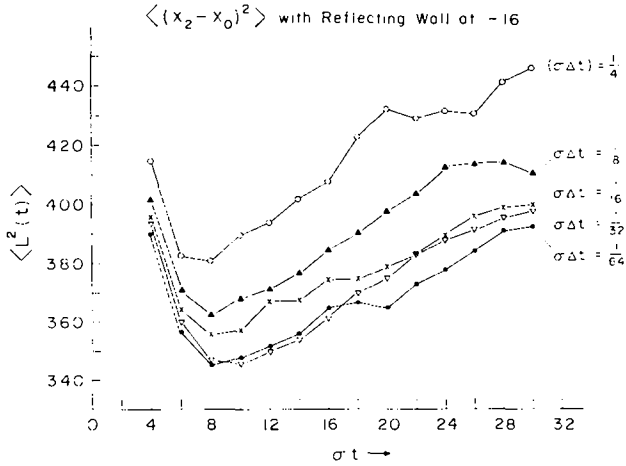


Fig. 4. The mean square end-to-end distance of a linear chain with three beads and with the reflecting wall at $x = -16$. Initially, the beads are distributed by Eq. (8), where $d = -16$ and $h = 16$. The parameters in Eq. (7) are taken as $b = 16$ and $n = 1$, and 30,000 independent runs are taken.

where $\langle \xi_j \rangle = \xi_j(0)\, e^{-\sigma\lambda_j t}$. The $\Psi$ obtained from the Gaussian initial distribution function is expressed in terms of the distance between successive beads $u_{i,i+1}$ as given by Eq. (37). However, Eq. (39) does not reduce to a function of $u_{i,i+1}$. From Eq. (39), we find that the mean and mean square end-to-end distances have the same expression as those given by Eqs. (10) and (24), respectively. Equation (39) was obtained by Wang and Uhlenbeck (Note IV in Appendix of Ref. 9). However, the time-dependent distribution function for a linear tensile relaxation as given by Eq. (37) is derived for the first time in this paper.

## 5. DISCUSSION

When a boundary condition is imposed on Eq. (7), it is not possible to obtain $\langle L(t, B_x) \rangle$ in a closed form. Only the Monte Carlo method is available for this case. Since this method is an iterative process starting from an initial position of beads, the error accumulates as the time progresses if we choose too large $\Delta t$. Too small a value of $\Delta t$, however, would take too much computer time. Equations (21) and (23) give a good estimate of the right magnitude of $\Delta t$ for given $\sigma$ and $N$. Since $\lambda_i$ is inversely proportional to $(N + 1)^2$ for small $i$, and only low values of $i$ contribute to the summation for sufficiently large $t$, $\Delta t$ could be chosen bigger for larger $N$. In order to demonstrate this numerically, we have computed the mean and mean square end-to-end distances of the linear chain by the Monte Carlo method with $\nu = \Delta t = 1$, $\sigma = 0.125$, and $b = 16$. Initially, the beads are distributed by Eq. (8) where $d = -hN/2$ and $h = 16$. The crosses in Figs. 1 and 2 are obtained by taking 50,000 and 400 independent runs, respectively, where the vertical lines indicate the magnitude of the standard deviations. The solid lines are obtained from Eqs. (10) and (24). As shown in these figures, the Monte Carlo result is very good for $N = 10$, while it is quite poor for $N = 2$. We have also studied the effect of a choice of $\Delta t$ on Eq. (7) by placing a simple boundary condition (Figs. 3 and 4). Initially, the zeroth, first, and second beads are placed at $x = -16$, 0, and 16 along the $x$ axis, respectively. The reflecting wall is located at $x = -16$. The parameters in Eq. (7) are taken to be $b = 16$ and $n = 1$. As we see from Fig. 4, we find that the computed values of $\langle L^2(t) \rangle$ differ for each $\Delta t$ in the interval of $1/4 \leqslant \sigma \Delta t \leqslant 1/64$.

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