

**REACTIONS GOVERNED BY  
A BINOMIAL REDISTRIBUTION PROCESS—  
THE EHRENFEST URN PROBLEM\***

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A distributive process of the binomial type in a one-dimensional discrete space with an absorbing barrier is studied. A simple expression for the particle number  $\Sigma(t)$  is derived. The analysis is based on recursion relationships and sum rules for the underlying eigenvectors, the Krawtchouk polynomials. The first passage time is determined, and the validity of the passage time approximation to  $\Sigma(t)$  tested. The continuous limit, corresponding to the diffusion and reaction of a harmonically bound particle, is briefly described.

## 1. Introduction

In this paper we will reconsider the Ehrenfest urn problem which characterises the simplest stochastic process giving rise to a binomial equilibrium distribution<sup>1,2</sup>). This problem derives its importance from the fact that it appears in various disguises in many situations of statistical mechanics. Our treatment given here differs from previous studies in that we will consider the problem in the context of a reaction process.

The Ehrenfest urn problem was devised originally to model the heat exchange between two containers. In regard to current interests in intramolecular relaxation, it may be assumed to model the exchange of vibrational quanta between two modes of a molecule<sup>3</sup>). The questions traditionally asked concerned the distribution of particles, assuming a random transfer of particles between the containers. However, one may envisage the situation that a reaction takes place whenever the particles in one of the containers exceed a certain maximum number (absorbing barrier). A realisation may be a molecule highly excited in a non-reactive vibrational mode which exchanges vibrational quanta between this mode and a reactive mode. One may then ask how the reaction will proceed in time. One may also want to estimate the

\* Dedicated to Ernst Ruch on the occasion of his 60th birthday.

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mean time for the reaction to take place. In the following we will derive the corresponding answers.

Our treatment below follows the solution of the Ehrenfest urn problem by Kac<sup>1)</sup> in that it relies on eigenvectors given by the Krawtchouk polynomials, generalizations of the Hermite polynomials<sup>4,5)</sup>. We drew much guidance from the relationship between the Krawtchouk and the Hermite polynomials by generalizing some needed properties of the latter.

The Ehrenfest urn problem gives rise also to the simplest description of the end-to-end diffusion of a polymer molecule, entailing the most important features of the realistic behaviour. As this notion allows for a clear physical language, we want to consider the Ehrenfest model in this disguise only. In section 2 we introduce the polymer formulation and solve the Ehrenfest model under reaction-free conditions. The aim of this section, which does not go beyond the Kac solution, is mainly pedagogical and to define our notation. In section 3 we assume reaction conditions and solve for the particle number. In section 4 the mean reaction time  $\tau$  will be evaluated. We will demonstrate that the polymer reaction is approximated rather well by an exponential decay,  $\exp(-t/\tau)$ . In section 5 we briefly rederive the results of sections 2 to 4 in the continuous limit, i.e. for an Einstein-Smoluchowski diffusion process giving rise to a Gaussian equilibrium distribution. As a trivial departure from most previous studies, we will assume all processes to proceed along a continuous time axis, i.e. we model the particle transfer between containers by first order kinetics, and not as events discrete in time.

## 2. End-to-end motion of one-dimensional polymer

We want to consider in this section the simplest model of a polymer. The archetype polymer is confined to a one-dimensional space and consists of  $2N$  segments of length one. Each segment can achieve two possible orientations, one in the positive and one in the negative direction. The polymer can assume thereby  $2^{2N}$  different conformations. We wish to focus, however, solely on the end-to-end distance of the polymer.

The end-to-end distance  $x$  assumes the value

$$x = 2j, \quad (2.1)$$

when  $N - j$  polymer segments are in the negative direction ( $j = -N, -N + 1, \dots, N$ ). The end-to-end distance  $x = 2j$  is realized for  $\binom{2N}{N+j}$  conformations. The vast majority (for large  $N$ ) of polymer conformations obviously corresponds to small  $x$  values. Assuming that at equilibrium all conformations

are equally likely, the equilibrium end-to-end distribution  $P_{0j}$  is

$$P_{0j} = 2^{-2N} \binom{2N}{N+j}. \quad (2.2)$$

We want to describe, however, the behaviour of the polymer under non-equilibrium conditions. A typical question may be: How fast is the equilibrium distribution attained by an ensemble of polymers after all polymers have been extended to a length  $x = 2m$ ?

For a description of the stochastic motion of the end-to-end distribution one needs to know the rate of fluctuation between positive and negative segment orientations. We assume that the fluctuations of all segments are independent and are governed by the rate equation

$$\frac{d}{dt} \begin{bmatrix} p \\ n \end{bmatrix} = \frac{1}{\tau_R} \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \begin{bmatrix} p \\ n \end{bmatrix}, \quad (2.3)$$

where the vector  $\begin{bmatrix} p \\ n \end{bmatrix}$  accounts for the occupation of positive ( $p$ ) and negative ( $n$ ) segment orientations. With these assumptions, the problem of describing the end-to-end diffusion of the polymer through its  $2^{2N}$ -dimensional configuration space can be reduced to a diffusion problem described by a master equation in the much more confined  $(2N + 1)$ -dimensional space of the end-to-end distribution  $P(j, t)$ :

$$\tau_R \frac{d}{dt} P(j, t) = -2NP(j, t) + (N + j + 1)P(j + 1, t) + (N - j + 1)P(j - 1, t). \quad (2.4)$$

This equation follows directly from the observation that single segment reorientations yield  $2N$  ways to change a  $x = 2j$  conformation either into a  $x = 2j + 2$  or  $x = 2j - 2$  conformation,  $N - j + 1$  ways to change a  $x = 2j - 2$  conformation into a  $x = 2j$  conformation, and  $N + j + 1$  ways to change a  $x = 2j + 2$  conformation into a  $x = 2j$  conformation. Eq. (2.4) is equivalent to the master equation in ref. 1 describing an elastically bound particle and to the Ehrenfest model, except for the trivial difference of a continuous time variable.

We may note here for later use that eq. (2.4) may also be cast into the operator form

$$\tau_R \frac{d}{dt} \mathbf{P}(t) = \mathbf{O} \mathbf{P}(t), \quad (2.5)$$

where the vector

$$[\mathbf{P}(t)]_j = P(j, t) \quad (2.6)$$

describing the time-dependent end-to-end distribution and the stochastic operator  $O$  is a tri-diagonal matrix with elements

$$O_{ji} = \begin{cases} N-j+1 & \text{if } i=j-1 \\ -2N & \text{if } i=j \\ N+j+1 & \text{if } i=j+1 \\ 0 & \text{otherwise.} \end{cases} \quad (2.7)$$

As a demonstration of the behaviour described by eq. (2.4) we will show that any polymer extended to some end-to-end distance  $x = 2m$  described by the initial condition

$$P(j, t=0) = \delta_{jm} \quad (2.8)$$

decays towards the equilibrium distribution. For this purpose we define the generating function

$$g(x, t) = \sum_{j=-N}^{+N} P(j, t | m, 0) x^j. \quad (2.9)$$

Eq. (2.4) implies then the differential equation

$$\tau_R \frac{\partial}{\partial t} g(x, t) = N(x + x^{-1} - 2)g(x, t) + (1 - x^2) \frac{\partial}{\partial x} g(x, t) \quad (2.10)$$

and the initial condition (2.8) imposes

$$g(x, t=0) = x^m. \quad (2.11)$$

Eq. (2.10) gives rise to the eigenvalue problem

$$\left[ (1 - x^2) \frac{\partial}{\partial x} + N(x + x^{-1} - 2) \right] g_k(x) = \lambda(k) g_k(x), \quad (2.12)$$

which is solved by ( $k = 0, 1, 2, \dots, 2N$ )

$$g_k(x) = x^{-N} (1+x)^{2N-k} (1-x)^k, \quad (2.13)$$

$$\lambda(k) = -2k. \quad (2.14)$$

The generating function  $g(x, t)$  is profitably expanded in terms of these eigenfunctions

$$g(x, t) = x^{-N} \sum_{k=0}^{2N} a_k (1+x)^{2N-k} [\exp(-2t/\tau_R)(1-x)]^k, \quad (2.15)$$

for as the initial condition (2.11) may be written

$$g(x, t=0) = 2^{-2N} x^{-N} [(1+x) + (1-x)]^{N-m} [(1+x) - (1-x)]^{N+m} \quad (2.16)$$

one can immediately conclude

$$g(x, t) = 2^{-2N} x^{-N} [1 + x + \exp(-2t/\tau_R)(1-x)]^{N-m} \times [1 + x - \exp(-2t/\tau_R)(1-x)]^{N+m}. \quad (2.17)$$

According to the definition (2.9) of the generating function the distribution  $P(j, t | m, 0)$  can be abstracted from this expression by expansion in terms of powers of  $x$ . Inspection of (2.17) shows that at long times  $g(x, t)$  becomes independent of the starting distance  $x = 2m$

$$g(x, t) \underset{t \rightarrow \infty}{\sim} 2^{-2N} x^{-N} (1+x)^{2N} = 2^{-2N} \sum_{j=-N}^{+N} \binom{2N}{N+j} x^j, \quad (2.18)$$

i.e.  $P(j, t | m, 0)$  approaches the equilibrium distribution (2.2) at long times. Because any initial distribution can be regarded as a superposition of (2.8), we have, thus, shown that any solution of the master equation (2.4) decays towards the equilibrium distribution. This is, of course, to be expected: according to (2.15) the relaxation times for the contributions of  $g_k(x)$  are  $\tau_R/2k$  so that at long times only  $g_0(x)$  remains.

### 3. End-end reaction of one-dimensional polymer

We will describe now by means of the master equation (2.4) polymers which undergo a reaction when their ends meet at  $x=0$ . The aim is to evaluate for such situation the fraction of polymers unreacted yet at time  $t$

$$\Sigma(t) = \sum_{j=1}^N P(j, t) \quad (3.1)$$

for any initial distribution  $P(j, t=0)$ . We will assume here and in the following  $\Sigma(0) = 1$ . As the reaction at  $x=0$  depletes the corresponding polymers, one has to impose the boundary condition

$$P(j=0, t) = 0. \quad (3.2)$$

Since the occurrence of the reaction effectively divides the diffusion space into two halves, i.e.  $j > 0$  and  $j < 0$ , the sum in (3.1) may involve only positive  $j$  values.

$\Sigma(t)$  is most conveniently evaluated starting from the expression for the reaction rate

$$\frac{d}{dt} \Sigma(t) = -\frac{N+1}{\tau_R} P(1, t), \quad (3.3)$$

which results from a summation of (2.4). The eigenvector expansion of the initial distribution,

$$P(0) = \sum_{k=0}^{2N} \alpha_k P_k, \quad (3.4)$$

leads to

$$P(j, t) = \sum_{k=0}^{2N} \alpha_k \exp[\lambda(k)t/\tau_R] P_{kj}, \quad (3.5)$$

or

$$\frac{d}{dt} \Sigma(t) = -\frac{N+1}{\tau_R} \sum_{k=0}^{2N} \alpha_k \exp[\lambda(k)t/\tau_R] P_{k1}. \quad (3.6)$$

Integration yields

$$\Sigma(t) = -(N+1) \sum_{k=0}^{2N} \alpha_k \lambda(k)^{-1} \exp[\lambda(k)t/\tau_R] P_{k1}. \quad (3.7)$$

For an evaluation of  $\Sigma(t)$  one needs to determine the (right) eigenvectors  $P_k$  of  $O$ . They are provided by the generating function  $g_k(x)$  defined in eq. (2.13) by means of<sup>6</sup>

$$g_k(x) = \sum_{j=-N}^{+N} P_{kj} x^j, \quad (3.8)$$

viz.

$$P_{kj} = \sum_s (-1)^s \binom{k}{s} \binom{2N-k}{N+j-s}. \quad (3.9)$$

The spectrum  $\lambda(k)$  of  $O$  is given by (2.14). The properties of the eigenvectors needed in the further calculation are best abstracted from the generating function

$$\begin{aligned} G(x, y) &= x^{-N} [1 + x + y(1-x)]^{2N} \\ &= \sum_{k=0}^{2N} \sum_{j=-N}^{+N} \binom{2N}{k} P_{kj} y^k x^j, \end{aligned} \quad (3.10)$$

which follows directly from (2.13) and (3.8). One can immediately derive from this relationship the symmetry property

$$P_{k-j} = (-1)^k P_{kj}. \quad (3.11)$$

This implies  $P_{k0} = 0$  for  $k$  odd, and together with

$$(2k-2N)P_{kj} + (N-j+1)P_{kj+1} + (N-j+1)P_{kj-1} = 0, \quad (3.12)$$

a restatement of the eigenvector property  $OP_k = -2kP_k$ , it implies  $P_{k0} \neq 0$  for  $k$  even. From this follows that the expansion (3.5) and, hence, (3.7) entails only

odd  $k$  values:

$$\Sigma(t) = (N+1) \sum_{k=1}^N \frac{\alpha_{2k-1}}{4k-2} \exp[-(4k-2)t/\tau_R] P_{2k-11}. \quad (3.13)$$

Clearly,

$$\lim_{t \rightarrow \infty} \Sigma(t) = 0, \quad (3.14)$$

i.e. all polymers finally undergo reaction. The decay of  $\Sigma(t)$  is dominated at long times by the longest relaxation time  $\frac{1}{2}\tau_R$ .

As  $O$  is not a symmetric operator, its eigenvectors are not orthogonal. The transformation  $S^{-1}OS$

$$S_{ij} = \left( \frac{2N}{N+j} \right)^{1/2} \delta_{ij} \quad (3.15)$$

brings  $O$  to a symmetric form and, hence, provides an orthogonal basis  $S^{-1}P_k$ , i.e.

$$\sum_{j=-N}^{+N} \left( \frac{2N}{N+j} \right)^{-1} P_{kj} P_{kj} = \sigma_k \delta_{kk}. \quad (3.16)$$

This orthogonality relationship allows us to determine the expansion coefficients  $\alpha_k$  defined in (3.4)

$$\alpha_k = S^{-2} P_k \cdot P(0) / S^{-2} P_k \cdot P_k. \quad (3.17)$$

In the appendix we derive for the case that the initial distribution is equal to the equilibrium distribution for  $j > 0$ , but vanishes for  $j \leq 0$ ,

$$\alpha_{2k-1} = \frac{N+1}{2k-1} 2^{-2N} \binom{2N}{2k-1} P_{2k-11}. \quad (3.18)$$

Hence,

$$\Sigma(t) = 2^{-2N-1} \sum_{k=1}^N \frac{(N+1)^2}{(2k-1)^2} \binom{2N}{2k-1} P_{2k-11}^2 \exp[-(4k-2)t/\tau_R]. \quad (3.19)$$

This expression is readily evaluated. The result is presented in fig. 1 for a polymer with 40 bonds ( $N = 20$ ).

#### 4. First passage time approximation

Expression (3.19) demonstrates that the end-end reaction of polymers is described by relaxation times  $(1/2)\tau_R$ ,  $(1/6)\tau_R$ ,  $(1/10)\tau_R$ , etc. The longest

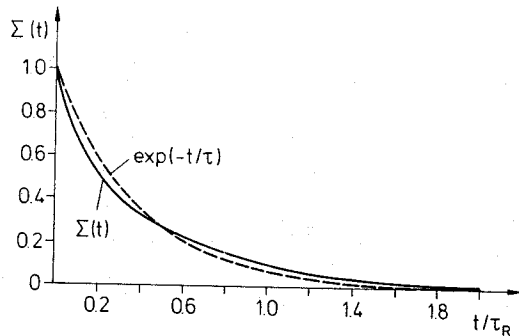


Fig. 1. One-dimensional discrete polymers ( $2N = 40$ ) undergoing binomial end-end diffusion and an end-end reaction: comparison of the fraction of polymers yet unreacted at time  $t$ ,  $\Sigma(t)$  as given by eq. (3.19), and its first passage time approximation  $\exp(-t/\tau)$ ,  $\tau$  evaluated from eq. (4.17).

relaxation time  $(1/2)\tau_R$  will dominate the behaviour of  $\Sigma(t)$  as the contribution of the shorter relaxation time should decay fast. The question arises how well  $\Sigma(t)$  can be approximated over its whole time course by a single exponential, i.e.

$$\Sigma(t) \approx \exp(-t/\tau). \quad (4.1)$$

The effective relaxation time  $\tau$ , the so-called first passage time<sup>7</sup>, is determined by

$$\tau = \int_0^{\infty} dt \Sigma(t). \quad (4.2)$$

We want to show now that  $\Sigma(t)$  can indeed be approximated rather well by (4.1), (4.2) and demonstrate furthermore that the first passage time  $\tau$  can be evaluated with little effort.

Let  $P(j, t | m, 0)$ ,  $\Sigma(t | m)$ ,  $\tau_m$  be the distribution, fraction of polymers unreacted yet, and the first passage time for a polymer ensemble which starts to diffuse at time  $t = 0$  with an end-to-end distance  $x = 2m$  and subsequently undergoes an end-end reaction. One can derive from (2.5)

$$P(j, t | m, 0) = \left[ \exp\left(\frac{t}{\tau_R} O\right) \right]_{jm} = \left[ \exp\left(\frac{t}{\tau_R} O^T\right) \right]_{mj}, \quad (4.3)$$

where  $O^T$  stands for the transpose of  $O$ . The first equation entails the recursion equation (2.4). The second equation, though seemingly trivial, yields an important new master equation, the adjoint equation

$$\tau_R \frac{d}{dt} P(j, t | m, 0) = \sum_n O_{kn} P(j, t | n, 0) \quad (4.4)$$

or

$$\begin{aligned} \tau_R \frac{d}{dt} P(j, t | m, 0) = & -2NP(j, t | m, 0) + (N - m)P(j, t | m + 1, 0) \\ & + (N + m)P(j, t | m - 1, 0). \end{aligned} \quad (4.5)$$

Summation over  $j$  results in

$$\begin{aligned} \tau_R \frac{d}{dt} \Sigma(t | m) = & -2N\Sigma(t | m) + (N - m)\Sigma(t | m + 1) \\ & + (N + m)\Sigma(t | m - 1), \end{aligned} \quad (4.6)$$

an equation which has to be supplemented by the boundary condition

$$\Sigma(t | 0) = 0. \quad (4.7)$$

Integration over  $t$  yields by virtue of  $\Sigma(0 | m) = 1$  [for  $m \neq 0$ ] a recursion relationship and boundary condition for the first passage times  $\tau_m$  ( $m = 1, 2, \dots, N$ )

$$-2N\tau_m + (N - m)\tau_{m+1} + (N + m)\tau_{m-1} = -\tau_R, \quad (4.8)$$

$$\tau_0 = 0. \quad (4.9)$$

This equation will be solved now.

The solution of (4.8), (4.9) goes in two steps: first the differences

$$d_m = \tau_m - \tau_{m-1}, \quad m = 1, 2, \dots, N \quad (4.10)$$

will be determined, and then the first passage times by means of

$$\tau_m = \sum_{n=1}^m d_n. \quad (4.11)$$

The differences  $d_m$  obey the inhomogeneous equation

$$(N - m)d_{m+1} - (N + m)d_m = -\tau_R. \quad (4.12)$$

Multiplication by  $\binom{2N}{N+m}$  results in

$$2N \binom{2N-1}{N-m-1} d_{m+1} - 2N \binom{2N-1}{N-m} d_m = -\binom{2N}{N+m} \tau_R, \quad (4.13)$$

from which follows

$$d_m = \frac{\tau_R}{2N} \binom{2N-1}{N-m}^{-1} \sum_{i=m}^N \binom{2N}{N+i}. \quad (4.14)$$

The resultant first passage times  $\tau_m$  are

$$\tau_m = \frac{\tau_R}{2N} \sum_{n=1}^m \binom{2N-1}{N-n}^{-1} \sum_{i=n}^N \binom{2N}{N+i}. \quad (4.15)$$

The first passage time  $\tau$  for the initial equilibrium distribution  $P_0$ ,  $j > 0$ , defined as

$$\tau = \sum_{m=1}^N \binom{2N}{N+m} \tau_m / \sum_{m=1}^N \binom{2N}{N+m}, \quad (4.16)$$

is given by the expression

$$\tau = \tau_R \left[ 2N \sum_{j=1}^N \binom{2N}{N+j} \right]^{-1} \sum_{j=1}^N \binom{2N-1}{N-j}^{-1} \left[ \sum_{i=j}^N \binom{2N}{N+i} \right]^2. \quad (4.17)$$

Fig. 1 demonstrates for a polymer with 40 bonds that the agreement between the exact  $\Sigma(t)$  and its first passage time approximation  $\exp(-t/\tau)$  is very close. The first passage time  $\tau$  is in this case  $0.389\tau_R$ . As to be expected,  $\tau$  is shorter than the longest relaxation time of the exact expression of  $\Sigma(t)$ , which is  $\tau_1 = \frac{1}{2}\tau_R$  but longer than the shorter relaxation times  $\tau_2, \tau_3, \dots = (1/6)\tau_R, (1/10)\tau_R, \dots$

## 5. The continuum limit

For long polymers ( $N$  large) the equilibrium distribution (2.2) is approximated well by the continuous Gaussian distribution ( $x = 2bj$ )

$$P_0(x) = (4\pi b^2 N)^{-1/2} \exp(-x^2/4b^2 N). \quad (5.1)$$

This suggests that the discrete master equation (2.4) may be represented by a diffusion equation which yields (5.1) as its equilibrium distribution. The corresponding equation is the Einstein-Smoluchowski equation<sup>1)</sup>

$$\tau_R \frac{\partial}{\partial t} p(x, t) = \left( 4Nb^2 \frac{\partial^2}{\partial x^2} + 2 \frac{\partial}{\partial x} x \right) p(x, t), \quad (5.2)$$

where  $b$  stands for the bond length of the polymer and  $x = 2bj$  denotes the end-to-end distance.

We want to describe now continuous one-dimensional polymers which undergo a reaction when their ends meet, i.e. at  $x = 0$ . The fraction of polymers unreacted is

$$\Sigma(t) = \int_0^{\infty} dx p(x, t). \quad (5.3)$$

The occurrence of the reaction imposes the boundary condition

$$p(x = 0, t) = 0 \quad (5.4)$$

on the solution of (5.2). The diffusion space is thereby divided into two disjunct intervals,  $x > 0$  and  $x < 0$ . In order to keep a close analogy to the derivation in section 4, we will obtain  $\Sigma(t)$  by means of an eigenfunction expansion:

$$P(x, t) = \sum_k c_k \exp[\lambda(k)t/\tau_R] P_k(x/2b\sqrt{N}), \quad (5.5)$$

where ( $y = x/2b\sqrt{N}$ )

$$\left( \frac{\partial^2}{\partial y^2} + 2 \frac{\partial}{\partial y} y \right) P_k(y) = \lambda(k) P_k(y). \quad (5.6)$$

The solutions of (5.6) are given by the Hermite polynomials  $H_k$

$$P_k(y) = \exp(-y^2) H_k(y), \quad (5.7)$$

$$\lambda(k) = -2k. \quad (5.8)$$

Eqs. (5.7) and (5.8) imply that the Hermite polynomials, i.e.  $P_k(y = j/\sqrt{N})$ , represent the continuous limits of the eigenvectors  $P_{kj}$  above, a relationship which has been derived by Krawtchouk<sup>4)</sup>. Fig. 2 compares the orthonor-

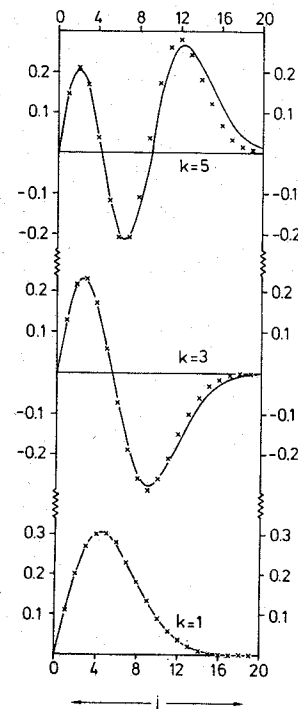


Fig. 2. Comparison of the orthonormalized eigenvectors of the binomial diffusion operator  $2^{-N} \binom{2N}{k}^{1/2} \binom{2N}{N+j}^{-1/2} P_{kj}$  presented by (x), and of the orthonormalized Hermite polynomials  $[2^k N k! \sqrt{\pi}]^{-1/2} \exp(-j^2/2N) H_k(j/\sqrt{N})$  presented by (—), for  $2N = 40$ .

malized polynomials

$$2^{-N} \binom{2N}{k}^{1/2} \binom{2N}{N+j}^{-1/2} P_{kj}$$

and  $[2^k N k! \sqrt{\pi}]^{-1/2} \exp(-j^2/2N) H_k(j/\sqrt{N})$  for  $N = 20$  to illustrate that only for small  $k$  or  $j$  the agreement between the polynomials is satisfactory.

The boundary condition (5.4) eliminates all even eigenfunctions from expansion (5.5), i.e.

$$p(x, t) = \sum_{k=0}^{\infty} c_{2k+1} \exp[-(4k+2)t/\tau_R - y^2] H_{2k+1}(y). \quad (5.9)$$

The coefficients  $c_{2k+1}$  have to comply with the initial condition

$$p(x, t=0) = P_0(x) \quad \text{for } x > 0, \quad (5.10)$$

hence,

$$(b\sqrt{\pi N})^{-1} = \sum_{k=0}^{\infty} c_{2k+1} H_{2k+1}(y). \quad (5.11)$$

One obtains<sup>8)</sup>

$$c_{2k+1} = (-1)^k [b\pi 2^{2k} (2k+1)k! \sqrt{N}]^{-1}, \quad (5.12)$$

and for  $\Sigma(t)$  then

$$\begin{aligned} \Sigma(t) &= \frac{2}{\pi} \sum_{k=0}^{\infty} (-1)^k [2^{2k} (2k+1)k!]^{-1} \\ &\times \exp[-(4k+2)t/\tau_R] \int_0^{\infty} dy \exp(-y^2) H_{2k+1}(y). \end{aligned} \quad (5.13)$$

Integration of (5.6) yields

$$\int_0^{\infty} dy \exp(-y^2) H_{2k+1}(y) = H_{2k}(0) \quad (5.14)$$

and, finally<sup>9)</sup>,

$$\Sigma(t) = \frac{2}{\pi} \sum_{k=0}^{\infty} (2k)! [2^{2k} (k!)^2 (2k+1)]^{-1} \exp[-(4k+2)t/\tau_R], \quad (5.15)$$

which is recognized as the Taylor expansion of

$$\Sigma(t) = \frac{2}{\pi} \sin^{-1}(e^{-2t/\tau_R}). \quad (5.16)$$

The derivation of eqs. (5.12)–(5.15) involves those properties of Hermite

polynomials which, in the course of obtaining (3.19), have been generalized to Krawtchouk polynomials.

As in the case of discrete polymers, it is to be expected that the longest relaxation time  $\tau_R/2$  in (5.15) will dominate the decay of  $\Sigma(t)$ . The question again arises if  $\Sigma(t)$  can be approximated over its whole time course by a single exponential, i.e. through eqs. (4.1) and (4.2). The evaluation of the corresponding first passage time  $\tau(x_0)$  for an ensemble of polymers starting at time  $t = 0$  at an end-to-end distance  $x_0$  follows closely the treatment in section 4.

Let  $p(x, t | x_0, 0)$  and  $\Sigma(t | x_0)$  be the polymer distribution and polymer fraction unreacted at time  $t$ . Eq. (4.4) in the continuous case has to be replaced by the adjoint equation<sup>10)</sup> of (5.2)

$$\tau_R \frac{\partial}{\partial t} p(x, t | x_0, 0) = \left( 4Nb^2 \frac{\partial^2}{\partial x_0^2} - 2x_0 \frac{\partial}{\partial x_0} \right) p(x, t | x_0, 0), \quad (5.17)$$

together with the adjoint boundary condition

$$p(x, t | x_0 = 0, 0) = 0. \quad (5.18)$$

Integration over  $x$  yields

$$\tau_R \frac{\partial}{\partial t} \Sigma(t | x_0) = \left( 4Nb^2 \frac{\partial^2}{\partial x_0^2} - 2x_0 \frac{\partial}{\partial x_0} \right) \Sigma(t, x_0). \quad (5.19)$$

Integration over  $t$  by virtue of the initial condition  $\Sigma(0, x) = 1$  results then in the first passage time equation

$$4Nb^2 \frac{d^2}{dx_0^2} \tau(x_0) - 2x_0 \frac{d}{dx_0} \tau(x_0) = -\tau_R, \quad (5.20)$$

together with

$$\tau(0) = 0. \quad (5.21)$$

The solution of (5.20) and (5.21) goes again in two steps, solving first for  $d\tau(x_0)/dx_0$  and then for  $\tau(x_0)$  to obtain, instead of (4.15),

$$\tau(x_0) = (\tau_R/4Nb^2) \int_0^{x_0} dx \exp(x^2/4Nb^2) \int_x^{\infty} dy \exp(-y^2/4Nb^2). \quad (5.22)$$

The first passage time for an ensemble of polymers initially in the equilibrium distribution (5.1), i.e.

$$\tau = (b\sqrt{\pi N})^{-1} \int_0^{\infty} dx_0 \tau(x_0) \exp(-x_0^2/4Nb^2) \quad (5.23)$$

is now [cf. eq. (4.17)]

$$\tau = (2\tau_R/\sqrt{\pi}) \int_0^\infty dx \exp(x^2) \left[ \int_x^\infty dy \exp(-y^2) \right]^2. \quad (5.24)$$

But only in the continuous case can  $\tau$  be reduced to the simple expression {note<sup>11</sup>}  $[\int_x^\infty dy \exp(-y^2)]^2 = \int_x^\infty dt (1+t^2)^{-1} \exp[-x^2(1+t^2)]$

$$\tau = (\tau_R/2) \ln 2. \quad (5.25)$$

Fig. 3 demonstrates the agreement between the exact  $\Sigma(t)$  given by (5.16) and its first passage time approximation  $\exp(-t/\tau)$ . The first passage time for the continuous case, i.e. eq. (5.25), amounts to 0.347, and that for a discrete polymer with  $N = 40$  to 0.389. An illustration of the merit of the passage time approximation for more general situations has been given in ref. 12.

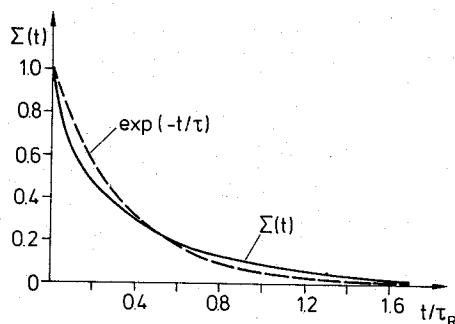


Fig. 3. One-dimensional continuous polymers undergoing Gaussian end-end diffusion and an end-end reaction: comparison of the fraction of polymers yet unreacted at time  $t$ ,  $\Sigma(t)$  as given by eq. (5.16), and its first passage time approximation  $\exp(-2t/\tau_R \ln 2)$ .

## Appendix

### Sum rules for $P_{kj}$

We want to evaluate the two sums

$$S^{-2} P_k \cdot P(0) = \sum_{j=1}^N P_{kj}, \quad (A.1)$$

$$S^{-2} P_k \cdot P_k = \sum_{j=1}^N \binom{2N}{N+j}^{-1} P_{kj}^2. \quad (A.2)$$

Summation over the eigenvalue equation (3.12) yields for odd  $k$ , i.e.  $P_{k0} = 0$

$$\sum_{j=1}^N P_{kj} = \frac{N+1}{2k} P_{k1}. \quad (A.3)$$

The evaluation of (A.2) is somewhat more elaborate. Starting points are two differential equations for the generating function (3.10)

$$[1+x+y(1-x)] \frac{\partial}{\partial y} G(x,y) = 2N(1-x)G(x,y), \quad (A.4)$$

$$(1-y) \frac{\partial}{\partial y} G(x,y) = (1-x) \frac{\partial}{\partial x} G(x,y) + ((N/x) - N)G(x,y), \quad (A.5)$$

which imply the recursion equations

$$P_{kj} - P_{k+1j} - P_{k+1j-1} - P_{kj-1} = 0, \quad (A.6)$$

$$(2N-k)P_{k+1j} - (N+j+1)P_{kj+1} + (N+j-k)P_{kj} = 0. \quad (A.7)$$

Combination of these relationships yields

$$(2N-k)P_{k+1j} + 2jP_{kj} + kP_{k-1j} = 0. \quad (A.8)$$

Multiplying (A.8) by  $P_{k-1j}$  and subtracting the same recursion equation taken for  $k-1$  and multiplied by  $P_{kj}$  we obtain

$$kP_{k-1j}^2 + (2N-k)P_{k+1j}P_{k-1j} - (k-1)P_{k-2j}P_{kj} - (2N-k+1)P_{kj}^2 = 0. \quad (A.9)$$

Multiplying this relationship by  $\binom{2N}{N+j}^{-1}$  and summing over  $j$  yields by virtue of the orthogonality relationship (3.16)

$$\sigma_k = \frac{k}{2N-k+1} \sigma_{k-1} \quad (A.10)$$

or, by iteration,

$$\sigma_k = \binom{2N}{k}^{-1} \sigma_0. \quad (A.11)$$

As  $\sigma_0$  is readily evaluated, one has

$$\sigma_k = 2^{2N} \binom{2N}{k}^{-1}. \quad (A.12)$$

For odd  $k$  the sum in (A.2), which involves only positive  $j$  values, is just  $\frac{1}{2}\sigma_k$ . Combination of this result and (A.3) yields finally

$$\alpha_k = 2^{-2N} \frac{N+1}{k} \binom{2N}{k} P_{k1}. \quad (A.13)$$

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## References

- 1) M. Kac, *Am. Math. Monthly* **43** (1947) 369.
- 2) W. Feller, *An Introduction to Probability Theory and its Applications*, (John Wiley, New York, 1968), Vol. 1, rev. ed.
- 3) This problem has been addressed recently in the context of discrete statistical models and functions by M.R. Hoare and M. Rahman, *Physica* **97A** (1979) 1.
- 4) M. Krawtchouk, *C.R. Acad. Sci. Paris* **189** (1929) 620.
- 5) G. Szegő, *Orthogonal Polynomials*, Amer. Math. Soc. Colloquium Publications **23** (1959) rev. ed.
- 6) The  $P_{ij}$  are identical with the coefficients  $C_{j+N}^{(k-N)}$  of Kac<sup>1</sup>, and with  $\binom{2N}{j+N} \binom{2N}{+k}^{-1/2} P_k(j+N)$ , where  $P_k(x)$  stands for the Krawtchouk polynomials as defined in ref. 4 for  $p = q = \frac{1}{2}$ . These latter polynomials have also been studied by J.P. Gram, *J. für Math.* **114** (1982) 41 and by H.E.H. Greenleaf, *Ann. Math. Statistics* **3** (1932) 204.
- 7) An excellent introduction to first passage times for discrete and continuous models is N.S. Goel and N. Richter-Dyn, *Stochastic Models in Biology* (Academic Press, New York, 1974).
- 8) N.N. Lebedev, *Special Functions and their Applications*, (Prentice-Hall, Englewood Cliffs, 1965), eq. (4.9.6).
- 9) Ref. 8, eq. (4.9.4).
- 10) See for example P.M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw Hill, New York, 1953).
- 11) Ref. 8, page 29.
- 12) A. Szabo, K. Schulten and Z. Schulten, *J. Chem. Phys.* (in press).