First-passage problem for the Rouse polymer chain: An exact solution

A. E. Likhtman[1] and C. M. Marques[2]

[1] *Department of Applied Mathematics, University of Leeds - Leeds LS2 9JT, UK*
[2] *Institut Charles Sadron-CNRS UP 22 - 6 rue Boussingault*
67083 Strasbourg Cedex, France

Abstract. – We solve the first-passage problem of a non-Markovian process arising in the reaction diffusion theory of polymer chains. By considering the Rouse chain, a free-draining dynamic model of a polymer where the chain monomers are represented by beads and the chain connectivity by harmonic springs, we develop an exact analytical method for describing the kinetics of end-chain reactions. Our analytical results illuminate the approximations used previously and are in perfect agreement with numerical stochastic simulations.

Introduction. – The first-passage problem, also known as the Kramers problem in reaction theory, arises in many areas of physics [1]. In its simplest form it refers to a Brownian particle that diffuses until it comes within the capture radius of a reactive site and a reaction takes place. Other more complex situations include systems with many particles and many reaction sites, reactions with moving traps or interactions between the particles and the reaction targets [2]. Kramers seminal work and later developments of his method [3] have allowed in many cases the calculation of relevant physical quantities such as the survival probability $\rho(t)$, the fraction of particles which have not yet reacted at time t.

In polymer physics, first-passage problems have received much attention since it was first realized [4] that the study of fast reactions between groups attached to a polymer chain can provide a direct measure of the relaxation mechanisms governing polymer dynamics [5]. Theoretical studies have been devoted to chain cyclization, to reactions between different polymer chains leading to branching or polymerization and to reactions between polymer chains and stationary traps [6–9]. Interestingly, the first-passage time is also a key ingredient of the tube theory for the dynamics of entangled polymer melts. The tube theory assumes that stress relaxation in a strained melt is provided by the diffusive motion of a given chain out of its confinement tube, which represents the average topological influence of other chains. The stress relaxation is thus proportional to $\mu(t)$, the fraction of the tube length not visited by the chain ends after time t [10–12].

The motion of a monomer attached to a polymer chain has a strong non-Markovian character due to chain connectivity. Because of this, analytical theories of reaction diffusion in polymer physics have so far relied exclusively on approximated methods. In fact, numerical simulations show that the best existing theoretical predictions for the reaction times can be significantly different from the simulated results [13]. In this letter we present exact results for

the first-passage problem of the Rouse chain model, and show that results from our method are in perfect agreement with stochastic numerical simulations.

The model. – The Rouse model describes a polymer chain by $N + 1$ Brownian beads with friction coefficient ζ, connected by harmonic springs with spring constant $3k_BTb^{-2}$, where b is a Kuhn segment length, k_B is the Boltzman constant and T the temperature. The harmonic energy associated with a given configuration of the chain is therefore given by $U(\boldsymbol{R}_0, \ldots, \boldsymbol{R}_N) = 3/2 \, k_BTb^{-2} \sum_{i=1}^{N} (\boldsymbol{R}_i - \boldsymbol{R}_{i-1})^2$, where $\boldsymbol{R}_i$ are the coordinates of i-th segment. The motion of the chain can be described by the Langevin equations

$$\zeta \mathrm{d}\boldsymbol{R}_i = -\frac{\partial U}{\partial \boldsymbol{R}_i}\mathrm{d}t + \sqrt{2k_BT\zeta}\mathrm{d}\boldsymbol{W}_i, \tag{1}$$

where $\boldsymbol{W}_i$ is a Wiener process representing random Gaussian noise. The corresponding probability distribution $\Psi(\boldsymbol{R}_0, \ldots, \boldsymbol{R}_N)$ for the monomer coordinates obeys the diffusion equation

$$\hat{L}\Psi \equiv \frac{\partial \Psi}{\partial t} - \sum_i \left[\frac{k_BT}{\zeta}\frac{\partial^2 \Psi}{\partial \boldsymbol{R}_i^2} + \frac{1}{\zeta}\frac{\partial}{\partial \boldsymbol{R}_i}\left(\Psi\frac{\partial U}{\partial \boldsymbol{R}_i}\right)\right] = \delta(t)\Psi_0 \tag{2}$$

with $\hat{L}$ being the usual multidimensional diffusion operator including intrachain potential and Ψ_0 being the initial value of the distribution.

The first-passage problem for the chain end can be formulated as a boundary condition problem. The probability density for configurations where the chain end $\boldsymbol{R}_0$ has not visited the reactive site $\boldsymbol{Z}$ can be obtained from a solution of equation (2) with boundary condition

$$\Psi(\boldsymbol{R}_0 = \boldsymbol{Z}, \boldsymbol{R}_1, \ldots, \boldsymbol{R}_N) = 0. \tag{3}$$

If this solution $\Psi(\boldsymbol{R}, t)$ is available, then the fraction of unreacted molecules is given by the integral over the whole configuration space:

$$\rho(t) = \int \Psi(\boldsymbol{R}, t)\mathrm{d}\boldsymbol{R}. \tag{4}$$

Equation (2) without the boundary condition can be easily solved using transformation to Rouse modes [11]. The immense complexity of the problem arises from the fact that the boundary condition eq. (3) couples all Rouse modes. making it impossible to reduce the N-dimensional problem to a set of one-dimensional problems.

Previous work. – Reaction diffusion problems in polymers were first addressed theoretically by Wilemski and Fixman [4] (WF) who considered a more general formulation of the reaction problem by introducing the sink operator $q \, Q(\boldsymbol{R})$, which is proportional to the probability that the system with coordinates $\boldsymbol{R}$ will react. The shape of $Q(\boldsymbol{R})$ can accommodate some molecular information concerning the local reaction landscape. The parameter q measures the probability of the reaction and allows to tune the binding frequency. The diffusion equation (2) then becomes

$$\hat{L}\Psi = \delta(t)\Psi_0 - qQ\Psi. \tag{5}$$

The absorbing boundary condition (3) is recovered with a delta function for the sink shape $Q(\boldsymbol{R}) = \delta(\boldsymbol{R}_0 - \boldsymbol{Z})$ and an infinitely large strength $q \to \infty$. Equation (5) can be rewritten as an integral equation for $\Psi(\boldsymbol{R}, t)$:

$$\Psi(\boldsymbol{R}, t) = \Psi_{eq}(\boldsymbol{R}) - q\int\limits_0^t \mathrm{d}t' \int \mathrm{d}\boldsymbol{R}^0 G_0(\boldsymbol{R}^0, \boldsymbol{R}, t - t')Q(\boldsymbol{R}^0)\Psi(\boldsymbol{R}^0, t'), \tag{6}$$

where $\Psi_{eq}(\boldsymbol{R})$ and $G_0(\boldsymbol{R}^0, \boldsymbol{R}, t)$ are, respectively, the equilibrium distribution and the Green's function in the absence of reactions. Superscript 0 refers to the initial values $\boldsymbol{R}^0 = \boldsymbol{R}(t = 0)$. Formally, the Green's function is the solution of eq. (2) with initial condition $\Psi(\boldsymbol{R}, t = 0) = \delta(\boldsymbol{R} - \boldsymbol{R}^0)$. It represents the probability density to find the system at point $\boldsymbol{R}$ at time t provided it was at $\boldsymbol{R}^0$ at time zero. Equation (6) has a simple physical meaning: the surviving configurations are all those that have not reacted by visiting the reaction site at any time before the present. The validity of eq. (6) can be checked by direct substitution in eq. (2). For the end chain reactions $Q(\boldsymbol{R})$ depends only on one coordinate: the distance between the monomer and the reactive site or a distance between chain ends in the case of cyclization. For simplicity, we name this single coordinate $\boldsymbol{x}$ and all other coordinates $\boldsymbol{y}$, *i.e.* $\boldsymbol{R} = \{\boldsymbol{x}, \boldsymbol{y}\}$. Representing the sink function at locus $\boldsymbol{z}$ as $Q(\boldsymbol{R}) = \delta(\boldsymbol{x} - \boldsymbol{z})$, eq. (6) can be rewritten in Laplace space $(f(s) = \int_0^\infty f(t) \exp[-st] \mathrm{d}t)$ as

$$\Psi(\boldsymbol{x}, s) = \frac{\Psi_{eq}(\boldsymbol{x})}{s} - q \int \mathrm{d}\boldsymbol{y}^0 G_0(\boldsymbol{z}, \boldsymbol{y}^0, \boldsymbol{x}, s) \ \Psi(\boldsymbol{z}, \boldsymbol{y}^0, s) \tag{7}$$

if one introduces the density of reactive monomers $\Psi(\boldsymbol{x}, s) = \int \Psi(\boldsymbol{x}, \boldsymbol{y}, s) \mathrm{d}\boldsymbol{y}$ and the analogous Green's function. Equation (7) is still a formidable integral equation for $\Psi(\boldsymbol{x}, s)$. The WF closure relation assumes [4] that the presence of the reaction does not affect the distribution of other variables $\boldsymbol{y}_0$. In our notation it leads to the simple separation:

$$\int \mathrm{d}\boldsymbol{y}^0 G_0(\boldsymbol{z}, \boldsymbol{y}^0, \boldsymbol{x}, s) \Psi(\boldsymbol{z}, \boldsymbol{y}^0, s) \simeq G_0(\boldsymbol{z}, \boldsymbol{x}, s) \Psi(\boldsymbol{z}, s). \tag{8}$$

Inserting this closure relation into eq. (7), and taking the limit of infinite reaction strength, $q \to \infty$, one gets the surviving probability

$$\rho(s) = \frac{h(s)}{1 + sh(s)} \tag{9}$$

with $h(s)$ being the Laplace transform of the function $h(t)$ defined by $h(t) = G_0(\boldsymbol{z}, \boldsymbol{z}, t) \times \Psi_{eq}(\boldsymbol{z})^{-1} - 1$. In this expression the Green function is evaluated at the locus of reaction from $G_0(\boldsymbol{x}^0, \boldsymbol{x}, t) = \int \mathrm{d}\boldsymbol{y}^0 \mathrm{d}\boldsymbol{y} G_0(\boldsymbol{x}^0, \boldsymbol{y}^0, \boldsymbol{x}, \boldsymbol{y}, t)$, the probability density of the reactive monomer to be at point $\boldsymbol{x}$ at time t provided it was at $\boldsymbol{x}^0$ at time zero, calculated in the absence of reactions. The longest reaction time τ of the survival probability can be obtained by the smallest pole of eq. (9), *i.e.* by the largest root τ of the equation $\tau = h(-\tau^{-1})$; the average reaction time $\langle t \rangle$ is simply given by $\langle t \rangle = \rho(s \to 0)$ (see refs. [15] for more details).

A seemingly different approach was proposed by de Gennes [7] and later elaborated by Fredrickson *et al.* [15]. The method assumes that there exists an integro-differential operator $\hat{L}_{dG}$ such that the projected propagator $G_0(\boldsymbol{x}^0, \boldsymbol{x}, t) = \int G_0(\boldsymbol{x}^0, \boldsymbol{y}^0, \boldsymbol{x}, \boldsymbol{y}, t) \mathrm{d}\boldsymbol{y}^0 \mathrm{d}\boldsymbol{y}$ obeys $\hat{L}_{dG} G_0(\boldsymbol{x}^0, \boldsymbol{x}, t) = \delta(\boldsymbol{x} - \boldsymbol{x}^0)\delta(t)$ analogous to eq. (2), but in "projected" space of reaction coordinate only. Under this assumption, the reaction diffusion propagator is given by $\hat{L}_{dG} G(\boldsymbol{x}_0, \boldsymbol{x}, t) = -q\delta(\boldsymbol{x} - \boldsymbol{z})G(\boldsymbol{x}_0, \boldsymbol{x}, t) + \delta(\boldsymbol{x} - \boldsymbol{x}^0)\delta(t)$, an equation which has a solution analogous to eq. (6). In the limit $q \to \infty$ it reads

$$G(\boldsymbol{x}^0, \boldsymbol{x}, s) = G_0(\boldsymbol{x}^0, \boldsymbol{x}, s) - \frac{G_0(\boldsymbol{x}^0, \boldsymbol{z}, s)G_0(\boldsymbol{z}, \boldsymbol{x}, s)}{G_0(\boldsymbol{z}, \boldsymbol{z}, s)} \tag{10}$$

and it leads to eq. (9) after integration over $\boldsymbol{x}$ and $\boldsymbol{x}^0$. It is thus clear that the assumption of the existence of $\hat{L}_{dG}$ is similar to the WF closure relation (8), providing only an approximated treatment of this first-passage problem.

Different approximations were developed by des Cloizeaux and Granek [16] in the context of tube theory and with path integral methods by Nechaev *et al.* [9]. These methods and others [14] are based on poor approximations or wrong assumptions and thus fail to predict the chain behavior quantitatively and do not withstand comparison with simulations.

Solution. – In this letter we consider for the sake of simplicity a one-dimensional Rouse chain. The end reaction in one-dimensional polymer chains is relevant for instance to describe contour length fluctuations in branched polymers or to study specific adhesion mediated by tethered ligands, a problem discussed in Jeppesen *et al.* [17]. An extra advantage of 1d systems is that the capture radius can be set to zero. This eliminates one parameter from the model but keeps all its complexity. Generalizations of our method to higher dimensions and other reaction situations are straightforward. Our starting point is the exact Smoluchovski equation eq. (2) for the N-dimensional Green's function of the coordinates of all monomers $\boldsymbol{R} = \{x, \boldsymbol{y}\}$, where x is the coordinate of the reactive monomer and $\boldsymbol{y}$ is a vector representing all other monomer positions. The full Green's function $G(\boldsymbol{R}^0, \boldsymbol{R}, t)$ follows also eq. (7), with the simple sink function $Q(\boldsymbol{R}) = \delta(x - z)$:

$$G(\boldsymbol{R}^0, \boldsymbol{R}, t) = G_0(\boldsymbol{R}^0, \boldsymbol{R}, t) - q \int_0^t \mathrm{d}t' \int \mathrm{d}\boldsymbol{R}' \delta(x' - z) G_0(\boldsymbol{R}, \boldsymbol{R}', t - t') G(\boldsymbol{R}', \boldsymbol{R}^0, t'). \quad (11)$$

The presence of the delta sink function defines an hypersurface Ω for the integration of all coordinates except the reactive one. Let us denote all points on this surface by $\boldsymbol{Z}$. Let us also write with small letters the arguments of projected Green's functions, *i.e.* the arguments of Green's functions integrated over non-reacting monomers: $G(x^0, \boldsymbol{R}, t) = \int_\Omega G(\boldsymbol{R}^0, \boldsymbol{R}, t) \mathrm{d}\boldsymbol{y}^0$. Since G_0 does not depend on q and $G(x^0, \boldsymbol{Z}) \to 0$ as $q \to \infty$, we conclude (following the same steps as in de Gennes calculations [7, 15]) that the Green function at the absorbing surface asymptotically obeys $G(x^0, \boldsymbol{Z}', t) = q^{-1} g(x^0, \boldsymbol{Z}', t) + \mathrm{O}(q^{-2})$. With this notations, the projected, $q \to \infty$ form of eq. (11) is in Laplace time

$$G_0(x^0, \boldsymbol{Z}, s) = \int_\Omega g(x^0, \boldsymbol{Z}', s) G_0(\boldsymbol{Z}', \boldsymbol{Z}, s) \mathrm{d}\boldsymbol{Z}' . \quad (12)$$

This is an integral equation for $g(x^0, \boldsymbol{Z}, s)$, where $\boldsymbol{Z}$ lies on the surface Ω, and x^0 and s are parameters. The function $g(x^0, \boldsymbol{Z}, s)$ has a physical meaning of first-passage time density of arrival at the point $\boldsymbol{Z}$, and eq. (12) is called a renewal equation in the Markovian case. In the following we will omit common argument s from our notation.

At this stage the problem is reduced to finding $g(x^0, \boldsymbol{Z})$ as defined in eq. (12). If $g(x^0, \boldsymbol{Z})$ can be found, the final answer to the original problem is simply expressed as

$$G(x^0, \boldsymbol{R}) = G_0(\boldsymbol{R}_0, \boldsymbol{R}) - \int_\Omega \mathrm{d}\boldsymbol{Z}' g(x^0, \boldsymbol{Z}') G_0(\boldsymbol{Z}', \boldsymbol{R}). \quad (13)$$

Equation (12) can be solved by an iteration method. If we define integral operators $\hat{K} f(x^0, \boldsymbol{Z}) \equiv \int_\Omega f(x^0, \boldsymbol{Z}') G_0(\boldsymbol{Z}', \boldsymbol{Z}) \mathrm{d}\boldsymbol{Z}'$ and $\hat{I} f(x^0, \boldsymbol{Z}) = f(x^0, \boldsymbol{Z})$, eq. (12) can be recast as

$$g = \lambda G_0 - \left(\lambda \hat{K} - \hat{I} \right) g \quad (14)$$

by multiplying it by so far unspecified function $\lambda(x^0, s)$ and adding g to both sides. Here we omit arguments for simplicity. Equation (14) can be solved iteratively:

$$g^{(1)} = \lambda G_0; \qquad g^{(i+1)} = \lambda G_0 - \lambda \hat{K} g^{(i)} + g^{(i)}, \quad (15)$$

where the superscript refers to the order of the iteration. The first few iterations give

$$g^{(1)} = \lambda G_0; \quad g^{(2)} = 2\lambda G_0 - \lambda^2 \hat{K} G_0; \quad g^{(3)} = 3\lambda G_0 - 3\lambda^2 \hat{K} G_0 + \lambda^3 \hat{K}^2 G_0, \qquad (16)$$

which lead to the Green's functions

$$G^{(1)}(x^0, x) = G_0(x^0, x) - \lambda G_0(x^0, z, x),$$
$$G^{(2)}(x^0, x) = G_0(x^0, x) - 2\lambda G_0(x^0, z, x) + \lambda^2 G_0(x^0, z, z, x),$$
$$G^{(3)}(x^0, x) = G_0(x^0, x) - 3\lambda G_0(x^0, z, x) + 3\lambda^2 G_0(x^0, z, z, x) - \lambda^3 G_0(x^0, z, z, z, x), \qquad (17)$$

where we defined the n-point Green's functions as $G_0(x^0, z, x) = \int_\Omega G_0(x^0, \boldsymbol{Z}) G_0(\boldsymbol{Z}, x) \mathrm{d}\boldsymbol{Z}$, $G_0(x^0, z, z, x) = \int_\Omega \int_\Omega G_0(x^0, \boldsymbol{Z}) G_0(\boldsymbol{Z}, \boldsymbol{Z}') G_0(\boldsymbol{Z}', x) \mathrm{d}\boldsymbol{Z} \mathrm{d}\boldsymbol{Z}'$, and so on. The result (17) can be rewritten in a compact way if we formally define the operator $\hat{Z}$ as an operator that inserts one z argument in G_0; *i.e.* $\hat{Z} G_0(x^0, x) = G_0(x^0, z, x)$; $\hat{Z}^2 G_0(x^0, x) = G_0(x^0, z, z, x)$:

$$G^{(n)}(x^0, x) = (I - \lambda \hat{Z})^n G_0(x^0, x), \qquad (18)$$

where $\lambda(x^0)$ can be found self-consistently from the condition that

$$G^{(n)}(x^0, z) = (I - \lambda \hat{Z})^n G_0(x^0, z) = 0. \qquad (19)$$

This is an n-th order algebraic equation for $\lambda(x^0)$. For instance, the first-order iteration gives $\lambda(x^0) = G_0(x^0, z)/G_0(x^0, z, z)$ and

$$G^{(1)}(x^0, x) = G_0(x^0, x) - \frac{G_0(x^0, z, x) G_0(x^0, z)}{G_0(x^0, z, z)}, \qquad (20)$$

which for the simple Markovian process $G_0(x^0, x_1, x_2) = G_0(x^0, x_1) G_0(x_1, x_2)$ leads to the Wilemski-Fixman-de Gennes (WFdG) results eq. (10). All other iterations do not change this result. Thus, the WFdG method is exact only for Markovian processes. Equation (17) (or equivalently (18)) together with eq. (19) constitute the main result of the paper. It expresses the Green's function in the presence of reaction via a series involving all n-point Green's functions calculated without the reaction.

In order to use this result, let us calculate the n-point Green's function of 1d Rouse chain $G(x_0, 0, x_1, t_1, \ldots, x_n, t_n)$. It is defined as the probability density that the reaction coordinate will change from x_0 to x_1 in time t_1, then to x_2 in time t_2 and so on. It is given by

$$G_0(x_0, 0, x_1, t_1, \ldots, x_n, t_n) = \int_\Omega \prod_{j=1}^n G_0(\boldsymbol{R}_{j-1}, \boldsymbol{R}_j, t_j) \mathrm{d}\boldsymbol{R}_j, \qquad (21)$$

where $G_0(\boldsymbol{R}_0, \boldsymbol{R}, t)$ is the full N-dimensional Green's function for all monomers. Since the 2-point Green's function is Gaussian, the n-point projected function will also be Gaussian of the general form

$$G(x_0, 0, x_1, t_1, \ldots, x_n, t_n) P(x_0) = \frac{1}{\sqrt{(2\pi)^{(n+1)} \det A}} \exp\left[-\frac{1}{2} \sum_{j,k=0}^n A_{jk}^{-1}(x_j - \langle x \rangle)(x_k - \langle x \rangle)\right], \qquad (22)$$

where A_{ij}^{-1} are unknown functions of all times $t_1, \ldots, t_n$ and $\langle x \rangle$ is the average equilibrium value of the reaction coordinate. $P(x_0)$ in the left-hand side is the equilibrium probability distribution for the reactive monomer $P(x_0) = (2\pi j(0))^{-1/2} \exp[-(x_0 - \langle x \rangle)^2/(2j(0))]$. According to well-known properties of Gaussian distributions, the matrix elements A_{nm}^{-1} are to be obtained from the inversion of the matrix with elements $A_{nm} = j(\sum_{l=\min(m,n)}^{\max(m,n)-1} t_l)$ with $j(t)$ of the usual 2-point Green's function, obtained by WF and Doi [4,6].
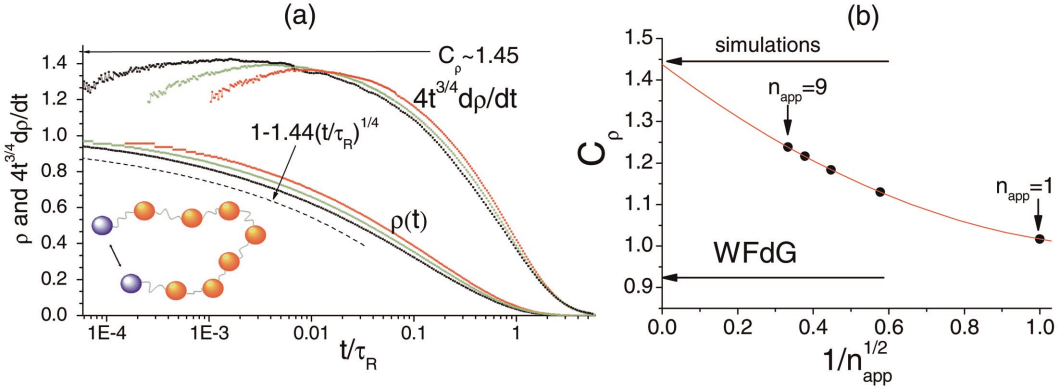
Fig. 1 – (a) Stochastic simulation results for $\rho(t)$ and its normalized derivative $-4t^{3/4}\frac{d\rho}{dt}$ for $N = 100, 200$ and 500 (from right to left). The plateau in the normalized derivative provides the value of C_ρ as $N \to \infty$. (b) C_ρ values as predicted by the WFdG closure approximation, by the stochastic simulations and by our iteration method up to order 9. The extrapolation of our results to infinite n by second-order polynomial of $\sqrt{n_{app}}$ exactly coincides with the simulation.

Results and discussion. – The most demanding test for a reaction diffusion theory is to calculate the cyclization rate $\rho(t)$ at early times, when the motion of the chain end is strongly non-Markovian. Let us consider a Rouse chain with the reactive sites attached to its ends. In this case reaction coordinate x is the end-to-end distance. Given its initial equilibrium distribution $P(x_0)$ and the first passage propagator $G(x_0, x, t)$, the fraction of unreacted chains reads

$$\rho(t) = \int_{-\infty}^{\infty} dx_0 P(x_0) \int_{-\infty}^{\infty} dx\ G(x_0, x, t). \tag{23}$$

From the scaling properties of the Rouse chain [12] we know that at early time the answer scales as

$$\rho(t) = 1 - C_\rho(t/\tau_R)^{1/4} \quad \text{or} \quad \rho(s) = s^{-1} - \Gamma(5/4)C_\rho s^{-5/4}\tau_R^{-1/4}\ . \tag{24}$$

Therefore in order to compare different theories at early times we need only one number, for example C_ρ. Direct stochastic simulations of eq. (1) using standard Brownian dynamics algorithms give

$$C_\rho^{\text{sim}} = 1.45 \pm 0.03. \tag{25}$$

The procedure used to extract the value of C_ρ from the $\rho(t)$ data is illustrated in fig. 1(a). In the context of contour length fluctuations, analogous simulations were presented in [12]. Indeed, one can also calculate C_ρ using the result for another coefficient C_μ from [12] as following. For short times, only the chain with the ends close to each other are important, and therefore the distribution $P(x_0)$ can be replaced by a constant $P(x_0) \approx \sqrt{3/(2\pi)}$. The constant C_μ in $\mu(t) \approx 1 - C_\mu(t/\tau_R)^{1/4}$ is thus $C_\mu = \sqrt{(\pi/3)}C_\rho \approx 1.5$, with τ_R the Rouse time [11]. From the WFdG method eq. (10) one gets

$$C_\rho^{\text{dG}} = 2\sqrt{(2)}\pi^{-7/4}\left(1 + \sqrt{2}\right) \approx 0.92 \tag{26}$$

which is slightly lower than the first iteration of our method and significantly lower than the exact result (fig. 1(b)).

In order to calculate $C_\rho^{(n)}$ using our iterative solutions, we numerically calculate $\lambda(x_0, s)$ from each x_0 at some fixed large s, and then perform numerical integrations in order to

calculate the value of the survival probability at order n, $\rho^{(n)}$. Integrals over $t_1, \ldots, t_n$ were performed by an integration method analogous to the Gauss method. The results for $C_\rho^{(n)}$ for $n = 1, 3, 5, 7$ and 9 are shown in fig. 1(b) as a function of $1/\sqrt{n}$. Even orders of n do not correspond to real solutions of eq. (19), and odd orders of n have one unique solution.

Figure 1(b) shows that the new method extrapolated to $1/\sqrt{n} = 0$ gives

$$C_\rho^\infty = 1.44 \tag{27}$$

in perfect agreement with the simulation results eq. (25).

Conclusions. – We have shown that the first-passage time for end-reactions in a Rouse polymer chain, which is a strongly non-Markovian problem, can be solved by an exact iteration method. We provided a solution for the most stringent case of polymer cyclization, and showed that it agrees exactly with stochastic simulations of the same problem. We are convinced that this method will allow solving a variety of other first-passage problems in non-Markovian processes.

$$* * *$$

REFERENCES

[1]   Redner S., *A Guide to First-passage Processes* (Cambridge University Press, Cambridge) 2001.
[2]   Berezhkovskii A. M., Makhnovskii Y. A., Bogachev L. V. and Molchanov S. A., *Phys. Rev. E*, **47** (1993) 4564.
[3]   Kramers H. A., *Physica*, **4** (1940) 284; Hanggi P., Talkner P. and Borkovec M., *Rev. Modern Phys.*, **62** (1990) 251.
[4]   Wilemski G. and Fixman M., *J. Chem. Phys.*, **60** (1974) 866; 878.
[5]   Bodunov E. N., Berberan-Santos M. N. and Martinho J. M. G., *Chem. Phys.*, **274** (2001) 243.
[6]   Doi M., *J. Chem. Phys.*, **9** (1975) 455; **11** (1975) 107; 115.
[7]   de Gennes P. G., *J. Chem. Phys.*, **76** (1982) 3316; 3322.
[8]   Friedman B. and O'Shaughnessy B., *Phys. Rev. Lett.*, **60** (1988) 64.
[9]   Nechaev S., Oshanin G. and Blumen A., *J. Stat. Phys.*, **98** (2000) 281.
[10] de Gennes P. G., *J. Chem. Phys.*, **55** (1971) 572; Doi M., *J. Polym. Sci., Polym. Phys. Ed.*, **21** (1983) 667.
[11] Doi M. and Edwards S. F., *The Theory of Polymer Dynamics* (Clarendon Press, Oxford) 1986.
[12] Likhtman A. E. and McLeish T. C. B., *Macromolecules*, **35** (2002) 6332.
[13] Pastor R. W., Zwanzig R. and Szabo A., *J. Chem. Phys.*, **105** (1996) 3878.
[14] Sokolov I. M., *Phys. Rev. Lett.*, **90** (2003) 080601. The paper contains a mistake in the first equation. The 3-point conditional probability should read as the probability to be at a given point provided it visited the previous point *for the first time*. If this is taken into account, the first-passage distribution drops out of the equation and one cannot proceed any further. Thus, the approach [14] is based on an uncontrolled assumption.
[15] Fredrickson G. H. and Leibler L., *Macromolecules*, **29** (1996) 2674; Kolb A., Marques C. M. and Fredrickson G. H., *Macromol. Theory Simul.*, **6** (1997) 169.
[16] des Cloizeaux J., *Macromolecules*, **23** (1990) 4678; Granek R., *Macromolecules*, **28** (1995) 5370.
[17] Jeppesen C., Wong J. Y., Kuhl T. L., Israelachvili J. N., Mullah N., Zalipsky S. and Marques C. M., *Science*, **293** (2001) 465.