Journal of Statistical Physics, Vol. 79, Nos. 1/2, 1995

Excursions for Polymers in Elongational Flows

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Received June 21, 1994; final October 3, 1994

The study of the configurational statistical mechanics of polymers in elongational flows requires the evaluation of quadratic path integrals. Here we present a new technique for the evaluation of such path integrals; the method relies on Ito excursion theory and the Ray–Knight theorem from probability theory. In addition to providing a powerful computational method in standard cases, the method generalizes to deal with quadratic path integrals for branching processes.

KEY WORDS: Brownian motion; excursion theory; path integration; polymers.

1. INTRODUCTION

Recently a new method for the computation of the laws of quadratic functionals of Brownian motion has been developed.[2] The motivation for this work came from the need to evaluate a class of path integrals for particles in quadratic potentials which are the partition functions for a polymer model in an elongational flow. The new method is based on the machinery of modern probability theory, especially Ito excursion theory. In this paper we extend the computational scope of the method to the evaluation of quadratic functionals for paths with fixed endpoints, that is, for Brownian bridges. We also see how one can compute statistical information about the shape of the polymer by dealing with source terms in the partition function. New insight, arising from geometrical considerations, is given to the calculation of the partition functions for star-shaped polymers.

The paper is largely self-contained; alternative proofs leading to the method in ref. 2 are given. The proofs rely on excursion theory and sample path considerations. Throughout we concentrate on the computational

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0022-4715/95/0400-0265$07.50/0

power of the method rather than dwelling on technical details. A number of new examples are included. We begin with a review of the polymer model that motivates the study. Many methods exist for the evaluation of quadratic path integrals and some of these are briefly reviewed in Section 3. The basics of Ito excursion theory are then expounded in an informal, calculationally orientated fashion. The basis for the computational method is then developed in Section 5, followed by some examples. In Section 6 the theory is used to deal with ring polymers and propagators; a nontrivial example calculation is included. The paper concludes by examining deterministically branching polymers (special emphasis being given to star-type polymers) and also by demonstrating how source terms may be included in order to analyze the statistics of the mean squared end-to-end distance for polymers in flows.

The authors would like to stress that while this paper concentrates on applications in polymer physics, the basic techniques provide a new mathematical method which may be applied in any area where quadratic path integrals arise. For example, results for quantum harmonic oscillators may be obtained via analytic continuation.

2. POLYMER PROBLEM

We begin with a brief description of the polymer model our analysis is aimed at. For a comprehensive introduction see ref. 5.

Polymers consist of chains of chemical units known as monomers. We shall be interested in the conformational equilibrium statistical mechanics of these chains, as opposed to any chemical or bulk properties. Two extreme models of polymers are (a) highly flexible chains, where the polymer appears as a random walk or, in the continuum limit, a diffusion, and (b) rigid rods. We shall consider the former model. In our analysis we shall neglect self-avoidance and take a continuum model where the polymer paths before Boltzmann reweighting (that is, in the absence of any potentials external or internal to the chain) are Brownian paths. Consequently we can apply the machinery of stochastic calculus in our study.[9]

To obtain information about the equilibrium configurational statistics of a polymer path, we define an energy functional on a path $(X_s)_{0 \leqslant s \leqslant t}$ given by

$$\mathscr{E}[X] = \int_0^t \left\{ \frac{1}{2} \dot{X}_s^2 + V(X_s) \right\} ds \tag{1}$$

where V is an (external) potential. (Internal potentials such as repulsive potentials generated by charges on polymers lead to more complicated

energy functionals with two time actions.) On exponentiation we obtain (up to a normalization factor) the Gibbs measure, the kinetic term in the original energy functional giving the Wiener measure on Brownian paths. In path integral notation the normalization factor for Gibbs measure is formally given by

$$Z = \int d[X] \exp\left(\frac{-\mathscr{E}[X]}{kT}\right) \tag{2}$$

Z is also known as the partition function. The constants k and T are the Boltzmann constant and temperature, respectively. In probabilistic notation this becomes

$$Z = \mathbb{E}\left[\exp\left\{-\int_0^t V(X_s)\, ds\right\}\right] \tag{3}$$

where the expectation is over Brownian motion and we have set kT to be equal to unity for notational simplicity. The ensemble average or statistical mechanical average of a functional F of a polymer path is given by the formula

$$\langle F[X]\rangle = Z^{-1}\mathbb{E}\left[F[X]\exp\left\{-\int_0^t V(X_s)\, ds\right\}\right] \tag{4}$$

the angled brackets indicating ensemble averaging.

The specific physical model we shall study is that for polymers in pure straining or elongational flows at zero Reynolds number,[2] i.e., in a limit where inertia forces are neglected. An elongational velocity field $u(x)$ is given by $u(x) = E \cdot x$, where E is a traceless (as the flow is incompressible) symmetric tensor, called the rate of strain tensor. The force on a single rigid particle in a zero-Reynolds-number flow is given by $F = R \cdot u$, where R is the resistance tensor of the particle; for simplicity we shall take R to be isotropic, so we can take R to be a scalar, the scalar resistance of the particle. For the isotropic case, the work done against the elongational flow is conservative, with potential energy $V(x)$ given by

$$V(x) = -\tfrac{1}{2}Rx^T Ex \tag{5}$$

If we consider a single-chain polymer as a Brownian path threaded through infinitesimal isotropic particles and neglect the effects of hydrodynamic interactions between the infinitesimal particles and self-avoidance, we can define the flow energy of the polymer by

$$V[X] = -\tfrac{1}{2}\int_0^t X_s^T E X_s\, R[ds] \tag{6}$$

The functional V is not quite appropriate for considering the statistical mechanics of polymer shapes in an elongational flow, since it is not invariant under translations of the whole polymer. To achieve translational invariance we must change to center of resistance coordinates, namely redefine the flow energy of the polymer by

$$V[X] = -\tfrac{1}{2}\int_0^t (X_s - \bar{X})^T E(X_s - \bar{X})\, R[ds] \tag{7}$$

where

$$\bar{X} = \frac{\int_0^t X_s\, R[ds]}{\int_0^t R[ds]} \tag{8}$$

is the center of resistance. Notice that the partition function factorizes:

$$Z = \prod_{i=1}^{3} Z_i \tag{9}$$

where

$$Z_i = \mathbb{E}\left[\exp\left\{\frac{\lambda_i}{2}\int_0^t (X_s^i - \bar{X}^i)^2\, R[ds]\right\}\right] \tag{10}$$

The λ_i are the eigenvalues of E and the X^i are the corresponding components of X. Thus in calculations where the functional F also factorizes, the three-dimensional system reduces to three independent one-dimensional systems. In what follows we shall restrict attention to one-dimensional systems and drop the index i.

The basic object we need to evaluate has the form

$$\phi = \mathbb{E}\left[\exp\left\{-\left(\int_0^t X_s^2\, d\mu - \rho\left(\int_0^t X_s\, d\mu\right)^2\right)\right\}\right] \tag{11}$$

where

$$\rho = \left(\int_0^t d\mu\right)^{-1} \tag{12}$$

A simple, but very useful trick for dealing with the evaluation of such objects is as follows. Define

$$\hat{\phi}(\xi) = \mathbb{E}\left[\exp\left\{-\int_0^t X_s^2\, d\mu + (2\rho)^{1/2}\,\xi\int_0^t X_s\, d\mu\right\}\right] \tag{13}$$

Hence if G is an $N(0, 1)$ random variable, that is to say a Gaussian random variable with zero mean and unit variance, then

$$\phi = \mathbb{E}(\hat{\phi}(G)) \tag{14}$$

where the expectation is over G; this trick is often referred to as the Hubbard–Stratonovich transformation. The translational invariance of the polymer energy functional (7) means that we can choose the starting point of the path to be at 0, i.e., $X(0) = 0$. Completing the square in (13) and then shifting the starting point of the path yields

$$\hat{\phi}(\xi) = \exp\left(\frac{\xi^2}{2}\right) \mathbb{E}^0\left[\exp\left\{-\int_0^t (X_s - (\rho/2)^{1/2}\,\xi)^2\, d\mu\right\}\right] \tag{15}$$

$$= \exp\left(\frac{\xi^2}{2}\right) \mathbb{E}^{(\rho/2)^{1/2}\xi}\left[\exp\left\{-\int_0^t X_s^2\, d\mu\right\}\right] \tag{16}$$

consequently we shall be interested in the computation of laws of the type

$$\psi(x) = \mathbb{E}^x\left[\exp -\left\{\int_0^t X_s^2\, d\mu\right\}\right] \tag{17}$$

3. METHODS FOR QUADRATIC PATH INTEGRALS

There exists a number of methods for evaluating laws of quadratic functionals of Gaussian processes. The earliest methods were based on eigenfunction expansions (e.g., see refs. 11, 8, and 17). In the context of path integration this is also the case; the propagator for the simple harmonic oscillator can be obtained by expansion with Fourier series.[7] More recently Yor[18] has showed how martingale techniques and stochastic calculus can be elegantly used to compute the laws of certain quadratic functionals of Gaussian processes.

3.1. The Diagonalization Method

The eigenfunction method is often called the diagonalization method and is still widely used in the literature. Here we shall explain the basic method based on ref. 17 and give a (new) example to illustrate its use.

Given an inner product $(\cdot, \cdot)$ and a Gaussian X process on $[0, 1]$, we wish to find $\mathbb{E}[\exp\{(z^2/2)(X, X)\}]$ for complex z. We write

$$X_s = \sum_{n \geq 1} \gamma_n g_n(s) \xi_n \tag{18}$$

where ξ_n are independent identically distributed $N(0, 1)$ random variables and $(g_n, g_m) = \delta_{m,n}$.

Assume the covariance $C(s, s')$ of X is known. Thus

$$\mathbb{E}(X_s X_{s'}) = \sum_{n \geqslant 1} \gamma_n^2 g_n(s)\, g_n(s') = C(s, s') \tag{19}$$

Define Γ so that

$$\Gamma f(s) = (C(s, \cdot), f) \tag{20}$$

Therefore

$$\Gamma = \sum_{n \geqslant 1} \gamma_n^2 g_n g_n \tag{21}$$

with respect to the inner product $(\cdot, \cdot)$. Therefore Γ has eigenfunctions g_n with corresponding eigenvalues γ_n^2, given by the equation

$$\Gamma g_n = \gamma_n^2 g_n \tag{22}$$

with respect to $(\cdot, \cdot)$. Consequently, when $\mathrm{Re}(\gamma_{\max}^2 z^2) < 1$ and $\sum_n \gamma_n^2$ is finite,

$$\mathbb{E}\left[\exp\left\{\frac{z^2}{2}(X, X)\right\}\right] = \mathbb{E}\left[\exp\left\{\frac{z^2}{2}\sum_{n \geqslant 1} \gamma_n^2 \xi_n^2\right\}\right] = \prod_{n \geqslant 1} (1 - z^2 \gamma_n^2)^{-1/2} \tag{23}$$

the aforementioned conditions on z and the γ_n ensuring the existence of the Gaussian integrals and infinite product, respectively. For example, one can easily show that, where defined,

$$\mathbb{E}^0\left[\exp\left\{\frac{z^2}{2}\int_0^1 X_s^2\, ds\right\}\right] = \{\cos(z)\}^{-1/2} \tag{24}$$

where X is standard Brownian motion. The infinite product is evaluated using the Weierstrass product formula.[1]

Example. We shall consider the case where X is Brownian motion on $[0, 1]$, started at 0, and where

$$(X, X) = \int_0^1 X_s^2\, d\mu \tag{25}$$

with

$$d\mu = (\alpha^2 I_{[0, a]} + \beta^2 I_{[a, 1]})\, ds \tag{26}$$

In this case $C(s, s') = s \wedge s'$ [$= \min(s, s')$] and the eigenvalue equation (22) is

$$\gamma_n^2 g_n(s) = \int_0^1 (s \wedge s')\, g_n(s')\, ds' \tag{27}$$

The boundary conditions imposed on the g_n can be read off from (27), namely $g_n(0) = 0$ and $g_n'(1) = 0$. The solution (unnormalized) to (27) is

$$g_n(s) = A \sin\left(\frac{\alpha s}{\gamma_n}\right), \qquad 0 < s < a \tag{28}$$

$$= \sin\left(\frac{\beta s}{\gamma_n} - \theta\right), \qquad a < s < 1 \tag{29}$$

where A and θ are constants. To avoid obtaining the eigenvalues explicitly, we may complete the calculation using an observation made in ref. 3 and a little more trickery. We note that $\prod_{n \geqslant 1} (1 - z^2\gamma_n^2)$ has simple zeros at $z = \pm \gamma_n^{-1}$; however, so does $\cos(\beta z - \theta)$ from the condition $g_n'(1) = 0$. Consequently one can show their ratio is a bounded entire function in $\mathbb{C}$ and hence is constant (this is essentially how one proves the Weierstrass product formulas). The continuity conditions at $s = a$ are

$$A \sin(\alpha a z) = \sin(\beta a z - \theta) \tag{30}$$

$$A\alpha \cos(\alpha a z) = \cos(\beta a z - \theta) \tag{31}$$

Using the addition formula for cosines, we may write

$$\cos(\beta z - \theta) = \cos\{\beta z(1-a)\}\, \cos(\beta z a - \theta) - \sin\{\beta z(1-a)\}\, \sin(\beta z a - \theta) \tag{32}$$

and then use (30) and (31) to show

$$\prod_{n \geqslant 1} (1 - z^2\gamma_n^2) = \left(\cos\{\beta z(1-a)\}\, \cos(\alpha z a) - \frac{\beta}{\alpha} \sin\{\beta z(1-a)\}\, \sin(\alpha z a)\right) \tag{33}$$

and hence

$$\mathbb{E}\left[\exp\left\{\frac{z^2}{2}(X, \dot{X})\right\}\right] = \left(\cos\{\beta z(1-a)\}\, \cos(\alpha z a) - \frac{\beta}{\alpha} \sin\{\beta z(1-a)\}\, \sin(\alpha z a)\right)^{-1/2} \tag{34}$$

3.2. The Pauli–Van Vleck Formula

The Pauli–Van Vleck formula has its origins in quantum mechanics; in the Euclidean setting corresponding to polymer physics the propagator for a quadratic action is given by

$$K(y, t \mid x, 0) = \int_x^y d[X] \exp(-S[X]) \tag{35}$$

$$= \left[\frac{1}{2\pi} \left| \frac{\partial^2 S_{cl}}{\partial x \, \partial y} \right| \right]^{1/2} \exp(-S_{cl}) \tag{36}$$

where $S[X]$ is the action functional for paths and S_{cl} is the action of the classical path between x and y (when it is unique). A number of proofs exist,[10] but essentially it comes from expanding the action about the classical paths X_{cl}, i.e.,

$$S[X] = S[X_{cl} + \eta] = S[X_{cl}] + \frac{1}{2} \eta \frac{\delta^2 S[X_{cl}]}{\delta X^2} \eta + \cdots \tag{37}$$

which is exact for quadratic actions. The Pauli–Van Vleck formula also provides the starting point for semiclassical methods such as the WKB approximation.

3.3. A General Result

We recall a result known to some as *the fundamental theorem of statistics*.

If X is a zero-mean, Gaussian, $\mathbb{R}^d$-valued random variable covariance matrix C, $a \in \mathbb{R}^d$, and M is a positive-definite symmetric matrix, then

$$\mathbb{E}[\exp\{-\tfrac{1}{2}(X+a)^T M(X+a)\}] = \det(I + MC)^{-1/2} \exp\{-\tfrac{1}{2} a^T (I + MC)^{-1} Ca\} \tag{38}$$

The results for continuous Gaussian processes on intervals of the real line follow via soft weak convergence arguments.[2] The statement of the result (familiar to field theorists) in this case is

$$\mathbb{E}\left[\exp -\left\{ \int_0^t (X_s + a(s))^2 \, d\mu \right\} \right] = \det(I + MC)^{-1/2} \exp\left\{ -\frac{1}{2} \int_0^t \int_0^t ds \, ds' \, a(s) \times [(I + MC)^{-1} M](s, s') \, a(s') \right\} \tag{39}$$

Here

$$Mf(s) = \frac{d\mu}{ds} f(s) \qquad \text{and} \qquad Cf(s) = \int_0^t ds'\, C(s, s')\, f(s') \tag{40}$$

where $C(s, s') = \mathbb{E}(X_s X_{s'})$, and I is the identity operator. In ref. 2 the above formulation of the problem is used to develop an analytical approach to the problem in terms of resolvent operators; via this the ultimate link with exclusion theory is made to simplify calculations when the operators involved become too unwieldy. However, it is only the structure of (39) that we shall use when we consider ring polymers and propagators.

4. ITO EXCURSION THEORY

The following section is a brief introduction to Ito excursion theory for Brownian motion; it is based on the introduction in ref. 4, where excursion theory is used to analyze diffusion on a generalized comb. Excursion ideas apply to any Markov process with a recurrent state.[15]

Consider a standard Brownian motion $(B_t)_{t \geqslant 0}$ on $\mathbb{R}$ starting at 0; then by the continuity of B we can write $\{t: B_t \neq 0\}$ as the disjoint countable union of maximal open intervals, i.e., $\bigcup_i (a_i, b_i)$. During each of these intervals B makes an *excursion* away from 0. An excursion can be considered as a point in the excursion space U, where

$$\begin{aligned} U \equiv \{ f \mid & f \text{ is a continuous function from } \mathbb{R}^+ \text{ to } \mathbb{R} \\ & \text{and } f^{-1}(\mathbb{R} \backslash \{0\}) \text{ is an open interval} \} \end{aligned} \tag{41}$$

The length of the interval $f^{-1}(\mathbb{R}\backslash\{0\})$ is the duration of the excursion. So an excursion for Brownian motion has the form

$$\{ B_{\min(t + a_i,\, b_i)} : t \geqslant 0 \} \tag{42}$$

On the intuitive level we may say that each time Brownian motion hits the origin it makes a loop away from the origin (an excursion). When the Brownian motion returns to the origin, the next excursion away is independent of all the previous excursions. This is because Brownian motion is a Markov process, so, conditional on knowing that we are at the origin, what happens next is independent of what has happened in the past. Given a *number* of visits to the origin, one can construct the Brownian path by joining together the loops in the order in which they occur. However, we may not talk of the number of visits of Brownian motion to the origin, as before making any significant (e.g., high-level) excursion away from the origin the Brownian motion will have *flicked* through the origin an infinite

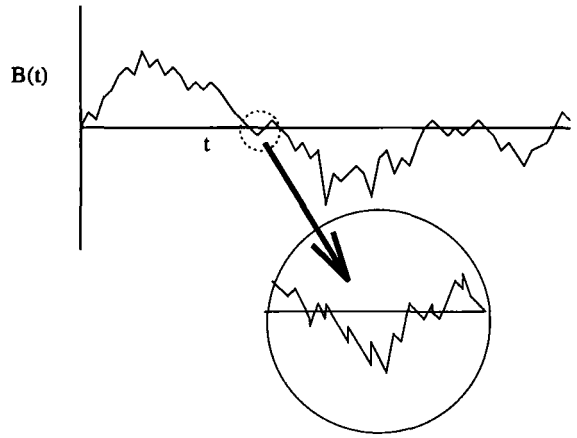

Fig. 1. Realization of a Brownian path, shown with part of the path magnified.

number of times (see Fig. 1). This is due to the nowhere differentiability of the Brownian path. However, a natural generalization for the number of visits to the origin does exist—it is called local time and we may use it to parameterize the order of excursions.

Theorem 1 (Trotter). There exists a jointly continuous process $\{L(t, x): t \geqslant 0,\ x \in \mathbb{R}\}$ such that for all bounded, measurable f and all $t \geqslant 0$

$$\int_0^t f(B_s)\, ds = \int_{-\infty}^{\infty} f(x)\, L(t, x)\, dx$$

The function $L(t, \cdot)$ is the occupation time density, called local time. A heuristic definition of L, useful for calculations, is

$$L(t, x) \equiv \int_0^t \delta(B_s - x)\, ds \tag{43}$$

where δ is the one-dimensional Dirac delta function with unit mass at 0. In the context of polymer physics we see that local time is simply the monomer density. Hence if $b < a'$, then the excursions occurring in the intervals (a, b) and (a', b') occur at local times at 0, l, and l', respectively, where $l < l'$. Using this, we can split a Brownian sample path apart into its excursions from 0 and represent a Brownian path as a point-process Ξ in $\mathbb{R}^+ \times U$, where $(l, \xi) \in \Xi$ if and only if the Brownian motion makes excursion ξ at local time l. This procedure can be reversed, as, if we know Ξ, we can join the excursions in the correct order to recover the original sample path. The fundamental result of excursion theory is the following.

Theorem 2 (Ito). The excursion point-process is Poisson with expectation measure Lebesgue $\times n$, where the σ-finite measure n on U is called the excursion measure.

Thus we deduce:

(i) If $A \subset U$, $0 \leqslant n(A) < \infty$, then

$$\mathbb{P}(\Xi \text{ has no point in } (0, l) \times A) = e^{-ln(A)} \tag{44}$$

(ii) If $A_1, \ldots, A_k \subset U$ are disjoint, $0 \leqslant n(A_i) < \infty$ for all i, $A = \bigcup_1^k A_i$, and $n(A) > 0$, then

$$\mathbb{P}(\Xi_l \in A_i) = n(A_i)/n(A) \tag{45}$$

where $l \equiv \inf\{u: \Xi_u \in A\}$.

We are now faced with the problem of calculating the excursion measure n of some set A. Ito's theorem means, however, that the local time at which a first excursion in A occurs is exponentially distributed with rate $n(A)$. Hence for a Brownian motion started at 0, we have

$$n(A) = (\mathbb{E}^0(L_A))^{-1} \tag{46}$$

where L_A is the local time at 0 at which the first excursion in A occurs. This can be found by calculating the expected local time spent at 0 by a Brownian motion which is killed when it has an excursion in A. There are many elegant methods for calculating excursion rates, but the method we shall use involves only standard mathematical methods.

Examples

Rates of Hitting Levels. Let A be the set of excursions hitting the point $-a$ or a. To find $n(A)$ we calculate the expected local time at 0 of a Brownian motion killed at $\pm a$; this expected local time is therefore $n(A)^{-1}$.

For a Brownian motion started at $x \in [-a, a]$ and killed at $\pm a$, define $\phi(x)$ to be the expected local time at 0 before the process is killed. It is easy to show, using the definition (43), that ϕ satisfies

$$\frac{1}{2}\frac{d^2\phi}{dx^2} + \delta(x) = 0 \tag{47}$$

with the (killing) boundary conditions $\phi(-a) = \phi(a) = 0$. Solving (47) yields $\phi(0) = a$, giving $n(A) = a^{-1}$. Excursions hitting $-a$ and a, by symmetry, occur at the same rate and are also disjoint, hence

$$n(\text{hit } -a) = n(\text{hit } a) = 1/2a \tag{48}$$

Marked Excursions. In the following examples we mark[3] the sample paths at an exponentially distributed real time of rate $\frac{1}{2}\alpha^2$, independent of the path.

(i) Let A be the set of excursions which are marked or hit $\pm a$. Therefore $n(A)^{-1}$ is equal to the expected local time spent at 0 by a Brownian motion which is killed at $\pm a$ and at real time rate $\frac{1}{2}\alpha^2$. In this case the equation for the expected local time at 0 for a Brownian motion started at $x \in [-a, a]$ and killed at rate $\frac{1}{2}\alpha^2$ is

$$\frac{1}{2}\frac{d^2\phi}{dx^2} - \frac{1}{2}\alpha^2\phi + \delta(x) = 0 \tag{49}$$

with the (killing) boundary conditions $\phi(-a) = \phi(a) = 0$. Solving (49) yields $\phi(0) = \alpha^{-1}\tanh(\alpha a)$. Hence $n(A) = \alpha\coth(\alpha a)$ and using the symmetry between upward and downward excursions, we obtain

$$n(\text{hit } -a \text{ or marked}) = n(\text{hit } a \text{ or marked}) = \tfrac{1}{2}\alpha\coth(\alpha a) \tag{50}$$

In the limit $a \to \infty$, (50) becomes

$$n(\text{marked in } [-\infty, 0]) = n(\text{marked in } [0, \infty]) = \tfrac{1}{2}\alpha \tag{51}$$

which can also be obtained by direct calculation.

(ii) If A is the set of excursions which hit a before they are marked, then we can use the Poisson nature of the excursions to find

$$\mathbb{P}^0(\text{hit } a \text{ before marked}) = \frac{n(A)}{n(B) + n(C)} \tag{52}$$

where B is the set of upward excursions hitting a or marked and C is the set of marked downward excursions. Since

$$\mathbb{P}^0(\text{hit } a \text{ before marked}) = e^{-\alpha a} \tag{53}$$

from (50) and (51) we find

$$e^{-\alpha a} = \frac{n(A)}{\frac{1}{2}\alpha\coth(\alpha a) + \frac{1}{2}\alpha} \tag{54}$$

giving

$$n(A) = \tfrac{1}{2}\alpha\,\mathrm{cosech}(\alpha a) \tag{55}$$

[3] These marked excursions, strictly, belong to a richer excursion space;[15] however, for our purposes we need not worry about the precise details here.

(iii) If the process is a Brownian motion reflected at $\pm a$, then the local-time rate of marked excursions is given by a measure m on excursions of reflected Brownian motion. If $\phi(x)$ is the expected local time at 0 for this process started at $x \in [-a, a]$, then $\phi(x)$ satisfies (49) subject to the (reflecting) boundary conditions $\phi'(-a) = \phi'(a) = 0$. This gives $\phi(0) = \alpha^{-1} \coth(\alpha a)$. Hence, using the symmetry between upward and downward excursions, we find

$$m(\text{marked in } [-a, 0]) = m(\text{marked in } [0, a]) = \tfrac{1}{2}\alpha \tanh(\alpha a) \quad (56)$$

We can derive (56) by an excursion argument (the basic form of which is used frequently in excursion problems). For Brownian motion in $(-\infty, a]$ with reflection at a and real time rate of marking as before, we proceed by noting that marked excursions from 0 into $[0, a]$ are either marked before hitting a or are marked coming back to 0 from a. Consequently,

$$\begin{aligned} m(\text{marked in } [0, a]) = {} & m(\text{marked in } [0, a] \text{ or hit } a) \\ & - n(\text{hit } a \text{ with no mark}) \cdot p \end{aligned} \quad (57)$$

where p is the probability of returning to the origin from a without a mark. In other words, we have used the fact that marked excursions from 0 are those which hit a or are marked, less those excursions which hit a without a mark and then return to 0 without a mark. We can carry out excursion theory from reflecting starting points, by ignoring any excursions above the level a. (We may neglect any renormalizations of rates from the reflecting point, as we shall only be interested in ratios of rates to give probabilities.) We find using the rates we already have

$$p = \frac{n^a(\text{hit 0 without a mark})}{n^a(\text{hit 0 or marked in } [0, a])} = \frac{\frac{1}{2}\alpha \operatorname{cosech}(\alpha a)}{\frac{1}{2}\alpha \coth(\alpha a)} \quad (58)$$

Hence we recover (56).

5. THE RAY–KNIGHT THEOREM AND QUADRATIC FUNCTIONALS OF BROWNIAN MOTION

Our methods for evaluating the laws of quadratic functionals for Brownian motion are based on the celebrated Ray–Knight theorem, (part of) which states the following

Theorem 3 (Ray–Knight). Let W_u be a Brownian motion with values in $(0, t]$, started at t and reflected at t, let $L(u, s)$, $s \leqslant t$, be the local time for W at s, and let $H_0 = \inf\{u: W_u = 0\}$. For independent Brownian

motions $B_1(s)$, $B_2(s)$ starting from 0, let $Z_s = B_1(s)^2 + B_2(s)^2$ be a squared two-dimensional Bessel [*BESQ(2)*] process. Then the two processes $\{L(H_0, s): 0 \leqslant s \leqslant t\}$ and $\{Z_s: 0 \leqslant s \leqslant t\}$ are identical in law, i.e.,

$$(Z_s; 0 \leqslant s \leqslant t) \overset{\text{(law)}}{=} \left(\int_0^{H_0} \delta(s - W_u)\, du; 0 \leqslant s \leqslant t \right) \tag{59}$$

Proofs of the Ray–Knight theorem are normally given for $t = 1$; the more general result follows from a scaling argument. A proof using excursion theory is sketched in ref. 14 and the full details are given in ref. 15. An alternative proof may be found in ref. 16.

Corollary 4. Let B be a standard Brownian motion and let W be a Brownian motion in $(-\infty, t]$ started at t, reflected at t, and marked at the (position-dependent) exponential real time rate $v(W_u) I_{\{W_u > 0\}}$. Then

$$\begin{aligned} \psi(x) &\equiv \mathbb{E}^x \left[\exp\left\{ -\int_0^t B_s^2 v(s)\, ds \right\} \right] \\ &= p^{1/2} e^{-dx^2} \end{aligned} \tag{60}$$

where $p = \mathbb{P}^t(W \text{ hits } 0 \text{ before being marked})$ and d is the local time rate of marked excursions of W from 0, i.e.,

$$d = n^0(\text{marked}) \tag{61}$$

with n^0 the excursion measure on Brownian motion which is reflected at the level t and marked at (position-dependent) exponential real time rate v in $[0, t]$.

The proof of this can be found in ref. 2, but in the spirit of our exposition we shall give an alternative (sketch) sample path proof.

Proof. If N is an $N(0, T)$ normal random variable for some $T \geqslant 0$, then

$$\mathbb{E}(\psi(N)) = \mathbb{E}^0 \left[\exp\left\{ -\int_0^t (B_s + N)^2 v(s)\, ds \right\} \right] \tag{62}$$

where the first expectation is over N and the second is over N and B. If $(\tilde{B}_s)_{-T \leqslant s \leqslant t}$ is a standard Brownian motion started from 0 at time $-T \leqslant 0$, then

$$\mathbb{E}(\psi(N)) = \mathbb{E} \left[\exp\left\{ -\int_{-T}^t \tilde{B}_s^2 v(s) I_{\{s > 0\}}\, ds \right\} \right] \tag{63}$$

If we square (63), we obtain

$$[\mathbb{E}(\psi(N))]^2 = \mathbb{E}\left[\exp\left\{-\int_{-T}^{t} Z_s \nu(s) I_{\{s>0\}}\, ds\right\}\right] \tag{64}$$

where $(Z_s)_{-T\leqslant s\leqslant t}$ is a *BESQ(2)* process started at 0 at time $-T$. Consequently we may apply Corollary 4 (taking advantage of time translation invariance) to obtain

$$[\mathbb{E}(\psi(N))]^2 = \mathbb{E}'\left[\exp\left\{-\int_0^{H_{-T}} \nu(W_u) I_{\{W_u>0\}}\, du\right\}\right] \tag{65}$$

where W is a Brownian motion in $(-\infty, t]$ started at t and reflected at t and $H_{-T} = \inf\{u\colon W_u = -T\}$, i.e., the first hitting time at $-T$. Therefore

$$[\mathbb{E}(\psi(N))]^2 = \mathbb{P}'(W \text{ hits } -T \text{ before being marked}) \tag{66}$$

By the Markov property of W

$$\begin{aligned}&\mathbb{P}'(W \text{ hits } -T \text{ before being marked})\\ &\quad = \mathbb{P}'(W \text{ hits } 0 \text{ before being marked})\\ &\qquad \times \mathbb{P}^0(W \text{ hits } -T \text{ before being marked})\end{aligned} \tag{67}$$

An excursion argument gives

$$\mathbb{P}^0(W \text{ hits } -T \text{ before being marked}) = \frac{n^0(\text{hit } -T)}{n^0(\text{hit } -T) + n^0(\text{marked})} \tag{68}$$

(Note the set of marked excursions and the set of excursions hitting $-T$ are disjoint because there is no marking in $[-T, 0]$.) Using the notation of the statement of the corollary and the result $n^0(\text{hit } -T) = 1/2T$ from Section 4, we find

$$\mathbb{P}^0(W \text{ hits } -T \text{ before being marked}) = \frac{1/(2T)}{1/(2T) + d} \tag{69}$$

and hence

$$\mathbb{E}(\psi(N)) = \frac{p^{1/2}}{(1+2dT)^{1/2}} \tag{70}$$

Because $\psi(x) = \psi(-x)$, we may write (70) as

$$\left(\frac{2}{\pi T}\right)^{1/2} \int_0^\infty dz\, e^{-z^2/2T} \psi(z) = \frac{p^{1/2}}{(1+2dT)^{1/2}} \tag{71}$$

The integral transform above is invertible (a change of variables makes it a Laplace transform) and consequently we obtain the required result.

We may now obtain the law ϕ as

$$\phi = \mathbb{E}\left[p^{1/2} \exp\left(\frac{G^2 - G^2 \rho d}{2}\right)\right] \tag{72}$$

$$= \left(\frac{p}{\rho d}\right)^{1/2} \tag{73}$$

Examples

Single-Strand Polymer with Uniform Resistance. This is the simplest case; we shall take a path of length t with measure $d\mu(s) = (\alpha^2/2)\, ds$. In this case the real time rate of marking is simply constant and $\rho = 2/(\alpha^2 t)$. It is then well known (or a trivial exercise to show) $p = 1/\cosh(\alpha t)$ and from (56) we know $d = (\alpha/2)\tanh(\alpha t)$. Therefore

$$\phi = \left(\frac{\alpha t}{\sinh(\alpha t)}\right)^{1/2} \tag{74}$$

Note that in this calculation we have implicitly assumed that the eigenvalue associated with the particular component of the flow was negative. For positive eigenvalues we may obtain the corresponding result by analytic continuation. In this particular case the continuation is $\alpha \to i\alpha$ and we obtain

$$\phi = \left(\frac{\alpha t}{\sin(\alpha t)}\right)^{1/2} \tag{75}$$

Positive eigenvalues of the flow correspond to directions in which the flow tends to stretch the polymer and negative eigenvalues ones where the flow tends to compress the polymer. The factors of the partition function corresponding to positive eigenvalues become singular for flow strengths sufficiently high. Physically this divergence signals the coil–stretch transition, where the polymers cease to be well modeled by Brownian motion and are instead highly aligned in the stretching directions of the flow. Note that in the simple case above the transition occurs at $\alpha t = \pi$, i.e., increasing either the length of the polymer or the flow strength takes it closer to the coil–stretch transition—this is physically intuitive.

Single-Strand Polymer with Piecewise Constant Resistance. Here we take the length of the path to be 1 and the resistance measure to be proportional to the one in (26), i.e.,

$$d\mu = \left(\frac{\alpha^2}{2} I_{[0,a]} + \frac{\beta^2}{2} I_{[a,1]}\right) ds \tag{76}$$

Physically we could think of this as a polymer strand formed by joining two homogeneous polymers of different resistances. This calculation can be done with minimal computation using excursion theory.

By the Markov property

$$p = \mathbb{P}^1(\text{hits } a \text{ without a mark}) \cdot \mathbb{P}^a(\text{hits } 0 \text{ without a mark}) \tag{77}$$

We know

$$\mathbb{P}^1(\text{hits } a \text{ without a mark}) = 1/\cosh[\beta(1-a)] \tag{78}$$

and

$$\mathbb{P}^a(\text{hits } 0 \text{ without a mark}) = \frac{n^a(\text{hit } 0 \text{ without a mark})}{n^a(\text{hit } 0 \text{ or } \alpha \text{ marked}) + n^a(\beta \text{ marked})} \tag{79}$$

Using the rates in (4), we obtain

$$\begin{aligned}\mathbb{P}^a(\text{hits } 0 \text{ without a mark}) &= \frac{(\alpha/2)\operatorname{cosech}(\alpha a)}{(\alpha/2)\coth(\alpha a) + (\beta/2)\tanh(\beta(1-a))} \\ &= \frac{\cosh(\beta(1-a))}{\cosh(\alpha a)\cosh(\beta(1-a)) + (\beta/\alpha)\sinh(\beta(1-a))\sinh(\alpha a)}\end{aligned} \tag{80}$$

Hence

$$p = \left(\cosh(\alpha a)\cosh\{\beta(1-a)\} + \frac{\beta}{\alpha}\sinh\{\beta(1-a)\}\sinh(\alpha a)\right)^{-1} \tag{81}$$

Marked excursions of W from 0 are either marked before they hit a or they hit a without a mark but are then marked before returning to 0; therefore

$$\begin{aligned}d = {} & n^0(\alpha \text{ marked or hit } a) \\ & - n^0(\text{hit } a \text{ without a mark}) \cdot \mathbb{P}^a(\text{hits } 0 \text{ without a mark})\end{aligned} \tag{82}$$

Substituting in the relevant excursion rates yields

$$\begin{aligned}d &= \frac{\alpha}{2}\coth(\alpha a) - \frac{(\alpha/2)\operatorname{cosech}(\alpha a)\cosh(\beta(1-a))}{\cosh(\alpha a)\cosh(\beta(1-a)) + (\beta/\alpha)\sinh(\beta(1-a))\sinh(\alpha a)} \\ &= \frac{1}{2}\frac{\alpha\cosh(\beta(1-a))\sinh(\alpha a) + \beta\cosh(\alpha a)\sinh(\beta(1-a))}{\cosh(\alpha a)\cosh(\beta(1-a)) + (\beta/\alpha)\sinh(\beta(1-a))\sinh(\alpha a)}\end{aligned} \tag{83}$$

Therefore

$$\phi = \left[\frac{\alpha^2 a + \beta^2 (1-a)}{\alpha \cosh(\beta(1-a)) \sinh(\alpha a) + \beta \cosh(\alpha a) \sinh(\beta(1-a))} \right]^{1/2} \tag{84}$$

The previous two results are in agreement with those already obtained in ref. 2 via calculations with the resolvent operator for Brownian motion rather than by the excursion method used here.

6. RING POLYMERS AND PROPAGATORS

In order to deal with ring polymers we need to be able to condition the endpoints of our Brownian paths to *tie up*, that is, we need to be able to compute the laws of quadratic functional of Brownian bridges. We shall show here how to accomplish this; in addition we shall show how our methods can be used to obtain the propagators for generalized simple harmonic oscillators.

Lemma 5. Let $(B_s)_{0 \leqslant s \leqslant t}$ be a Brownian motion conditioned so that $B_0 = x$ and $B_t = 0$; then

$$\mathbb{E}^{x \to 0} \left[\exp \left\{ -\int_0^t B_s^2 v(s)\, ds \right\} \right] = (2bt)^{1/2} \exp \left\{ -\left(\tilde{a} - \frac{1}{2t} \right) x^2 \right\} \tag{85}$$

where

$$\tilde{a} = n^t(\text{hit 0 or } \mu \text{ marked}) \tag{86}$$

$$b = n^t(\text{hit 0 without being } \mu \text{ marked}) \tag{87}$$

and n is the excursion measure on Brownian motion marked at real time rate v in $[0, t]$.

Proof. First we use

$$\mathbb{E}^{x \to 0} \left[\exp \left\{ -\int_0^t B_s^2 v(s)\, ds \right\} \right] = \lim_{\lambda \to \infty} \frac{\mathbb{E}^x [\exp\{ -\int_0^t B_s^2 v(s)\, ds - \lambda B_t^2 \}]}{\mathbb{E}^x [\exp\{ -\lambda B_t^2 \}]} \tag{88}$$

This is clearly true on physical grounds and is a standard form of argumentation in polymer physics (the statement can also be mathematically justified in terms of Doob h-transforms). For $\lambda \in (0, \infty)$ we may write

$$\mathbb{E}^x \left[\exp \left\{ -\int_0^t B_s^2 v(s)\, ds - \lambda B_t^2 \right\} \right] = \mathbb{E}^x \left[\exp \left\{ -\int_0^t B_s^2 v^*(s)\, ds \right\} \right] \tag{89}$$

where $v^*(s) = v(s) + \lambda\delta(s-t)$. We now apply Corollary 4; the process W, having state space $[0, t]$, is marked at real time rate v^*, which is real time marking of rate v with local time marking of rate λ at t. [Elaborating,

$$\int_0^{H_0} v^*(W_u)\, du = \int_0^{H_0} \{v(W_u) + \lambda\delta(t - W_u)\}\, du \tag{90}$$

$$= \int_0^{H_0} v(W_u)\, du + \lambda L(H_0, t) \tag{91}$$

where L is the local time process for W.] Therefore, in the notation of Corollary 4,

$$p = \frac{n'(\text{hit 0 without a mark})}{n'(\text{hit 0 or } v \text{ marked}) + \lambda} \tag{92}$$

$$= \frac{b}{a+\lambda} \tag{93}$$

and

$$d = \tilde{a} - \frac{\tilde{b}b}{a+\lambda} \tag{94}$$

where

$$a = n'(\text{hit 0 or } \mu \text{ marked}) \tag{95}$$

$$\tilde{b} = n^0(\text{hit } t \text{ without being } \mu \text{ marked}) \tag{96}$$

where all the excursion measures n are for the process W. Finally it is easy to see

$$\mathbb{E}^x[\exp(-\lambda B_t^2)] = \left(\frac{1}{1+2\lambda t}\right)^{1/2} \exp\left(-\frac{x^2\lambda}{1+2t\lambda}\right) \tag{97}$$

and hence the result.

A Brownian motion started at some point x and conditioned to be at point y at time t is called a Brownian bridge on $[0, t]$ between x and y. It has the representation $\beta_s + x + (y-x)s/t$, where $(\beta)_{0 \leqslant s \leqslant t}$ is the standard Brownian bridge on $[0, t]$, i.e., starting and ending at 0 (for example, see ref. 13); it is clear that its time reversal is the Brownian bridge on $[0, t]$ between y and x. Therefore a consequence of Lemma 5 is

$$\mathbb{E}^{0 \to x}\left[\exp\left(-\int_0^t B_s^2\, d\mu\right)\right] = (2\tilde{b}t)^{1/2} \exp\left\{-\left(a - \frac{1}{2t}\right)x^2\right\} \tag{98}$$

If we set $x=0$, then we find

$$\mathbb{E}^{0\to 0}\left[\exp\left(-\int_0^t B_s^2\,d\mu\right)\right]=(2bt)^{1/2}$$
$$=(2\tilde{b}t)^{1/2} \tag{99}$$

and hence $b=\tilde{b}$. Using (99) and the excursion rate (55), we recover the well known result[17, 2] (where once again it was obtained by calculations using resolvent operators)

$$\mathbb{E}^{0\to 0}\left[\exp\left(-\frac{1}{2}\int_0^t B_s^2\alpha^2\,ds\right)\right]=\left(\frac{\alpha t}{\sinh(\alpha t)}\right)^{1/2} \tag{100}$$

One can see that the expressions for (100) and (74) are the same; this is explained elegantly in ref. 6.

We are now in the position to give the general form of the law of the quadratic functional for a path with both endpoints fixed at arbitrary points.

Lemma 6. We have

$$\mathbb{E}^{x\to y}\left[\exp\left(-\int_0^t B_s^2\,d\mu\right)\right]=(2bt)^{1/2}\exp\left\{-\tilde{a}x^2+2bxy-ay^2+\frac{1}{2t}(x-y)^2\right\} \tag{101}$$

Proof. The basis of the proof is to note that

$$\mathbb{E}^{x\to y}\left[\exp\left(-\int_0^t B_s^2\,d\mu\right)\right]=\mathbb{E}\left[\exp\left\{-\int_0^t(\beta_s+a(s))^2\,d\mu\right\}\right] \tag{102}$$

where β is the standard Brownian bridge on $[0,t]$ and $a(s)=x+(y-x)s/t$. Hence the result (39) implies that

$$\mathbb{E}^{x\to y}\left[\exp\left(-\int_0^t B_s^2\,d\mu\right)\right]=C\exp(R[x,y]) \tag{103}$$

where C is independent of x and y, and R is quadratic in x and y. We may read off the value of C and the diagonal terms of R from (85) and (98), giving

$$\mathbb{E}^{x\to y}\left[\exp\left(-\int_0^t B_s^2\,d\mu\right)\right]=(2bt)^{1/2}\exp\left\{-\tilde{a}x^2+2rxy-ay^2+\frac{1}{2t}(x-y)^2\right\} \tag{104}$$

leaving only the value of r to be determined. Using Eq. (104) and Corollary 4, we may write

$$\mathbb{E}^x\left[\exp\left(-\int_0^t B_s^2\,d\mu\right)\right]$$

$$= \mathbb{E}\left[(2bt)^{1/2}\exp\left\{-\tilde{a}x^2 + 2rx(x+N) - a(x+N)^2 + \frac{1}{2t}(N)^2\right\}\right] \tag{105}$$

$$= \left(\frac{b}{a}\right)^{1/2}\exp\left\{-\left(\tilde{a} - \frac{b^2}{a}\right)x^2\right\} \tag{106}$$

where the expectation on the right-hand side of (105) is over N, a normal $N(0, t)$ random variable (i.e., we are simply averaging over all possible endpoints of the path starting at x). Taking the expectation over N and equating the two right-hand sides above, we obtain the required result.

The propagator for the polymer path is given by

$$K(y, t \mid x, 0) = \mathbb{E}^x\left[\delta(y - B_t)\exp\left(-\int_0^t B_s^2\,d\mu\right)\right] \tag{107}$$

$$= \mathbb{E}^{x\to y}\left[\exp\left(-\int_0^t B_s^2\,d\mu\right)\right]\cdot\mathbb{E}^x[\delta(y - B_t)] \tag{108}$$

$$= \left(\frac{b}{2\pi}\right)^{1/2}\exp(-\tilde{a}x^2 + 2bxy - ay^2) \tag{109}$$

If we set $d\mu = \frac{1}{2}\alpha^2\,ds$, then substituting the relevant excursion rates into (109), we obtain the (analytic continuation) of the well-known propagator for the simple harmonic oscillator,[7] i.e.,

$$K(y, t \mid x, 0) = \left(\frac{\alpha}{2\pi\sinh(\alpha t)}\right)^{1/2}\exp\left\{-\frac{1}{2}\alpha\coth(\alpha t)\right.$$

$$\left.\times(x^2 + y^2 - 2xy\,\mathrm{sech}(\alpha t))\right\} \tag{110}$$

This is directly a consequence of the fact that the analytic continuation of the polymer measure to imaginary time gives the path integral measure for quantum mechanics (in suitably chosen units). Less directly, one can use the Feynman–Kac formula to show that $K(y, t \mid x, 0)$ satisfies a diffusion equation[12]; this diffusion equation is the analytic continuation of the Schrödinger equation for the simple harmonic oscillator into imaginary time.

When the polymer in which we are interested is a ring polymer, then we find

$$\psi(x) = \mathbb{E}^{x \to x}\left[\exp\left(-\int_0^t B_s^2 \, d\mu\right)\right] \tag{111}$$

$$= (2bt)^{1/2} \exp\{-x^2(\tilde{a} + a - 2b)\} \tag{112}$$

and consequently

$$\phi = \left(\frac{2bt}{\rho(a + \tilde{a} - 2b)}\right)^{1/2} \tag{113}$$

Examples

Ring Polymer of Uniform Resistance. In this case we take $d\mu = \frac{1}{2}\alpha^2 \, ds$ and take the bridge to be run for time t. Substituting the relevant excursion rates into (113), we obtain

$$\phi = \frac{\alpha t}{2 \sinh(\alpha t/2)} \tag{114}$$

Once again this is in agreement with the resolvent-based calculation to be found in ref. 2. If we examine the analytic continuation to a direction where the flow is stretching, we find that the coil–stretch transition lies at $\alpha t = 2\pi$. The fact that the endpoints are joined makes the polymer less susceptible to stretching. In fact, comparing the partition functions (114) and (74) reveals that the partition function for the ring polymer of time length t is equal to the product of the partition functions of two identical single-strand, free-end polymers of half the time length (i.e., $t/2$) and the same resistance. Unfortunately, this result is not the sign of anything deeper to be uncovered, as we shall see in the next example.

Ring Polymer of Piecewise Constant Resistance. Here we shall take the polymer path to be a ring with resistance measure given by (76). We can think of this as a ring polymer made up of two single-strand polymers joined at their free ends. In order to simplify the forthcoming excursion arguments, we make the following observation. Because it is a measure on a ring polymer, the resistance measure $d\mu$ can be thought of as a measure on $[0, t]$ with the points 0 and t topologically identified, i.e., a circle of circumference t, S_t^1. We can now consider excursions Brownian motion W on the space S_t^1 with marking generated by the measure $d\mu$; however, we note that excursions from 0 or t end both when they return

to 0 and when they hit t. Let m denote the excursion measure on excursions of W. Marked excursions can be either clockwise or anticlockwise (the two sets being disjoint) and hence

$$m^0(\text{marked}) = m^0(\text{clockwise marked}) + m^0(\text{anticlockwise marked}) \quad (115)$$

If we take s to be increasing in the anticlockwise direction, then

$$m^0(\text{anticlockwise marked}) = \tilde{a} - b \quad (116)$$

and

$$m^0(\text{clockwise marked}) = a - b \quad (117)$$

Therefore

$$m^0(\text{marked}) = \tilde{a} + a - 2b \quad (118)$$

giving us an alternative interpretation for the excursion rate in the exponential in Eq. (112).

In our example

$$m^0(\text{marked}) = m^0(\text{marked or hit } a) - m^0(\text{hit } a \text{ with no mark}) \cdot \mathbb{P}^a(\text{hit 0 without a mark}) \quad (119)$$

Using the rates from Section 4, we find

$$m^0(\text{marked or hit } a) = \frac{\alpha}{2}\coth(\alpha a) + \frac{\beta}{2}\coth\{\beta(1-a)\} \quad (120)$$

and

$$m^0(\text{hit } a \text{ without a mark}) = \frac{\alpha}{2}\operatorname{cosech}(\alpha a) + \frac{\beta}{2}\operatorname{cosech}\{\beta(1-a)\} \quad (121)$$

A straightforward excursion argument gives

$$\mathbb{P}^a(\text{hit 0 without a mark}) = \frac{\alpha \operatorname{cosech}(\alpha a) + \beta \operatorname{cosech}(\beta(1-a))}{\alpha \coth(\alpha a) + \beta \coth(\beta(1-a))} \quad (122)$$

We also have

$$b = \frac{\alpha}{2}\operatorname{cosech}(\alpha a) \cdot \frac{\beta \operatorname{cosech}(\beta(1-a))}{\alpha \coth(\alpha a) + \beta \coth(\beta(1-a))} \quad (123)$$

Putting these rates into (113) yields

$$\phi = \left(\frac{\alpha^2 a + \beta^2 (1-a)}{(\alpha/\beta + \beta/\alpha)\sinh(\alpha a)\sinh(\beta(1-a)) + 2\cosh(\alpha a)\cosh(\beta(1-a)) - 2} \right)^{1/2} \tag{124}$$

So, unfortunately, there is no nice link between this partition function and the partition functions for the two polymers it is built up from.

7. PARTITION FUNCTIONS FOR DETERMINISTICALLY BRANCHING POLYMERS

The partition functions for deterministically branching polymers in elongational flows can be calculated by an extension of the techniques presented so far. The branching polymer is modeled by a Brownian motion whose time is indexed by a tree $\mathcal{T}$. Each interinternal node of the tree corresponds to a point where the Brownian motion has branched; segments of trees are the edges between nodes and correspond to the time intervals over which the corresponding path of the Brownian motion is run for (see Fig. 2). On each segment of the graph we once again have a measure μ, interpreted as the resistance of the corresponding segment of the polymer in the flow. The partition function of the branching polymer structure is

$$\phi = \mathbb{E}\left[\exp\left\{ -\left(\int_{\mathcal{T}} B_s^2 \, d\mu - \rho \left(\int_{\mathcal{T}} B_s \, d\mu \right)^2 \right) \right\} \right] \tag{125}$$

where we take $\rho = \mu(\mathcal{T})^{-1}$, making the expression (125) translation invariant.

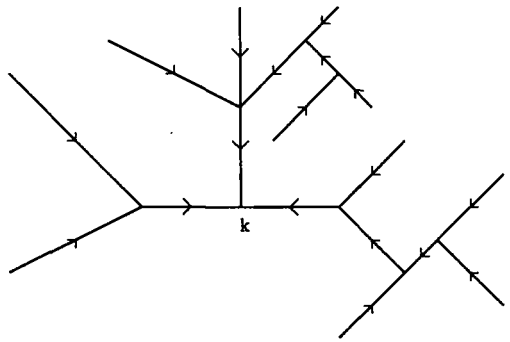

Fig. 2. Time free for a polymer with root k.

First we may make a particular choice of node of $\mathscr{T}$ as the root of the tree, say k corresponding to the starting point of the branching polymer. Now we consider a process W on $\mathscr{T}$ which is standard Brownian motion away from the nodes, is reflected at the free ends, and at each internal node its excursions are equally likely to go down any of the incident edges (in fact the construction of W is exactly the same as that for diffusion on a generalized comb in ref. 4). For each choice of node k as the root and each segment $\sigma = (i, j)$ connecting nodes i and j, where i is closer to the chosen root than j (so we can draw an arrow in the direction of k, see Fig. 2), define

$$P_{\sigma,k} \equiv \mathbb{P}^j(W \text{ reaches } i \text{ without being } \mu\text{-marked}) \tag{126}$$

and

$$\psi_k(x) \equiv \mathbb{E}^x\left[\exp\left(-\int_{\mathscr{T}} B_s^2 \, d\mu\right)\right] \tag{127}$$

where node k is chosen as the time origin of B and $B_k = x$.

Theorem 7. Let B be a deterministically branching Brownian motion indexed by tree $\mathscr{T}$ and choose node k of $\mathscr{T}$ as the root. Then if $B_k = x$,

$$\psi_k(x) = \left(\prod_{\sigma} P_{\sigma,k}\right)^{1/2} e^{-d_k x^2} \tag{128}$$

where d_k is the local time rate of μ-marked excursions by W from node k.

The proof is by induction on the number n of nodes and can be found in ref. 2. Using (128), we then obtain the partition function as

$$\phi = \left(\frac{\prod_{\mathscr{T},n}}{\rho d_n}\right)^{1/2} \tag{129}$$

where $\prod_{\mathscr{T},n} = \prod_{\sigma \in \mathscr{T}} P_{\sigma,n}$. One can readily check[2] that the above expression is independent of the choice of root, as we should expect from translational invariance. As a first simple, but illustrative, example we shall return to the single-strand polymer made by joining two polymers of uniform but differing resistances. The natural choice (with the benefit of

hindsight) for the root k is now at the joining point $s=a$ on $[0, 1]$. It is now trivial that

$$d_k = \frac{\alpha}{2}\tanh(\alpha a) + \frac{\beta}{2}\tanh(\beta(1-a)) \tag{130}$$

$$\prod_{\sigma} P_{\sigma,k} = \frac{1}{\cosh(\alpha a)\cosh(\beta(1-a))} \tag{131}$$

and

$$\rho = \frac{\alpha^2 a + \beta^2(1-a)}{2} \tag{132}$$

thus recovering the partition function (84).

General Star Polymer. We may construct a star polymer by taking n single-strand polymers, modeled by a Brownian path on $[0, \tau_i]$ with associated resistance measure μ_i, and joining them at the origin of their respective time segments (see Fig. 3). We choose the root k of the time graph to be the common origin. Using an obvious extension of the notations established in the previous section, we obtain the partition function for the star polymer as

$$\phi = \left(\frac{\prod_{i=1}^{n} p_i}{\rho \sum_{i=1}^{n} d_i}\right)^{1/2} \tag{133}$$

where $\rho = (\sum_{i=1}^{n} \int_0^{\tau_i} d\mu_i)^{-1}$. In particular, if each of the component *rays* consists of a single monomer type, and hence has a constant resistance measure $d\mu_i = \frac{1}{2}\alpha_i^2\, ds$, we obtain

$$\phi = \left(\frac{\prod_{i=1}^{n} \operatorname{sech}(\alpha_i \tau_i)}{\rho \sum_{i=1}^{n} \frac{1}{2}\alpha_i \tanh(\alpha_i \tau_i)}\right)^{1/2} \tag{134}$$

this being the general form of a result derived in ref. 2.

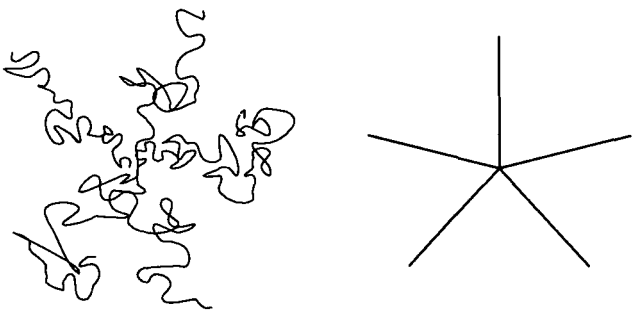

Fig. 3. A star polymer, pictured alongside its time graph.

Fig. 4. A "spider" polymer with its time graph.

8. MORE EXAMPLES

"Spider" Polymer. So far we have only considered branching polymer structures modeled on trees. By making use of our previous results for Brownian bridges, it is possible to handle polymers with rings. Consider a graph which consists of a loop (which we think of as the path of a Brownian bridge of length τ from x to x) with n trees $\mathcal{T}_m$, $m = 1,..., n$, attached by node k_m to the loop at time T_m (see Fig. 4). In this case

$$\psi(x) = \mathbb{E}^{x,x}\left[\exp\left(-\int_0^\tau X_s^2\, d\mu - \sum_{m=1}^n d_m X_{T_m}^2\right)\right]\left(\prod_{m=1}^n \Pi_{\mathcal{T}_m, k_m}\right)^{1/2} \tag{135}$$

$$= \mathbb{E}^{x,x}\left[\exp\left(-\int_0^\tau X_s^2\, d\mu^*\right)\right]\left(\prod_{m=1}^n \Pi_{\mathcal{T}_m, k_m}\right)^{1/2} \tag{136}$$

where X is now a Brownian bridge of length τ from x to x and $d\mu^* = d\mu + \sum_{m=1}^n d_m \delta_{T_m}\, ds$. The first factor on the right-hand side above can now be calculated using (112), giving the corresponding partition function ϕ to be

$$\phi = \left(\frac{2bt}{\rho(a^* + \tilde{a}^* - 2b^*)}\right)^{1/2}\left(\prod_{m=1}^n \Pi_{\mathcal{T}_m, k_m}\right)^{1/2} \tag{137}$$

the asterisk indicating that excursion rates are to be calculated for excursions with marking generated by the measure $d\mu^*$.

9. INCLUDING SOURCE TERMS

In order to gain statistical information about the geometry of a polymer path it is necessary to include source terms in the partition

function. We may analyze the statistics of the end-to-end distance for a single-strand polymer by considering the generating function

$$\phi(\lambda) = \mathbb{E}^0\left[\exp\left\{-\left(\int_0^t B_s^2\, d\mu - \rho\left(\int_0^t B_s\, d\mu\right)^2 + \lambda B_t\right)\right\}\right] \tag{138}$$

Given this, we may calculate

$$\langle \exp(-\lambda X_t)\rangle = \frac{\phi(\lambda)}{\phi(0)} \tag{139}$$

Here X is the actual physical polymer path obtained by using the correct Boltzmann weight given by (3), i.e., the measure on the process changed by the potential due to the flow. To compute $\phi(\lambda)$ we proceed as before: uncompleting the square by introducing the $N(0, 1)$ random variable G and shifting the origin, we obtain

$$\begin{aligned}\phi(\lambda) &= \mathbb{E}_G\left[\mathbb{E}^{G(\rho/2)^{1/2}}\left[\exp\left\{-\left(\int_0^t B_s^2\, d\mu + \lambda B_t\right.\right.\right.\right.\\ &\qquad \left.\left.\left.\left. - \lambda G\left(\frac{\rho}{2}\right)^{1/2}\right)\right\}\,\middle|\, G\right]\exp\left(\frac{G^2}{2}\right)\right]\\ &= \frac{1}{(2\pi)^{1/2}}\int_{\mathbb{R}} d\xi\, \mathbb{E}^{\xi(\rho/2)^{1/2}}\left[\exp\left\{-\left(\int_0^t B_s^2\, d\mu + \lambda B_t - \lambda\xi\left(\frac{\rho}{2}\right)^{1/2}\right)\right\}\right]\end{aligned} \tag{140}$$

We deal with the endpoint by writing (140) as

$$\begin{aligned}\phi(\lambda) = \frac{1}{(2\pi)t^{1/2}}\int_{\mathbb{R}^2} d\xi\, dy \left\{\exp\left(-\frac{y^2}{2t}\right)\right\}\\ \times \mathbb{E}^{\xi(\rho/2)^{1/2}\to y+\xi(\rho/2)^{1/2}}\left[\exp\left\{-\left(\int_0^t B_s^2\, d\mu + \lambda y\right)\right\}\right]\end{aligned} \tag{141}$$

i.e., we first condition on the endpoint and then average it out. We may now use (101), giving

$$\phi(\lambda) = \frac{(2b)^{1/2}}{2\pi}\int_{\mathbb{R}^2} dz \exp\left(-\frac{1}{2}z^T A z - c\cdot z\right) \tag{142}$$

where

$$A = \begin{pmatrix} \rho(a+\tilde{a}-2b) & (a-b)(2\rho)^{1/2} \\ (a-b)(2\rho)^{1/2} & 2a \end{pmatrix} \tag{143}$$

$$z = \begin{pmatrix} \xi \\ y \end{pmatrix} \tag{144}$$

and

$$c = \begin{pmatrix} 0 \\ \lambda \end{pmatrix} \tag{145}$$

Consequently,

$$\begin{aligned} \phi(\lambda) &= (2b)^{1/2} (\det(A))^{-1/2} \exp\left(\frac{1}{2} c^T A^{-1} c\right) \\ &= \left(\frac{p}{\rho d}\right)^{1/2} \exp\left[\frac{\lambda^2}{4}\left(\frac{a+\tilde{a}-2b}{a\tilde{a}-b^2}\right)\right] \end{aligned} \tag{146}$$

and where we have used the relations

$$d = \tilde{a} - \frac{b^2}{a} \tag{147}$$

and

$$p = \frac{b}{a} \tag{148}$$

Therefore, using (139), we obtain

$$\langle \exp(-\lambda X_t) \rangle = \exp\left[\frac{\lambda^2}{4}\left(\frac{a+\tilde{a}-2b}{a\tilde{a}-b^2}\right)\right] \tag{149}$$

$$\langle X_t^2 \rangle = \frac{1}{2}\left(\frac{a+\tilde{a}-2b}{a\tilde{a}-b^2}\right) \tag{150}$$

The reader may like to check that in the zero-resistance limit (150) gives the result for standard Brownian motion. In addition we note that X_t is a Gaussian random variable. [We should anticipate this, as the energy functional on the paths is still quadratic in X and hence the process $(X)_{0 \leqslant s \leqslant t}$ is Gaussian.]

In cases where the polymer resistance measure is invariant under time reversal, then we have $\tilde{a} = a$ and Eq. (150) simplifies to

$$\langle X_t^2 \rangle = \frac{1}{a+b} \tag{151}$$

In the case of a uniform resistance we find

$$\langle X_t^2 \rangle = \frac{2}{\alpha} \tanh\left(\frac{\alpha t}{2}\right) \tag{152}$$

As expected, the mean-squared end-to-end distance decreases as the compressing flow strength increases. If the component of the flow is instead stretching, then the substitution $\alpha \to i\alpha$ gives

$$\langle X_t^2 \rangle = \frac{2}{\alpha} \tan\left(\frac{\alpha t}{2}\right) \tag{153}$$

The stretching component of the flow increases the mean-squared end-to-end distance up to the coil–stretch transition, where it becomes infinite.

10. A REMARK ON STAR-TYPE POLYMERS

When we considered the partition function for star polymers in Section 7, the reader may have noticed that when the *rays* of the polymer are identical, the partition function takes on a much simpler form. Here we explain that simplification, in a slightly more general setting, as a consequence of the geometry of the original problem. Consider take n identical polymer types with the same time graph $\mathcal{T}$ (note that we need not restrict ourselves to trees here) and with the same resistance measure μ on each polymer. Now we choose a point x on the graph $\mathcal{T}$ and form a new *star-shaped* polymer by joining the individual polymers at the point x. The partition function for this new polymer is given by

$$\phi = \mathbb{E}\left[\exp\left\{-\left(\int_{\mathcal{T}} \sum_{i=1}^{n} B_i^2 \, d\mu - \frac{\rho}{n}\left(\int_{\mathcal{T}} \sum_{i=1}^{n} B_i \, d\mu\right)^2\right)\right\}\right] \tag{154}$$

where $\rho = \mu(\mathcal{T})^{-1}$. The process $B = (B_1, B_2, \ldots, B_n)$ can be viewed as a process in $\mathbb{R}^n$; so, defining the unit vector in $\mathbb{R}^n$

$$r = \frac{1}{\sqrt{n}}(1, 1, \ldots, 1) \tag{155}$$

we find

$$\phi = \mathbb{E}\left[\exp\left\{-\left(\int_{\mathscr{T}} B^2\, d\mu - \rho\left(\int_{\mathscr{T}} B\cdot r\, d\mu\right)^2\right)\right\}\right] \tag{156}$$

By rotating the coordinate axis in $\mathbb{R}^n$, taking the first orthonormal basis vector to r, one obtains

$$\begin{aligned}\phi &= \mathbb{E}\left[\exp\left\{-\left(\int_{\mathscr{T}} B^2\, d\mu - \rho\left(\int_{\mathscr{T}} B_1\, d\mu\right)^2\right)\right\}\right] \\ &= \mathbb{E}\left[\exp\left\{-\left(\int_{\mathscr{T}} B_1^2\, d\mu - \rho\left(\int_{\mathscr{T}} B_1\, d\mu\right)^2\right)\right\}\right] \\ &\quad \times \prod_{i=2}^{n} \mathbb{E}\left[\exp\left(-\int_{\mathscr{T}} B_i^2\, d\mu\right)\,\middle|\, B_x = 0\right]\end{aligned} \tag{157}$$

where we have used the independence of the B_i. Hence we need only calculate the partition function for a single ray with the center-of-mass correction to the energy functional. If in addition $\mathscr{T}$ itself had been a star and the connection point x had been the end of a ray, we could now compute the factor in the partition function with the center-of-mass correction in exactly the same way. For example, we shall take $\mathscr{T}$ to be a star polymer made by joining the endpoints of m identical single strands of length t and with uniform resistance measure $(\alpha^2/2)\, ds$. The new star polymer is then formed by joining n of these at a connection point x which is the free end of one of the single-strand rays. Applying (157) to the star polymer $\mathscr{T}$, we find

$$\begin{aligned}&\mathbb{E}\left[\exp\left\{-\left(\int_{\mathscr{T}} B_1^2\, d\mu - \rho\left(\int_{\mathscr{T}} B_1\, d\mu\right)^2\right)\right\}\right] \\ &\quad = [\operatorname{sech}(\alpha t)]^{(m-1)/2}\left(\frac{\alpha t}{\sinh(\alpha t)}\right)^{1/2}\end{aligned} \tag{158}$$

Application of Theorem 7 gives

$$\begin{aligned}&\mathbb{E}\left[\exp\left(-\int_{\mathscr{T}} B_i^2\, d\mu\right)\,\middle|\, B_x = 0\right] \\ &\quad = [\operatorname{sech}(\alpha t)]^{(m-1)/2}\left(\frac{\operatorname{cosech}(\alpha t)}{(m-1)\tanh(\alpha t) + \coth(\alpha t)}\right)^{1/2}\end{aligned} \tag{159}$$

for $2 \leqslant i \leqslant n$. Hence (157) yields the partition function as

$$\phi = [\operatorname{sech}(\alpha t)]^{n(m-1)/2} \left(\frac{\operatorname{cosech}(\alpha t)}{(m-1)\tanh(\alpha t) + \coth(\alpha t)} \right)^{(n-1)/2} \times \left(\frac{\alpha t}{\sinh(\alpha t)} \right)^{1/2} \tag{160}$$

11. DISCUSSION AND CONCLUSIONS

In this paper we have demonstrated how we can compute the laws of quadratic functionals of Brownian motion using ideas from excursion theory. These techniques give us a systematic method for computing the partition functions for a wide variety of polymer types in elongational flows. The basic excursion rates needed in our calculations are known when we are dealing with piecewise constant resistances; more general resistance measures may require numerical computation of the basic rates involved. However, the piecewise constant measure does describe a wide variety of polymers, known as block copolymers, made by constructing polymers from monomers of different types. Moreover, more general resistances can also be approximated by piecewise constant resistances.

The most obvious outstanding question in this work is whether a result analogous to Theorem 7 exists for a polymer whose time index is an arbitrary graph. We have seen that in the case of a ring polymer we can carry out some of the computations by considering Brownian motion on its time graph, i.e., some of the rates appearing have a natural interpretation in terms of Brownian motion on a circle. The main difference when we include loops is that, once a root is chosen, we lose the notion of directions on segments toward the root.

ACKNOWLEDGMENTS

One of us (D.S.D.) would like to acknowledge support from a Research Fellowship awarded by the U.K. EPSRC and also by E.U. grant CHRX-CT93-0411.

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