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Probability Theory and Polymer Physics

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This study applies the theory of stochastic processes to the equilibrium statistical physics of polymers in solution. The topics treated include random copolymers and randomly branching polymers, with self-consistent mean field effects. A new and more natural way of dealing with Boltzmann weighting is discussed, which makes it possible from the beginning of a calculation to consider only the "physical" polymer conformations. We also show that in general the random copolymer problem can be reduced to the ordinary polymer problem, and treat the self-consistent field problem for a general branching polymer.

KEY WORDS: Probability; Brownian motion; Boltzmann weighting; branching polymers; copolymers; potential; self-contrast mean-field correction; Markov process; h-transform; conditioning; infinitesimal generator; transition semigroup; resolvent; exponential distribution.

1. INTRODUCTION

The purpose of this study is first to introduce those topics in the theory of stochastic processes that can be used to simplify the calculations that often occur when analyzing the equilibrium statistical mechanics of polymer solutions, and second to illustrate the power of these methods on some new problems in this field. We have tried throughout to make this paper sufficiently self-contained that anyone familiar with standard methods of polymer physics will be able to use the methods discussed here with confidence, and we have avoided discussion of those methods from probability theory which are dangerous in the hands of the inexperienced. The discussion of probability theory may seem rather simple, and the reader may imagine that we are merely giving new names to old objects.

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But what probability can bring to polymer physics is not just new names, but new techniques, and above all, new concepts, allowing problems to be tackled at a much higher level than simply the calculation of solutions. We shall describe how to determine the distribution of a piece of chain polymer placed in a potential; then the distribution of a piece of chain polymer with random "special" monomers in a potential; then the distribution of a branching polymer in a potential; and finally the self-consistent mean-field correction for a branching polymer in a potential. These problems may appear to be of steeply increasing difficulty, but the probabilistic methods we use cope easily with them all.

In Section 2, we introduce the basic ideas of Markov processes, transition semigroups, generators, and conditioning a diffusion on an invariant event. Sections 2.1 and 2.2 serve partly to set up a common language between polymer physics and probability. In Section 2.3 we introduce the idea of a graveyard state: if we consider a polymer (before Boltzmann weighting) as the path of a diffusing particle, then a graveyard state is where the particle goes when it reaches the end of the path, i.e., when it dies. This is technically and conceptually convenient, in that it means that the particle does not just vanish when it reaches the end of the path. We end Section 2 with the theory and some examples of (Doob) *h*-transforming of a diffusion, which is the central technique used in the next section. For a more leisurely and thorough discussion of these topics, the reader is encouraged to consult Karlin and Taylor(4) to begin with, Øksendal(5) for a first account of stochastic calculus, and Rogers and Williams(6) for a more wide-ranging selection.

In Section 3, we begin by applying the methods of Section 2 to single-chain polymers in solution. For simplicity, in Section 3.1 we restrict attention to polymers that have an exponentially-distributed "length" (at least before Boltzmann weighting), but this is a restriction which will be relaxed later. By considering an applied potential field as a killing rate, we show that Boltzmann weighting can be replaced by conditioning (or *h*-transforming) the diffusing particle to go to a particular graveyard. This in turn is equivalent to adding a drift and modifying the killing rate of the diffusion. The rest of Section 3 consists of applications of this new approach to (i) random copolymers, (ii) randomly-branching polymers, and (iii) single-chain polymers of fixed length.

2. MARKOV PROCESSES

2.1. Markov Processes: Transition Semigroups

Informally, a (time-homogeneous) Markov process with state space S is a random process $(X_t)_{t \geqslant 0}$ which moves around S in a "memoryless" way: where it goes from time t onward depends on its history $\{X_u : u \leqslant t\}$ only through X_t, the current state. More precisely, for any bounded $f: S \to \mathbb{R}$,

$$E[f(X_{t+u}) \mid X_s : s \leqslant t] = P_u f(X_t) \tag{1}$$

where the operators $(P_u)_{u \geqslant 0}$ form the *transition semigroup* of the Markov process X.

The defining properties

$$P_{t+s} = P_t P_s \qquad \text{for all} \quad t, s \geqslant 0 \tag{2a}$$

$$0 \leqslant f \leqslant 1 \Rightarrow 0 \leqslant P_t f \leqslant 1 \qquad \text{for each} \quad t \geqslant 0 \tag{2b}$$

$$P_t 1 = 1 \qquad \text{for each} \quad t \geqslant 0 \tag{2c}$$

of a *Markov transition semigroup* are easy to verify.

Example (i). If $S = \mathbb{R}$, $X_t = X_0 + ct$, then $P_t f(x) = f(x + ct)$.

Example (ii). Brownian motion on $\mathbb{R}$ is a Markov process with

$$P_t f(x) = \int_{-\infty}^{\infty} \frac{e^{-y^2/2t}}{(2\pi t)^{1/2}} f(x+y)\, dy \tag{3}$$

Example (iii). If S is a countable set, then the Markov process X is called a *Markov chain*, and the transition semigroup can be expressed in terms of the transition matrices

$$p_{ij}(t) = P[X_t = j \mid X_0 = i] \qquad (i, j \in S, \quad t \geqslant 0)$$

In the case where S is finite, the behavior of X is very simple; it resides in its initial state i for a random time with an exponential distribution, and then jumps to some other state according to some distribution which may depend on i.

We shall later encounter *sub-Markovian* transition semigroups, which satisfy the defining properties (2a) and (2b) of a Markovian semigroup, but not (2c). Thus, from (2b), $P_t 1 \leqslant 1$ for all $t \geqslant 0$. As a trivial example of a sub-Markovian transition semigroup, fix some $\mu > 0$ and some Markovian semigroup $(P_t)_{t \geqslant 0}$, and just consider $(\bar{P})_{t \geqslant 0} = (e^{-\mu t} P_t)_{t \geqslant 0}$! For a less trivial example, fix some subset F of S, and let $T = \inf\{u : X_u \in F\}$. Then we can define a sub-Markovian transition semigroup $(\bar{P}_t)$ by

$$\bar{P}_t f(x) = E[f(X_t) I_{\{t < T\}} \mid X_0 = x] \tag{4}$$

Exercise. Check (2a). The semigroup $(\bar{P}_t)_{t \geqslant 0}$ corresponds to the process "killed when it reaches F." There is a simple and natural way to convert a sub-Markovian transition semigroup into a Markovian one; can the reader see how? Answer in Section 2.3.

2.2. Markov Processes: Generators and Resolvents

The *generator* G of a Markov process with transition semigroup $(P_t)_{t\geqslant 0}$ is defined to be

$$Gf \equiv \lim_{t\downarrow 0} \frac{1}{t}(P_t f - f) \tag{5}$$

(for those f for which the limit exists). G is a linear operator defined on a suitable vector space of functions. Informally, we can recover the semigroup from G by the recipe

$$P_t = \exp(tG) \tag{6}$$

The semigroup $(P_t)_{t\geqslant 0}$ is sometimes called the *propagator*. The transition semigroup $(P_t)_{t\geqslant 0}$ of a Markov process is in some sense less fundamental than its Laplace transform $(R_\lambda)_{\lambda\geqslant 0}$, the *resolvent* of the Markov process:

$$R_\lambda \equiv \int_0^\infty dt\, e^{-\lambda t} P_t \tag{7}$$

In view of (6), it would be no surprise if

$$R_\lambda = \int_0^\infty dt\, e^{-\lambda t} \exp(tG) = (\lambda - G)^{-1} \tag{8}$$

While it is not easy to make exact sense of (6), it *is* possible to make exact sense of (8). See Chapter XIII of Feller(3) for the basic ideas, and Chapter III of Williams(7) for more discussion.

Two interpretations of the resolvent are possible, and helpful. Let T be an $\exp(\lambda)$ random variable [that is, $P(T>t)=e^{-\lambda t}$ for $t\geqslant 0$] independent of X. Then

$$\begin{aligned}\lambda R_\lambda f(x) &= \int_0^\infty \lambda e^{-\lambda t} P_t f(x)\, dt \\ &= E[f(X_T) \mid X_0 = x] \end{aligned} \tag{9}$$

The other interpretation is exemplified by taking $f = I_A$ for some A, and then

$$\begin{aligned} R_\lambda I_A(x) &= E\left[\int_0^\infty e^{-\lambda t} I_A(X_t)\, dt \mid X_0 = x\right] \\ &= E\left[\int_0^\infty I_{\{t<T\}} I_A(X_t)\, dt \mid X_0 = x\right] \\ &= E[\text{total time in } A \text{ before } T \mid X_0 = x] \end{aligned} \tag{10}$$

The resolvent R_λ is the Green function for the process killed at rate λ; indeed, as $\lambda \downarrow 0$, we get in the limit the Green function of the process without killing. We shall later come to speak in terms of *killing* the process X at rate λ; the fatal blow comes at time T, and so $R_\lambda I_A(x)$ is the expected time spent in A before killing by the process started at x.

Exercise. Using the semigroup property (2a), obtain the *resolvent identity*

$$R_\lambda - R_\mu + (\lambda - \mu) R_\lambda R_\mu = 0 \qquad (\lambda, \mu > 0) \tag{11}$$

Example (iv). The generator of Example (i) is easily seen to be

$$Gf(x) = cf'(x) \qquad (f \in C^1)$$

Here, C^k denotes the space of functions with continuous derivatives of all orders up to and including the kth. Likewise, C_b^k denotes the space of all functions in C^k which, together with their derivatives of all orders up to the kth, are bounded.

Example (v). For $f \in C_b^2$

$$\begin{aligned}\frac{1}{t}\,[P_t f(x) - f(x)] &= \frac{1}{t}\int_{-\infty}^{\infty} \frac{e^{-y^2/2t}}{(2\pi t)^{1/2}}\,[f(x+y) - f(x)]\,dy\\ &= \frac{1}{t}\int_{-\infty}^{\infty} \frac{e^{-y^2/2t}}{(2\pi t)^{1/2}}\left[yf'(x) + \frac{1}{2}\,y^2 f''(x+\theta y)\right]dy\\ &\qquad \text{where} \quad |\theta| \leqslant 1\\ &\to \frac{1}{2} f''(x) \qquad \text{as} \quad t \downarrow 0\end{aligned}$$

and so for Brownian motion,

$$Gf(x) = \tfrac{1}{2} f''(x) \tag{12}$$

Remarks. The transition density

$$p_t(x, y) \equiv (2\pi t)^{-1/2} \exp[-(x-y)^2/2t] \tag{13}$$

of Brownian motion is the fundamental solution to the Kolmogorov backward equation

$$\frac{\partial p}{\partial t} = \frac{1}{2}\frac{\partial^2 p}{\partial x^2}, \qquad p_0(\cdot) = \delta_y(\cdot) \tag{14}$$

We can rewrite this as

$$\frac{\partial p}{\partial t}=Gp \tag{15}$$

In greater generality, any nice second-order elliptic differential operator $\bar{G}$ generates a diffusion in the sense that the fundamental solution $\bar{p}_t(x, y)$ to

$$\frac{\partial \bar{p}}{\partial t}=\bar{G}\bar{p}, \qquad \bar{p}_0(\cdot)=\delta_y(\cdot) \tag{16}$$

defines a transition semigroup $(\bar{P}_t)_{t\geqslant 0}$

$$\bar{P}_t f(x)=\int \bar{p}_t(x, y)\, f(y)\, dy$$

and the corresponding Markov process is a diffusion (has continuous paths). A physically interesting example comes from the Langevin equation with

$$\bar{G}=\frac{1}{2}\frac{\partial^2}{\partial x^2}-\lambda x\frac{\partial}{\partial x} \tag{17}$$

where $\lambda>0$ is some parameter. In this case, the Kolmogorov backward equation can be solved explicitly to give

$$\bar{p}_t(x, y)=[2\pi(1-e^{-2\lambda t})/2\lambda]^{-1/2}\exp[-\lambda(y-xe^{-\lambda t})^2/(1-e^{-2\lambda t})] \tag{18}$$

This can be obtained with a minimum of calculation if one knows some stochastic calculus; see Section V.5 of Rogers and Williams.(6)

Exercise. If B is Brownian motion, and $X_t=B_t+ct$, where c is constant, prove that the generator of X is $\frac{1}{2}\,\partial^2/\partial x^2+c\,\partial/\partial x$.

Example (vi). Assuming S is finite, let the exponential residence time in state i have mean $1/q_i$, and let the probability of a jump from i to j be p_{ij}. Then

$$\begin{aligned}\frac{1}{t}\,[P_t f(i)-f(i)]&=\frac{1}{t}\,\{E[f(X_t)\,|\,X_0=i]-f(i)\}\\&=\frac{1}{t}\left\{(1-q_i t)\,f(i)+\sum_{j\neq i} q_i t p_{ij} f(j)-f(i)+o(t)\right\}\end{aligned}$$

since with probability $1-q_i t+o(t)$ there is no jump between 0 and t, in which case $X_t=i$, and with probability $q_i t+o(t)$ there is a jump between 0 and t, in which case X jumps to j with probability p_{ij}. The probability of more than one jump in $[0, t]$ is $o(t)$. Hence

$$Gf(i)= -q_i f(i)+\sum_{j\neq i} q_i p_{ij} f(j) \tag{19}$$

One usually makes the notation more compact by thinking of the function f as the vector $(f(i))_{i\in S}$ and by defining the *Q-matrix* of this chain by

$$\begin{aligned} q_{ij} &= q_i p_{ij} \qquad (i\neq j) \\ &= -q_i \qquad (i=j) \end{aligned} \tag{20}$$

so that the row-sums of Q are zero, and off-diagonal entries are nonnegative. Then the generator G is just the matrix Q, with Gf equal to the function (vector) Qf:

$$Gf(i)=Qf(i)$$

Since S is finite, the matrix exponential

$$P_t=\exp(tQ) \tag{21}$$

is well defined, and is in fact the transition semigroup of the chain.

Exercise. Prove that (P_t) is a Markovian transition semigroup [so check properties (2a)–(2c)]. Prove that Q is the generator of (P_t).

2.3. Markov Processes: Death and Graveyards

We introduced sub-Markovian transition semigroups in Section 2.1, and now we show how to make the sub-Markovian transition semigroup $(\bar{P}_t)_{t\geqslant 0}$ into a Markovian one. Adjoin some state ∂ to the state space S, and now send the process to ∂ when it is killed. Once it is in ∂, it stays there. Such a state ∂ is called a *graveyard* state, not surprisingly! Formally, we define the new semigroup $(P_t)_{t\geqslant 0}$ by

$$P_t f(x)=\bar{P}_t f(x)+f(\partial)[1-\bar{P}_t 1(x)] \qquad (x\in S) \tag{22a}$$

$$P_t f(\partial)=f(\partial) \tag{22b}$$

for any $t\geqslant 0$, $f\colon S\cup\{\partial\}\to\mathbb{R}$. As an exercise, check that (22a)–(22b) does define a Markovian transition semigroup, and convince yourself that it corresponds to the intuitive descrition we gave in terms of killing.

The example we gave in Section 2.1 of the sub-Markovian semigroup $(e^{-\mu t}P_t)_{t\geqslant 0}$ has a useful probabilistic interpretation; take a random variable T with density $\mu e^{-\mu t}$, independent of X, and kill X at the time T. Then

$$E[f(X_t)I_{\{t<T\}}\,|\,X_0=x]=e^{-\mu t}P_tf(x)$$

so the semigroup $(e^{-\mu t}P_t)_{t\geqslant 0}$ corresponds to X killed at an independent exponentially-distributed time. We speak of X *killed at rate* μ, because

$$P[T-t\leqslant\varepsilon\,|\,T>t]=1-e^{-\mu\varepsilon}=\mu\varepsilon+o(\varepsilon) \tag{23}$$

as $\varepsilon\downarrow 0$; so, given that T has not yet happened, *the rate at which it happens is* μ.

Let us compute the generator of X killed at rate μ. If $f\colon S\cup\{\partial\}\to\mathbb{R}$, the transition semigroup of X killed at rate μ is $(P_t^\mu)_{t\geqslant 0}$ given by

$$\begin{aligned} &P_t^\mu f(x)=e^{-\mu t}P_tf(x)+(1-e^{-\mu t})f(\partial) \qquad (x\in S)\\ &P_t^\mu f(\partial)=f(\partial)\end{aligned} \tag{24}$$

Hence, for $x\in S$,

$$\begin{aligned} G^\mu f(x)&=\lim_{t\downarrow 0}\frac{1}{t}\,[P_t^\mu f(x)-f(x)]\\ &=\lim_{t\downarrow 0}\frac{1}{t}\,\{e^{-\mu t}[P_tf(x)-f(x)]-(1-e^{-\mu t})f(x)+(1-e^{-\mu t})f(\partial)\}\\ &=Gf(x)-\mu f(x)+\mu f(\partial) \end{aligned} \tag{25}$$

Often in practice one thinks of the generator G^μ as acting on functions defined only on S—in which case we set $f(\partial)=0$ by convention—and then the generator takes the simple form

$$G^\mu=G-\mu \tag{26}$$

We shall, however, have need of the full form (25) of G^μ.

One could envisage a situation where the Markov process was being killed in some part of S, but not elsewhere, or more generally, where the rate of killing depends on the position of the particle. We now explain how to treat this situation. The idea is to imagine that there is an exponential random variable T of rate 1 (so with density e^{-t}) given to us, independent of the process X. If the rate of killing when at x is $V(x)$, we compute the "accumulated risk" up to time t,

$$R_t \equiv \int_0^t V(X_s)\,ds \tag{27}$$

and kill X when $R_t = T$. Thus, when X is in regions where V is large, the accumulated risk climbs quickly, and we are more likely to see killing than in a region where V is small. The memoryless property of T

$$P[T-t>s \mid T>t] = P[T>s]$$

ensures that the probability of killing in $(t, t+dt)$ depends only on X_t and not on the accumulated risk R_t. Notice that the special case $V(x)=\mu$ for all x gives killing at time T/μ—which has density $\mu e^{-\mu t}$, exactly as before! To compute the (sub-Markovian) semigroup of X killed at rate V, note that if we condition on the whole of the process $\{X_s : s \geqslant 0\}$, then

$$\begin{aligned} P[\text{killing comes after } t \mid X] &= P[T>R_t \mid X] \\ &= \exp(-R_t) \end{aligned} \tag{28}$$

Hence the killed semigroup $(P_t^V)_{t \geqslant 0}$ is just

$$P_t^V f(x) = E[f(X_t) e^{-R_t} \mid X_0 = x] + f(\partial)\, E[1 - e^{-R_t} \mid X_0 = x] \tag{29}$$

Thus the generator is

$$\begin{aligned} G^V f(x) &= \lim_{t \downarrow 0} \frac{1}{t} \left[E(f(X_t) e^{-R_t} \mid X_0 = x) - f(x) + f(\partial)\, E(1 - e^{-R_t} \mid X_0 = x) \right] \\ &= Gf(x) - V(x) f(x) + V(x) f(\partial) \end{aligned} \tag{30}$$

We shall be using these ideas a lot in Section 3.

2.4. Markov Processes: *h*-Transforms

The notion of an h-transform of a Markov process is central to the discussion of polymer models which follows; it allows us to replace Boltzmann weighting as an equivalent conditioning. We begin with a concrete example.

Example (vii). Consider a random walk on $\{0, 1, \ldots, N\}$, which stays in state i for an exponentially distributed time mean λ^{-1}, then jumps with equal probability to $i+1$, $i-1$, for $i=1,\ldots,N-1$. Once the process reaches 0 or N, it stays still forever. Then

$$Q=\begin{pmatrix} 0 & 0 & 0 & \cdots \\ \lambda/2 & -\lambda & \lambda/2 & \cdots \\ \vdots & \vdots & \vdots & \end{pmatrix}$$

Let us compute for this example

$$h(i)\equiv P[X_t=N \text{ eventually} \mid X_0=i] \tag{31}$$

Evidently, $h(0)=0$, $h(N)=1$, and by considering what happens at the first jump of X,

$$h(i)=\tfrac{1}{2}h(i+1)+\tfrac{1}{2}h(i-1) \qquad (i=1,\ldots,N-1) \tag{32}$$

From this it follows easily that the unique solution is

$$h(i)=i/N \tag{33}$$

Notice that (32) says that $Qh=0$, so

$$P_t h=\exp(tQ)h=h \tag{34}$$

Now we investigate for this example the key concept of *conditioning the Markov process*. The event $F=\{X_t=N \text{ eventually}\}$ has the property that it is determined by $\{X_s: s\geqslant K\}$ for each K, however large. Thus,

$$\begin{aligned} &P[X_t=j \mid F, X_0=i] \\ &\quad=\frac{P[X_t=j, F\mid X_0=i]}{P[F\mid X_0=i]} \\ &\quad=\frac{P[F\mid X_t=j, X_0=i]\; p_{ij}(t)}{h(i)} \qquad \text{where} \quad p_{ij}(t)\equiv P[X_t=j\mid X_0=i] \\ &\quad=\frac{P[F\mid X_t=j]\; p_{ij}(t)}{h(i)} \\ &\qquad\qquad \text{since } X \text{ is Markovian and } F \text{ is determined by } (X_u)_{u\geqslant t} \\ &\quad=\frac{h(j)\, p_{ij}(t)}{h(i)} \end{aligned}$$

The importance of this is that *the old Markov chain has been trans-*

formed into a new Markov chain with transition semigroup $(\tilde{P}_t)_{t\geqslant 0} \equiv ((\tilde{p}_{ij}(t))_{i,j\in S})_{t\geqslant 0}$ defined by

$$\tilde{p}_{ij}(t) = p_{ij}(t)\, h(j)/h(i) \tag{35}$$

Exercise. Verify that $(\tilde{P}_t)_{t\geqslant 0}$ satisfies (2a)–(2c), using (34) for (2c).

In complete generality, a function $h: S \to [0, \infty)$ for which

$$P_t h = h \qquad (t \geqslant 0) \tag{36}$$

is said to be *harmonic* [with respect to the semigroup $(P_t)_{t\geqslant 0}$].

It follows from (36) and the definition (5) of the generator that if h is harmonic, then

$$Gh = 0 \tag{37}$$

One can again define a semigroup $(\tilde{P}_t)_{t\geqslant 0}$ by

$$\tilde{P}_t f = \frac{1}{h} P_t(hf) \tag{38}$$

The interpretation in terms of conditioning is now not quite so direct, but one can make up some sort of explanation, the details of which we shall not go into here.

In terms of generators, the h-transform of the original process has generator $\tilde{G}$ defined by

$$\tilde{G}f = \frac{1}{h} G(hf) \tag{39}$$

Returning to the random walk example, Example (vii), the h-transformed chain was just the chain *conditioned on the event F.* The original generator G was the matrix Q

$$q_{i,i+1} = \lambda/2 = q_{i,i-1}$$

and the harmonic function h was $h(i) = i/N$, so the new generator is

$$\tilde{q}_{i,i+1} = q_{i,i+1} \frac{h(i+1)}{h(i)} = \frac{i+1}{i} \frac{\lambda}{2}$$

$$\tilde{q}_{i,i-1} = \frac{i-1}{i} \frac{\lambda}{2}$$

Notice that $\tilde{q}_{10} = 0$, as it must be if the process is to get absorbed at N.

Our final examples of harmonic functions, also to do with Brownian motion, illustrate a simple but important trick for dealing with a lack of time homogeneity. Suppose, for example, that one considered

$$X_t = B_t + \mu(t)$$

where B is Brownian motion on $\mathbb{R}$, and μ is some nonrandom continuous function. Then X is *not* a Markov process, because the distribution of X_{t+s} given X_t is $N(\mu(t+s) - \mu(t) + X_t, s)$, which depends on t as well as on X_t. [Here we use the notation $N(\mu, \sigma^2)$ for a normal distribution with mean μ and variance σ^2.] However, if we consider the *space-time* process (t, X_t)—so we keep track of time as well as the position of the process X—we have a Markov process. Indeed,

$$\begin{aligned} Gf(t, x) &= \lim_{\varepsilon \downarrow 0} \frac{1}{\varepsilon} \left[P_\varepsilon f(t, x) - f(t, x)\right] \\ &= \lim_{\varepsilon \downarrow 0} \frac{1}{\varepsilon} \int \frac{e^{-y^2/2\varepsilon}}{(2\pi\varepsilon)^{1/2}} \{f(t+\varepsilon, x + y + \mu(t+\varepsilon) - \mu(t)) - f(t, x)\}\, dy \\ &= \frac{\partial f}{\partial t} + \frac{1}{2}\frac{\partial^2 f}{\partial x^2} + \mu'(t)\frac{\partial f}{\partial x} \qquad (40) \end{aligned}$$

(The sign of the first-order terms *is* correct, despite the apparent clash with the Kolmogorov backward equation; time here is running in the opposite direction to the direction in the Kolmogorov backward equation.)

Example (viii). For the space-time Brownian motion $(t, B_t)_{t \geq 0}$ in $\mathbb{R}^n$,

$$h(t, x) \equiv \exp\{c \cdot x - \tfrac{1}{2}|c|^2 t\} \qquad (41)$$

is a (space-time) harmonic function, as can easily be verified directly by computing $P_\varepsilon h(t, x)$. [It is trivial to check that $Gh = 0$, but a little care is needed; this is a necessary condition for h to be harmonic, but not sufficient. Consider, for example, the function $f(z) = \mathrm{Re}(\exp(z^3))$ of the complex variable z. Being the real part of an analytic function, it satisfies Laplace's equation, but $P_t f$ is not defined for $t > 0$, since f is not integrable with respect to the Brownian transition density.]

For the space-time Brownian motion h-transformed by $\exp(c \cdot x - \frac{1}{2}|c|^2 t)$ one gets

$$\tilde{G}f = \tfrac{1}{2}\Delta f + c \cdot \nabla f$$

As one knows if one did the earlier exercise, this is the generator of Brownian motion with *constant drift c*.

Example (ix). We consider the celebrated Brownian bridge, which is a Brownian motion in $\mathbb{R}^n$ "conditioned to be at $a \in \mathbb{R}^n$ at fixed time T." We take the space-time process

$$X_t = (t, B_t) \tag{42}$$

for $0 \leqslant t < T$. It is not hard to confirm that

$$h(t, x) = [2\pi(T-t)]^{-n/2} \exp[-|x-a|^2/2(T-t)], \qquad t < T \tag{43}$$

is harmonic, with the informal interpretation $h(t, x) = P(B_T = a \mid B_t = x)$.

For the Brownian motion "conditioned to be at $a \in \mathbb{R}^n$ at time T" we get

$$\tilde{G}f = \frac{1}{2}\Delta f - \frac{x-a}{T-t} \cdot \nabla f \qquad (t < T) \tag{44}$$

The process corresponding to this generator really does go to a at time T, as shown from Section IV.40 of Rogers and Williams,(6) for example.

3. POLYMERS

3.1. Single-Chain Polymers in Solution

All of the polymer examples we shall consider are of processes which can diffuse and jump, and we have just seen what happens when one conditions (or h-transforms) simple examples of such processes. "Putting the process into a potential" can be interpreted in terms of conditioning, and this renders the problem amenable to techniques of Markov process theory. The physical importance of putting a polymer into a potential is great enough to justify the effort required to understand these unfamiliar probabilistic ideas.

In this section, we shall apply the methods of Section 2 to the theory of polymers, as set forth in Edwards and Doi(1) or de Gennes,(2) for instance. We begin by considering the equilibrium statistical mechanics of a solution of ideal single-chain polymers in a potential field V when weakly coupled to a large reservoir (where the potential is zero) of polymers having an exponential "length" distribution. Since we model the polymers as Brownian paths (i.e., a scaling limit of random walk as the step size and time step tend to zero) $X(t)$, $0 \leqslant t \leqslant M$, it is better to refer to these polymers as having an exponential distribution of lifetimes rather than "lengths," as a Brownian path almost surely has infinite length. So we take M to have probability density function $\mu e^{-\mu t}$, where μ is the *rate* of the exponential random variable; this gives the mean life span $E(M)=\mu^{-1}$.

The reasons for considering this size distribution of polymers are (i) it is a good approximation in some applications, and (ii) it leads to much simpler mathematics than for polymers of fixed lifetime. Note that in principle results for polymers of exponential lifetimes can be turned into the corresponding results for fixed-size polymers by an inverse Laplace transform, when monomer–monomer interactions are neglected.

If $F[X]$ is a functional of the polymer shape X, its expectation (or ensemble average) is given by the usual Boltzmann weighted average, namely

$$Z_x^{-1}E^x\left\{F[X]\exp\left(-\frac{1}{kT}\int_0^M V(X(t))\,dt\right)\right\} \tag{45}$$

where V is the potential per unit time (which is proportional to the potential per monomer), Z_x is the partition function for polymers "starting" at x, and E^x denotes the expectation for polymers starting at x. [So $Z_x \equiv E^x\exp(-(1/kT)\int_0^M V(X(t))\,dt$.] In future we include the $(kT)^{-1}$ factor in V (or choose units so that $kT=1$). [In polymer physics (45) is often written informally as a path integral.] We now use the probability theory of the last section to rewrite (45) in a much more convenient form for further analysis, but for this we need to assume that $V(x)\geqslant 0$ for all x. The restriction to nonnegative V is not essential to the results, although it is essential to the probabilistic interpretation of the methods of proof.

Consider the Brownian path modeling the polymer before Boltzmann reweighting to be the path of a particle in "real" time. When $V=0$ the polymers have lifetimes that are exponential random variables of rate μ, so we can think of these polymers as being the paths of Brownian particles killed at rate μ. When particles are killed in this way we put them in a graveyard ∂. [Remember that one reason for introducing graveyard states is that the probability that a given particle is somewhere (i.e., in $\mathbb{R}^n$ or a graveyard) is always unity—so probability is conserved!] For convenience we shall say that particles in ∂ were *killed naturally*.

Now we are going to consider also *unnatural killing*: namely, when at x, the particle is killed unnaturally at rate $V(x)\geqslant 0$ and is sent to a different graveyard state Δ. As before at (28), the probability that there is no unnatural killing by time t, given $(X_u\colon u\geqslant 0)$, is

$$\exp(-R_t)\equiv\exp\left\{-\int_0^t V(X_s)\,ds\right\}$$

so the probability that there is no unnatural killing before the natural lifetime M, conditioned on $((X_u)_{u\geqslant 0}, M)$ is simply

$$\exp(-R_M)\equiv\exp\left\{-\int_0^M V(X_s)\,ds\right\}$$

Thus

$$\begin{aligned} Z_x &\equiv E^x\exp\left\{-\int_0^M V(X_s)\,ds\right\} \\ &\equiv P^x(\text{no unnatural killing before natural lifetime } M) \end{aligned} \tag{46}$$

and *the Boltzmann weighting* (45) *bears the simple probabilistic interpretation*

$$\begin{aligned} &Z_x^{-1}E^x\left\{F[X]\exp\left(-\int_0^M V(X_s)\,ds\right)\right\} \\ &\quad= E^x\{F(X)\,|\,X \text{ dies naturally}\} \\ &\quad= E^x\{F[X]\,|\,X \text{ ends up in } \partial\} \end{aligned} \tag{47}$$

[X will end up either in ∂ (if killed naturally) or in Δ (if killed unnaturally)].

It may appear that all we are doing is defining lots of new terms, but in a moment we show that the Boltzmann weighting can be "built into the path" in a very natural way. Indeed, the reason that Boltzmann weighting is necessary is that we are using the "wrong" measure, so we now change to the "right" measure and put the Boltzmann factor out of sight! To do this we need $\psi(x)\equiv P^x(X$ dies naturally), which is simply the partition function described in probabilistic language; we write $\psi(x)$ instead of Z_x to remind ourselves that we are dealing with the case $V\geqslant 0$, when the partition function Z_x *may* be interpreted as a probability. We can find a partial differential equation for ψ by arguing informally as follows: consider what can happen to the Brownian particle started at x in the first dt of its life and then consider the rest of its life (if "alive") from where it is at time dt. In the first dt the probability that it is not killed is $1-(\mu+V(x))\,dt$ and the probabilities that it goes to ∂ or Δ are $\mu\,dt$ and $V(x)\,dt$, respectively. If the particle is not killed in the first dt, then the expected value of ψ from its position at time dt is $P_{dt}\psi(x)=\psi(x)+G_0\psi(x)\,dt$, where $G_0\equiv\frac{1}{2}\nabla^2$ is the generator of the (unkilled) Brownian motion. Thus, ignoring terms of order dt^2,

$$\begin{aligned} \psi(x) &= \{1-(\mu+V(x))\,dt\}\,P_{dt}\psi(x)+\mu\,dt\,\psi(\partial)+V(x)\,dt\,\psi(\Delta) \\ &= \{1-(\mu+V(x))\,dt\}\,\{\psi(x)+G_0\psi(x)\,dt\}+\mu\,dt \end{aligned} \tag{48}$$

since clearly $\psi(\partial)=1$ and $\psi(\Delta)=0$ by the definition of ψ. So

$$\psi(x)=\psi(x)+\{G_0\psi(x)+\mu(1-\psi(x))-V(x)\,\psi(x)\}\,dt$$

This gives the equation for $\psi(x)$, namely

$$G_0\psi(x)+\mu(1-\psi(x))-V(x)\,\psi(x)=0 \tag{49}$$

The "boundary conditions" follow from the fact that $\psi(x)$ is a probability, so that for all x we require $0\leqslant\psi(x)\leqslant 1$.

We can also derive (49) quickly using resolvents as follows. From (46),

$$\begin{aligned}\psi(x)&=E^x\exp\left\{-\int_0^M V(X_s)\,ds\right\}\\&=E^x\int_0^\infty \mu\exp(-\mu t)\exp\left\{-\int_0^t V(X_s)\,ds\right\}dt\\&=\mu R_\mu^V 1(x)\end{aligned} \tag{50}$$

where $(R_\lambda^V)_{\lambda>0}$ is the resolvent if the process killed at rate V: if $f(\partial)=f(\Delta)=0$, then

$$\begin{aligned}R_\lambda^V f(x)&=E^x\int_0^\infty \exp\left\{-\lambda t-\int_0^t V(X_u)\,du\right\}f(X_t)\,dt\\&=(\lambda-G^V)^{-1}f(x)\\&=(\lambda+V-G_0)^{-1}f(x)\end{aligned} \tag{51}$$

from (8) and (30). Applying $(\mu+V-G_0)$ to both sides of (50) gives (49).

We now return to (47) and reformulate it in terms of ψ. The generator for (the μ and V killed process) X is

$$G\equiv\tfrac{1}{2}\nabla^2-(\mu+V(x)) \tag{52}$$

(at least on functions which vanish at ∂, Δ). This can now be transformed into the generator $\tilde{G}$ for the process conditioned on natural death, which is the ψ-transform of G; we shall denote this new process by $\tilde{X}$. As explained in the last section, for any test function f vanishing at ∂, Δ, we have $\tilde{G}f=\psi^{-1}G(\psi f)$. Thus, using the differential equation (49) for ψ,

$$\tilde{G}f=\tfrac{1}{2}\nabla^2 f+\psi^{-1}\nabla\psi\cdot\nabla f-\frac{\mu}{\psi}f \tag{53}$$

i.e., the generator for $\tilde{X}$ is

$$\tilde{G} = \tfrac{1}{2}\nabla^2 + \psi^{-1}\nabla\psi\cdot\nabla - \frac{\mu}{\psi} \tag{54}$$

It is important to note that the conditioned process $\tilde{X}$ always goes to ∂ (i.e., dies naturally), but with a new rate $\tilde{\mu}(x) \equiv \mu/\psi(x)$. Note that the only other effect of conditioning on natural death is the drift term, $\psi^{-1}\nabla\psi\cdot\nabla$, in the generator, i.e., the conditioned particle tends to drift away from places where V is large. To sum up, *Boltzmann weighting is equivalent to drift* $u(x) \equiv \nabla(\log\psi(x))$ *and a new killing at rate* $\tilde{\mu}(x) \equiv \mu/\psi(x)$, *now natural.* Indeed, (47) becomes

$$Z_x^{-1}E^x\left\{F[X]\exp\left(-\int_0^M V(X_s)\,ds\right)\right\} = E^x\{F[\tilde{X}]\}$$

This approach is expected to be useful in both numerical and analytical work, since only the paths that represent naturally-killed polymers need to be considered. This is particularly useful in problems where natural death is unlikely or in limits where it is zero!

To compare the two ways in which Boltzmann weighting can be performed, namely either by building it into the generator $\tilde{G}$ for $\tilde{X}$ at the beginning of the calculation, or by working with the unconditioned process X and then throwing away the unphysical paths, we consider a simple example.

Example (x). Consider polymers in a half-space, which we may treat as a one-dimensional problem. In this system

$$V(x) = \begin{cases} +\infty & \text{for} \quad x < 0 \\ 0 & \text{for} \quad x \geqslant 0 \end{cases}$$

Thus, the partition function for polymers starting at x is

$$\begin{aligned} \psi(x) &\equiv P^x(\text{dies naturally}) \\ &= P^x(X(t) \geqslant 0 \quad \text{for} \quad 0 \leqslant t \leqslant M) \\ &= 1 - e^{-\theta x} \qquad (x \geqslant 0) \end{aligned}$$

where $\theta \equiv (2\mu)^{1/2}$. Hence the generator for the process $\tilde{X}$ conditioned on natural death is

$$\tilde{G} = \frac{1}{2}\frac{\partial^2}{\partial x^2} + \frac{\theta}{e^{\theta x} - 1}\frac{\partial}{\partial x} - \frac{\mu}{1 - e^{-\theta x}} \tag{55}$$

Notice how the drift away from the boundary $x=0$ tends to infinity like x^{-1} as $x \downarrow 0$. In fact, any drift that is asymptotic to b/x as $x \downarrow 0$ will prevent a particle hitting 0 (whatever the killing rate) if and only if $b \geqslant 1/2$. Observe that the natural killing rate also tends to infinity as $x \downarrow 0$. This behavior is typical of any system with killing boundaries.

For this system consider $x > a > 0$ and let us determine the probability $\tilde{\phi}(x)$ that $\tilde{X}$ hits a. Since $\tilde{\phi}(x)$ is harmonic for $\tilde{X}(t \wedge H_a)$, i.e., the process that is like $\tilde{X}(t)$ up to the time $H_a \equiv \inf\{t: \tilde{X}(t) = a\}$ (which may not happen!) and sticks at a until natural death, we have

$$\tilde{G}\tilde{\phi}(x) = 0 \qquad \text{for} \quad a \leqslant x < \infty \tag{56}$$

with $\tilde{\phi}(a) = 1$, i.e., it is sure to hit a if it starts there. Since $\tilde{\phi}(x)$ is a probability, and so $0 \leqslant \tilde{\phi}(x) \leqslant 1$, we clearly want the solution that remains bounded as x tends to infinity. Thus,

$$\tilde{\phi}(x) = \frac{e^{\theta a} - 1}{e^{\theta x} - 1}$$

An alternative method of calculating $\tilde{\phi}(x)$, which would be much more usual in polymer physics, is to work throughout with conditional probabilities rather than conditioned processes as above. Thus, if $0 < a < x$,

$$\begin{aligned}
\tilde{\phi}(x) &\equiv \tilde{P}^x(\tilde{X} \text{ hits } a) \\
&= P^x(X \text{ hits } a \mid X \text{ dies naturally}) \\
&= \frac{P^x(X \text{ hits } a \text{ and } X \text{ dies naturally})}{P^x(X \text{ dies naturally})} \\
&= \frac{P^x(X \text{ hits } a) P^a(X \text{ dies naturally})}{P^x(X \text{ dies naturally})} \\
&= \frac{e^{-\theta(x-a)}(1 - e^{-\theta a})}{1 - e^{-\theta x}} \\
&= \frac{e^{\theta a} - 1}{e^{\theta x} - 1}
\end{aligned}$$

as before.

In the above example there is little advantage in considering the process $\tilde{X}$ explicitly. However, the advantage becomes much greater in more complex problems, and the physics is much clearer when every path considered corresponds to a physical polymer.

3.2. Random Copolymers

Consider a generalization of the theory in the previous section to include the effect of random "special" monomers. Again we consider systems in equilibrium with a large reservoir of (ideal) polymers of exponential lifetimes. In the reservoir we suppose that the potential fields for both the ordinary monomers and the special monomers are zero, and we suppose further that the rate of the special monomers is a constant γ (in "time" along the path) and independent of the path. Clearly, outside the reservoir, where in general the potentials are nonzero, the rate of special monomers will usually depend on the path.

Suppose the potential energy of the polymers has the form

$$\int_0^M V(X(t))\,dt+\sum_{i=1}^N U(X(T_i)) \tag{57}$$

where T_i, $1\leqslant i\leqslant N$, are the times of the special monomers and $U(x)$ is the potential energy of a special monomer at x. If we assume that $U(x)\geqslant 0$ for all x, then we can interpret the effect of the ith special monomer on the Boltzmann factor as a probability $1-e^{-U(X(T_i))}$ of unnatural death. In many applications we are interested in properties of the polymer shape and are not concerned with the special monomers explicitly, though the special monomers do have an effect on polymer shape through the Boltzmann factor. For example, we may wish to compute

$$Z_x^{-1}E^x\left\{F[X]\exp\left\{-\int_0^M V(X_t)\,dt-\sum_{i=1}^N U(X(T_i))\right\}\right\} \tag{58}$$

where $F[X]$ is a functional of the polymer shape X only. In such problems we can average out the effect of the special monomers and include it in the definition of V in the following way. Consider that part of the Boltzmann factor that depends explicitly on the special monomers, namely

$$\exp\left\{-\sum_{i=1}^N U(X(T_i))\right\} \tag{59}$$

Given a path $X(t)$, $0\leqslant t\leqslant M$, we must average (59) over all positions and numbers of the special monomers. Let $E(\cdot\,|\,X, M)$ denote the expectation given the path X and the lifetime M. Then

$$\begin{aligned}&E\left(\exp\left\{-\sum_{i=1}^N U(X(T_i))\right\}\middle|\,X, M\right)\\&\quad=E\left\{E\left(\exp\left\{-\sum_{i=1}^N U(X(T_i))\right\}\middle|\,X, M, N\right)\middle|\,X, M\right\}\end{aligned} \tag{60}$$

i.e., we may first average along X with a given number of special monomers N and then average over N. Since before Boltzmann weighting the special monomers occur with constant rate γ, we know that N is a Poisson random variable with mean γM, given X and M. Also given X, M, and N, the positions of the special monomers are independent and uniform in time along X. Thus,

$$E\left(\exp\left[-\sum_{i=1}^{N} U(X(T_i))\right]\middle| X, M, N\right)=\left(\frac{1}{M}\int_0^M \exp[-U(X(t))]\,dt\right)^N$$

and so

$$\begin{aligned}
&E\left(\exp\left[-\sum_{i=1}^{N} U(X(T_i))\right]\middle| X, M\right)\\
&\quad=\sum_{n=0}^{\infty} \exp(-\gamma M)\frac{(\gamma M)^n}{n!}\left\{\frac{1}{M}\int_0^M \exp[-U(X(t))]\,dt\right\}^n\\
&\quad=\exp(-\gamma M)\exp\left\{\gamma\int_0^M \exp[-U(X(t))]\,dt\right\}\\
&\quad=\exp\left\{-\gamma\int_0^M (1-\exp[-U(x(t))])\,dt\right\}
\end{aligned}$$

Thus, the full Boltzmann factor for the random copolymer after we have averaged out the effect of the special monomers is

$$\exp-\int_0^M \{V(X(t))+\gamma(1-\exp[-U(X(t))])\}\,dt \tag{61}$$

So this is exactly the same Boltzmann factor as for an ordinary polymer in a potential

$$V_e(x)\equiv V(x)+\gamma(1-e^{-U(x)}) \tag{62}$$

that is, *we have reduced the random copolymer problem to the ordinary polymer problem.*

Thus, for example, $\psi(x)\equiv E^x(X$ dies naturally) solves the analogue of (49):

$$G_0\psi-(\mu+V_e)\psi+\mu=0 \tag{63}$$

One property that is of some interest is the rate of special monomers $\tilde{\gamma}$, say, for the process conditioned on natural death $\tilde{X}$. On the conditioned path the only monomers we see are those that did not lead to unnatural death. Consider this as follows. Since each special monomer leads to unnatural death with probability $1-e^{-U(x)}$, we can split the special monomers into two groups: (i) lethal special monomers occurring with rate $\gamma_L(x) \equiv \gamma(1-e^{-U(x)})$ and (ii) harmless special monomers occurring with rate $\gamma_H(x) \equiv \gamma e^{-U(x)}$. [Note $\gamma_L(x)+\gamma_H(x)=\gamma$.] Since the lethal and harmless special monomers are independent, given the path, the effect of conditioning on natural death is to simply remove the lethal special monomers. Thus, the rate of special monomers on the conditioned path $\tilde{X}$ is

$$\tilde{\gamma}(x)=\gamma_H(x)=\gamma e^{-U(x)} \tag{64}$$

We can in fact generalize a little more. In the above, all we have really used is that the probability that a special monomer is harmless is $e^{-U(x)}$. Thus, equally we could consider anything we like attached on the special monomers provided we know the probability $\Gamma(x)$, say, that a special monomer at x and anything attached to it is harmless, i.e., does not lead to unnatural death. For example, we could attach rods or Brownian paths of fixed lengths to form a bottle-brush-shaped molecule like a proteoglycan. For all such systems the effective potential is

$$V_e(x) \equiv V(x)+\gamma(1-\Gamma(x)) \tag{65}$$

and the rate of the special monomers on the conditioned path $\tilde{X}$ is $\gamma\Gamma(x)$, i.e., the rate of harmless special monomers before conditioning.

Another example of a general special monomer is provided by randomly branching polymers, which we now consider in detail.

3.3. Randomly Branching Polymers

A randomly branching polymer may be modeled as a branching Brownian motion, in the absence of potential fields. So consider a system in equilibrium with a large reservoir of ideal branching polymers. In detail, before Boltzmann weighting, we model these polymers as Brownian paths that split into two at constant rate λ and die (naturally) at constant rate μ ($\geqslant \lambda$). Many other distributions of branching polymers can be constructed in a similar way, although here we are more concerned with the mathematical techniques available to analyze such systems.

As before, if the external potential per unit time V is positive, then we can interpret V as a rate of unnatural death. Thus, in this case the partition function $\psi(x)$ for polymers starting at x can be calculated along the lines of (48)–(49) as follows:

$$\begin{aligned}\psi(x) &\equiv P^x(\text{natural death on all branches}) \\ &= \{1-[\lambda+\mu+V(x)]\,dt\}[\psi(x)+\tfrac{1}{2}\nabla^2\psi(x)\,dt] \\ &\quad +\lambda\,dt\,\psi^2(x)+\mu\,dt\,\psi(\partial)+V(x)\,dt\,\psi(\Delta)\end{aligned} \tag{66}$$

where $\psi(\partial)=1$ and $\psi(\Delta)=0$ by the definition of ψ. This gives

$$\tfrac{1}{2}\nabla^2\psi-\lambda\psi(1-\psi)+\mu(1-\psi)-V\psi=0 \tag{67}$$

where the boundary conditions follow from the requirement that for all x we must have $0\leqslant\psi(x)\leqslant 1$, as ψ is a probability.

Once again, we can calculate (67) just as easily using the resolvent. At rate μ, natural death occurs, and at rate λ two independent particles are created, both of which must die naturally. Thus

$$\psi=R^V_{\lambda+\mu}(\lambda\psi^2+\mu) \tag{68}$$

Since $R^V_{\lambda+\mu}=(\lambda+\mu+V-G_0)^{-1}$ [see (51)], (67) follows immediately.

Note that we could have determined ψ by using the theory of the last section, by setting the splitting rate $\lambda=\gamma$, the rate of special monomers, and setting the probability $\Gamma(x)$ that the special monomer is harmless (i.e., does not lead to unnatural death) to be equal to $\psi(x)$. The reader should try calculating $\psi(x)$ by this method, and show that conditioning on natural death leads to a new splitting rate $\tilde{\lambda}(x)$ and killing rate $\tilde{\mu}(x)$ (now all natural) given by

$$\begin{aligned}\tilde{\lambda}(x)&=\lambda\psi(x)\\ \tilde{\mu}(x)&=\mu/\psi(x)\end{aligned} \tag{69}$$

We now derive the motion of a "randomly-chosen path" through the (conditioned) polymer. One way to think of this is that the polymer starts as a single particle at x, diffusing until it dies, or splits into two particles. If it splits, then one of the particles is chosen at random and followed, until that one either dies or splits. At each splitting, one of the descendants is chosen at random and followed. Another way to think of this is to consider the original particle as the "parent" particle, which retains its identity at the times of splittings. Thus, the "randomly-chosen path" can be thought of simply as the *path of the parent particle.* Before Boltzmann weighting, this parent particle is marked at rate λ with special monomers (= descendant particles), killed naturally at rate μ, and unnaturally at rate V. Each special monomer is lethal with probability $1-\psi(x)$. Thus, if we condition on no unnatural killing for all branches, then we are back in the situation of

Section 3.2; after weighting, the generator of the movement of the parent particle is the conditioned generator

$$\begin{aligned}\tilde{G}f &= \frac{1}{\psi} G(f\psi) \\ &= \frac{1}{\psi}\left\{\frac{1}{2}\nabla^2(f\psi) - \mu f\psi - [V + \lambda(1-\psi)]\, f\psi\right\} \\ &= \frac{1}{2}\nabla^2 f + \nabla \log \psi\, \nabla f - \frac{\mu f}{\psi}\end{aligned}$$

for f vanishing at ∂, Δ. So after conditioning (i.e., Boltzmann weighting), *the parent particle moves like a Brownian motion with drift* $\nabla \log \psi$, *killed at rate* μ/ψ.

We end this section by solving the self-consistent mean-field problem for a branching polymer, assuming that the splitting rate λ is strictly less than the death rate μ. We consider the equilibrium statistical mechanics of a solution of branching polymers in a potential V, where

$$V(x) = V_0(x) + f(\rho(x)) \tag{70}$$

with V_0 the external potential and f a nonnegative function of the mean monomer density ρ. The potential in the large reservoir is identically zero, and the mean monomer density there is equal to ρ_0, given by

$$\rho_0 \equiv \frac{m}{\mu - \lambda}$$

where m is the mean number of polymers per unit volume. We shall now derive an expression for the monomer density ρ when in a potential V; the relation (70) between V and ρ will be the self-consistency condition which must be satisfied.

Let us consider a single branching polymer started at x, killed at rate V. We take some set A and define

$$h(x) \equiv E^x(\text{total time spent in } A\text{: no } V\text{-killing on the polymer}) \tag{71}$$

The time spent in A decomposes into the time spent in A before the first killing/split, plus the time spent in A afterwards. Thus

$$\begin{aligned}&E^x(\text{time spent in } A \text{ before first killing/split:} \\ &\qquad \text{no } V\text{-killing on the polymer}) \\ &= R^V_{\lambda+\mu} I_A \psi(x)\end{aligned} \tag{72}$$

where ψ is as at (66)–(67). The appearance of ψ in (72) is explained by noticing that the time spent in A before the first killing/split only contributes to the expectation defining h if there is no subsequent V-killing—and the probability of no subsequent V-killing is given by ψ. After the first killing/split, there will only be time spent in A if there was a split. Now there are two particles which may (together with their descendants) spend time in A. Each will contribute on average h, but only if the other particle and its descendants do not suffer V-killing. Thus, the contribution to h from time in A after the first killing/split is simply

$$\lambda R^V_{\lambda+\mu}(2h\psi) \tag{73}$$

Hence

$$h = R^V_{\lambda+\mu}(I_A\psi) + \lambda R^V_{\lambda+\mu} 2h\psi \tag{74}$$

from which we immediately obtain

$$(\lambda + \mu + V - \tfrac{1}{2}\nabla^2)h = I_A\psi + 2\lambda h\psi$$

or equivalently

$$(\mu - \lambda + U - \tfrac{1}{2}\nabla^2)h = I_A\psi \tag{75}$$

where

$$U = V + 2\lambda(1-\psi)$$

Thus, the expected time (which is proportional to the expected number of monomers) in A is

$$\begin{aligned} m\int_{\mathbb{R}^n} h(x)\,dx &= m\int_{\mathbb{R}^n} R^U_{\mu-\lambda}(I_A\psi)(x)\,dx \\ &= m\int_{\mathbb{R}^n} dx \int_A r^U_{\mu-\lambda}(x, y)\,\psi(y)\,dy \end{aligned} \tag{76}$$

where $r^U_\lambda(\cdot, \cdot)$ is the resolvent density of R^U_λ. This is symmetric in x and y, so (76) becomes

$$= m\int_A (\mu-\lambda)^{-1}\,\psi(y)\,P^y(\text{no } U\text{-killing of Brownian motion before } T_{\mu-\lambda})\,dy \tag{77}$$

where $T_{\mu-\lambda}$ is an independent $\exp(\mu-\lambda)$ random variable. Defining

$$\tilde{\psi}(y) \equiv P^y(\text{no } U\text{-killing of Brownian motion before } T_{\mu-\lambda}) \tag{78}$$

then

$$\tilde{\psi} = (\mu - \lambda) R^{U}_{\mu - \lambda} 1 \tag{79}$$

so that from (76)–(77) the monomer density is simply

$$\rho = \frac{m}{\mu - \lambda} \psi \tilde{\psi} \tag{80}$$

Hence Boltzmann weighting is given by ψ, where ψ is determined from the pair of coupled partial differential equations

$$\frac{1}{2} \nabla^2 \psi - \left(V_0 + f\left(\frac{m\psi\tilde{\psi}}{\mu - \lambda} \right) \right) \psi + (\lambda\psi - \mu)(\psi - 1) = 0 \tag{81a}$$

$$\frac{1}{2} \nabla^2 \tilde{\psi} - \left(V_0 + f\left(\frac{m\psi\tilde{\psi}}{\mu - \lambda} \right) + \mu + \lambda - 2\lambda\psi \right) \tilde{\psi} + \mu - \lambda = 0 \tag{81b}$$

and $0 \leqslant \psi, \tilde{\psi} \leqslant 1$.

3.4. Back to Single-Chain Polymers

We end this study with a brief look at systems of single ideal chains of fixed lifetimes (or "lengths"). The reason we shall not spend long on this topic is that basically the same methods as in previous sections are still applicable, but it is much harder to obtain closed-form solutions (even in some seemingly simple problems). Without loss of generality, suppose that all the polymers in our system are of unit lifetimes, i.e., in the large reservoir they may be modeled as Brownian paths $X(t)$ with $0 \leqslant t \leqslant 1$. The only mathematical difference between this system and a system of exponential polymers is the explicit time dependence. This can be removed by working with space-time Brownian motion $(t, X_t)_{t \geqslant 0}$ rather than $(X_t)_{t \geqslant 0}$ itself. Space-time Brownian motion has generator

$$G = \frac{\partial}{\partial t} + \frac{1}{2} \nabla^2.$$

As in previous sections, an external potential $V(x)$ ($\geqslant 0$) can be interpreted as a rate of unnatural death. Thus, the partition function $\psi(t, x)$ for polymers "starting" at (t, x) is given by

$$\begin{aligned} \psi(t, x) &\equiv P^{(t,x)}(\text{natural death}) \\ &= P^{(t,x)}(\text{no } V\text{-killing before time } 1) \qquad (0 \leqslant t \leqslant 1) \end{aligned}$$

Thus, the equation for ψ can be determined as follows:

$$\psi(t,x) = (1 - V(x)\,dt)(\psi(t,x) + G\psi(t,x)\,dt) + V(x)\,dt\,\psi(\Delta)$$

where $\psi(\Delta) = 0$ by definition. Thus,

$$G\psi(t,x) - V(x)\,\psi(t,x) = 0$$

where $0 \leqslant \psi(t,x) \leqslant 1$ for all x and $0 \leqslant t \leqslant 1$. Clearly, if we had wanted to, we could have considered a potential V which is also a function of time.

As in earlier sections, we can condition on natural death, which for these polymers means living until $t = 1$. The new generator $\tilde{G}$ for the conditioned process $(t, \tilde{X}_t)$ is given by

$$\tilde{G}f(t,x) = \psi^{-1}(t,x)\{(G - V)(\psi(t,x)\,f(t,x))\}$$

Thus

$$\begin{aligned}\tilde{G}f &= \psi^{-1}\{\psi Gf + \nabla\psi\cdot\nabla f + (G\psi - V\psi)\,f\}\\ &= Gf + \nabla(\log\psi)\cdot\nabla f\end{aligned}$$

or

$$\tilde{G} = \frac{\partial}{\partial t} + \frac{1}{2}\nabla^2 + \nabla\log\psi(t,x)\cdot\nabla$$

which is the generator of space-time Brownian motion with an additional drift $(0, \nabla\log\psi(t,x))$.

Exercise. Consider ideal single chain polymers in a slot of width a, say, *with killing boundaries*, and investigate the behavior of both fixed-time polymers and exponential polymers. Show that the typical end-to-end distance for exponential polymers is always less than, or of the order of, a, whatever the natural killing rate μ.

This exercise highlights the differences between fixed-time and exponential-time polymers.

4. CONCLUSION

We have demonstrated the power of some of the techniques of the theory of stochastic processes on polymer problems. The most important result is that Boltzmann weighting a diffusion (modeling a polymer) is equivalent to having an additional drift and a new killing rate. This observation is likely to be useful in numerical work, as well as analytical, since only the realizations of the path that correspond to "physical" polymer conformations need to be generated. We have also shown that random copolymer problems can be reduced to ordinary polymer problems, and have discussed randomly-branching polymers, including the effect of a self-consistent mean field.

Several more applications of this approach to polymer physics will appear elsewhere, together with some more probabilistic "power tools"!

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