

REACTION-DIFFUSION ON METRIC GRAPHS AND CONVERSION PROBABILITY

RENATO FERES, MATT WALLACE

ABSTRACT. We consider a mathematical model of a class of first order reaction-diffusion systems in which gas reactants and products diffuse in a domain U and reaction takes place at relatively small catalytic sites in U . The central problem is to determine the probability of reaction, or, equivalently, the yield of the reaction, in terms of the geometric parameters of the system and the chemical reaction constant. This is shown to be solved by a boundary value problem for the time-independent Feynman-Kac equation. Our focus here is on network-shaped (reactor) domains. The main result of the paper is a factorization formula for reaction yield that separates the purely geometric from the chemical kinetic characteristics of the process. The formula is shown to hold exactly for systems described by metric graphs.

1. INTRODUCTION

In many reaction-diffusion systems that arise in applied chemical kinetics and engineering, a problem of central interest is to find approaches for extracting values of overall chemical reaction rates. One experimental method used for this purpose, which motivates the mathematical model of reaction-diffusion system explored in this paper, was introduced in 1988 by J.T. Gleaves and is called the *TAP system* [9] and has proven very successful in the theoretical and laboratory analysis of heterogeneous (gas-metal) catalytic systems. The essential elements of such systems are describe briefly in section 2 below. In [4, 5] a theoretical approach was introduced for obtaining reaction yields in TAP-systems of very general configurations. This area of applied science turns out to be a rich source of new problems in the mathematics of reaction-diffusion systems. Our focus here is on the purely mathematical side of the subject.

This paper has two main goals. The first is to provide a rigorous foundation for the stochastic approach introduced in more heuristic form in [4, 5] for the analysis of first order heterogeneous reaction systems. In particular, we wish to explain carefully and generalize the useful *factorization formula* for reactant conversion observed in [4]. Second, we wish to explore these kinds of reaction-diffusion systems in the context of graph-like domains; that is, for reactors that can be approximated by metric graphs in the spirit of the theory of *quantum graphs* [3]. In the simplest case of linear chain graphs, as in the so-called *thin zone* reactors described in [17], this type of approximation has already proven very useful. Our analysis extends to a much more general setting what has been obtained so far for thin zone systems.

2. IDEALIZED HETEROGENEOUS DIFFUSION-REACTION SYSTEMS

In this paper, we consider an irreversible heterogeneous (gas-solid) first-order reaction of the form $A \rightarrow B$. A concrete example of such a reaction is the platinum

catalyzed oxidation of carbon monoxide: $CO \rightarrow CO_2$. This notation is meant to summarize a possibly highly complex reaction mechanism involving adsorption and binding to the metal surface, surface diffusion, various surface reactions, and final desorption of the product. However, these many steps happening at the catalyst site need not be explicitly modeled if the interest lies in the reaction rate of the overall $A \rightarrow B$ process.

A feature we wish to impose on the system that distinguishes it from other reaction-diffusion systems often studied is that the catalyst occupies a relatively small region relative to the total reactor space. Outside those chemically active sites the gas mixture of A and B undergoes ordinary (Fickian) diffusion and no reaction can occur. In other words, reaction events can only happen at well localized sites, and reactants have to travel (diffuse) to those sites for a reaction to take place.

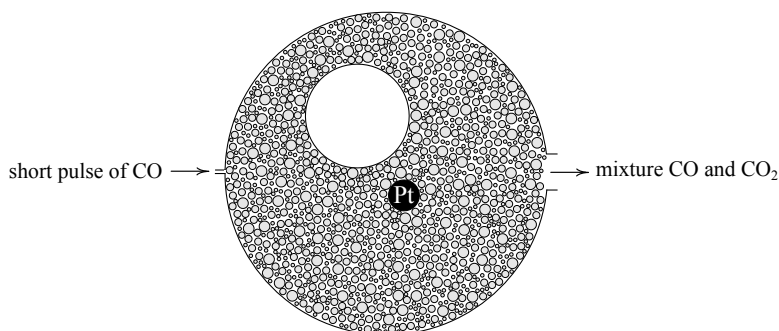


FIGURE 2.1. A typical reaction-diffusion system in an idealized TAP-reactor. (The roughly annular shape shown here is completely arbitrary. Figures will be drawn in dimension 2 for simplicity.)

Figure 2.1 shows a typical set up in idealized form. The medium through which gas diffuses is a chemically inert, porous (i.e., permeable to gas diffusion) solid material such as closely packed small quartz particles. The precise conditions of the packing will determine the diffusion characteristics of the medium. For example, if the medium is assumed uniform and isotropic, then the diffusion is characterized by a single constant diffusion coefficient. A particle of metal catalyst, such as oxidized platinum, is placed somewhere inside the packed bed. Then a short pulse of CO gas is injected at some point into the reactor, assumed to be in a vacuum, and diffuses through the packed bed. The amount of gas in the pulse is sufficiently small that gas molecules can be assumed to move independently of each other (this is the so-called *Knudsen regime* condition) and so that the state of the catalyst surface is not greatly altered in the course of a single experiment. Furthermore, the duration of the initial pulse is so narrow that we can model the initial conditions as a delta function at the injection site.

After the initial pulse has been injected, it diffuses through the reactor, possibly coming in contact with the catalyst and reacting to produce CO_2 . The gas mixture is then collected at another part of the reactor and the proportion of CO_2 is measured by a mass spectrometer.

The fundamental mathematical problem is to determine the fraction of reaction product, CO_2 , in the gas outflow. We call this quantity the *reaction yield* or, perhaps more appropriately, *reaction probability*. Since a primary concern in practice is to extract chemical kinetics information, we wish to express the reaction yield as explicitly as possible in terms of the chemical reaction constant. We also wish to understand how geometric parameters of the system such as shape of reactor, size and location of the catalyst particle, point of injection of the gas pulse, and region where gas outflow is collected, affect yield. Our main result, which will apply to the setting of *metric graphs* with catalyst particles located at some of the vertices, gives an exact expression for the dependence of reaction yield on the chemical reaction constant and indicates how geometric features of the system influence yield. The result will be stated after we describe the mathematical problem in more precise terms.

3. MATHEMATICAL FORMULATION OF THE MAIN PROBLEM

Before formulating the problem on metric graphs, we describe it on general domains. A more pedestrian study was undertaken in [4] and [5]. The main observation there was that the problem of obtaining reaction yield for a TAP-like experiment can be formulated as a time-independent boundary value problem for the Feynman-Kac equation. To understand these findings, consider the diagram in Figure 3.1.

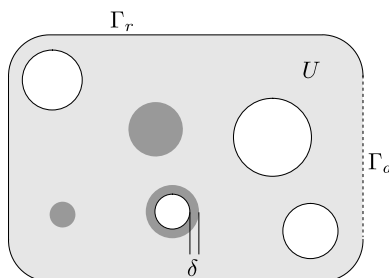


FIGURE 3.1. The reaction probability is the solution of a time independent boundary value problem for the Feynman-Kac operator on the domain U with Neumann boundary condition on the *reflecting boundary* Γ_r and boundary value 0 on the *absorbing boundary* Γ_a . The reaction rate term $kq(\mathbf{x})$ is assumed to be supported on a relatively small region of U , indicated by the darker grey sets, called *active sites*. Active sites are permeable to gas diffusion.

In this diagram, the shaded region U represents the region inside the reactor accessible to gas transport. Note that U does *not* include the interiors of the regions assigned to the solid catalyst. Within U , we assume that reaction can occur at only a few relatively small sites, which we call *active sites*. These are represented in the figure by regions in darker grey. Active sites could form a narrow collar neighborhood of one or more components of the reflecting boundary of U representing surfaces of catalyst particles. They may also correspond to small regions of U permeable to gas diffusion, in which case we think of them as consisting of many small solid particles comparable in size to the inert particles filling up the

reactor. The boundary of U is the union of Γ_r , the *reflecting* boundary, and Γ_a , the *absorbing* boundary. The latter is the open side of U through which gas outflow is collected.

Now let $\psi(\mathbf{x})$ represent the probability that a single gas molecule of type A , injected into U at the initial position \mathbf{x} , will eventually leave U through Γ_a without having converted into B . We call ψ the *survival function*. The complementary probability of conversion to B will be denoted $\alpha(\mathbf{x}) = 1 - \psi(\mathbf{x})$. If the overall reaction constant is k and the diffusion constant is \mathcal{D} (assuming uniform Fickian diffusivity) then it will be seen shortly that $\psi(\mathbf{x})$ satisfies the following boundary value problem:

$$\mathcal{D}\Delta\psi - kq(\mathbf{x})\psi = 0 \text{ on } U$$

where $q(\mathbf{x})$ is the indicator function of the union of the active sites, with boundary conditions

$$\begin{aligned} \mathbf{n} \cdot \nabla\psi &= 0 \text{ on } \Gamma_r \\ \psi &= 1 \text{ on } \Gamma_a, \end{aligned}$$

where \mathbf{n} is the outward-pointing unit normal vector field on the reflecting boundary.

If the active sites are all collar regions of thickness δ as in Figure 3.1, it was shown in [5] by a heuristic argument that for small δ the problem of finding the survival function can be restated in terms of Laplace's equation $\Delta\psi = 0$ in U with mixed Dirichlet-Neumann-Robin conditions on the boundary. Specifically, with Γ_c denoting the boundary of the region occupied by catalyst particles, and Γ_r now denoting the complement of Γ_c in the reflecting boundary, we have:

$$\begin{aligned} \mathbf{n} \cdot \nabla\psi &= 0 \text{ on } \Gamma_r \\ \mathbf{n} \cdot \nabla\psi &= \kappa\psi \text{ on } \Gamma_c \\ \psi &= 1 \text{ on } \Gamma_a \end{aligned}$$

Here $\kappa := \frac{\delta k}{\mathcal{D}}$ can be regarded as an *effective* reaction constant. Without a more detailed model of the reaction mechanism near the surface of the catalyst, it is not possible to say what value should be assigned to δ or even its scale—i.e. whether it be a microscopic length, or of the order of the diameter of the particles filling up the reactor bed, or something else. With this set-up, we now state the

Main question. *Determine the conversion $\alpha(\mathbf{x})$ as a function of κ or k .*

In principle, the boundary value problems above already answer this question. However, this answer is hardly satisfactory because it does not present the relationship in terms of any readily computable quantities. In [4] it is indicated that the conversion probability $\alpha(\mathbf{x})$ can be approximated by the following *factorization formula* when the catalyst is a single particle of a relatively small size:

$$(3.1) \quad \alpha(\mathbf{x}) = P(\mathbf{x}) \frac{\lambda\kappa}{1 + \lambda\kappa}$$

Here, $P(\mathbf{x})$ is the probability that a molecule of A injected at \mathbf{x} will hit the catalyst particle. Note that $P(\mathbf{x})$ depends only on the geometric configuration of the system and not on the chemical parameter. Indeed, under the assumption that gas molecules diffuse like a Brownian motion, $P(\mathbf{x})$ is well-known to solve Laplace's

equation $\Delta P(\mathbf{x}) = 0$ in U , together with the boundary conditions:

$$\begin{aligned} \mathbf{n} \cdot \nabla P &= 0 \text{ on } \Gamma_r \\ P &= 1 \text{ on } \Gamma_c \\ P &= 0 \text{ on } \Gamma_a \end{aligned}$$

Comparing with the boundary conditions characterizing α above, we see that P can be interpreted as the limit of α for very fast reactions, i.e. as $\kappa \rightarrow \infty$. As for the parameter λ , it too depends only on the geometric configuration of the system in a way which is best phrased in terms of local times. This will be explained later. For now it suffices to note that (3.1) relates the experimentally measurable quantity $\alpha(\mathbf{x})$ to the readily computable quantities $\alpha(\mathbf{x})$ and λ via the kinetic constant κ . Therefore it can be used to determine κ .

It will be shown that formula (3.1) holds exactly when the catalyst can reasonably be modeled as a single point in its state space. In fact, we can obtain (3.1) as a special case of a more general formula that supposes the catalyst to comprise a finite number of points in its state space. This result, based on Kac's method of moments, expresses reaction conversion as a rational function of the kinetic parameter κ :

$$\alpha(\mathbf{x}) = P_0(\mathbf{x}) - \sum_{v \in \mathcal{C}} P_v(\mathbf{x}) \frac{\lambda_v(\kappa)}{\lambda(\kappa)}$$

In this formula, $P_0(\mathbf{x})$ is the probability that a diffusing molecule hits \mathcal{C} at all, and $P_v(\mathbf{x})$ is the probability that a diffusing molecule hits \mathcal{C} for the first time at the vertex v . On the other hand, λ and λ_v are polynomial functions whose coefficients depend only on geometric properties of the graph. These results will be stated more precisely after we introduce some definitions concerning metric graphs.

3.1. The stochastic model. Let U be a bounded domain in \mathbb{R}^n with a piecewise smooth boundary Γ , and Γ_a a relatively closed subset of Γ . The motion of gas molecules of species A will be modeled by diffusion process $(X_t, \mathbb{P}^{\mathbf{x}})$ in U . Here, $\mathbb{P}^{\mathbf{x}}$ is the probability law of X with initial distribution $\delta_{\mathbf{x}}$. That is, the distribution of X_0 on U under $\mathbb{P}^{\mathbf{x}}$ is a point mass at \mathbf{x} . This corresponds to injecting a unit pulse of gas at \mathbf{x} .

Within U , the process X behaves like a Brownian motion with diffusion coefficient \mathcal{D} . As for the boundary, X is reflected instantaneously on $\Gamma_r := \Gamma \setminus \Gamma_a$ and absorbed on Γ_a . We write T for the first hitting time of X to Γ_a and demand that $\mathbb{P}^{\mathbf{x}}[T < \infty] = 1$ for all $\mathbf{x} \in U$. That is, the process has to hit the absorbing boundary. This condition will be met in almost every situation that occurs in practice.

Now, let q be a nonnegative function on U , and k a constant parameter with physical dimension 1/time, which we call the *reaction constant*. The function kq will be called the *reaction rate* function. We typically take q to be the indicator function of a subset of U , representing the chemically active region in U .

The main modeling assumption is that the reaction $A \rightarrow B$ corresponds to *killing* X at a rate determined by kq . The intuitive idea is that the probability that a molecule following sample path ω *hasn't* reacted decreases exponentially with the amount of time spent "in the vicinity of" the catalyst. Since the integral $\int_0^t q(X_s(\omega)) ds$ represents the amount of time spent in the vicinity of the catalyst up till time t , the

expression

$$\exp \left\{ -k \int_0^{T(\omega)} q(X_s(\omega)) ds \right\}$$

should represent the probability that the molecule hasn't reacted by the time it escapes the reactor. Therefore the quantity of interest, $\alpha(\mathbf{x}) = 1 - \psi(\mathbf{x})$, where $\psi(\mathbf{x})$ is the survival probability, is given by averaging over all sample paths that start at \mathbf{x} , i.e. by taking the expectation:

$$\alpha(\mathbf{x}) = 1 - \mathbb{E}^{\mathbf{x}} \left[\exp \left\{ -k \int_0^T q(X_s) ds \right\} \right].$$

It is well-known [16] that the survival function $\psi(\mathbf{x})$ solves the Feynmann-Kac equation in U :

$$\begin{aligned} \mathcal{D}\Delta u - kqu &= 0 \text{ in } U \\ \mathbf{n} \cdot \nabla u &= 0 \text{ on } \Gamma_r \\ u &= 1 \text{ on } \Gamma_a. \end{aligned}$$

We are particularly interested in studying the problem of determining the conversion rate function α for network-shaped domains, for which the above boundary value problem on U can be approximated by a similar problem on a metric graph. We next describe the problem on graphs.

3.2. Network shaped domains. We are interested in network shaped domains of the kind studied, for example, in [6, 12, 14]. A detailed comparison of the solutions to the Feynman-Kac boundary value problem on the initial domain and the corresponding graph-like approximation will be taken up elsewhere in the spirit of [6] and [12]. Here we derive on heuristic grounds the graph equations from the boundary value problem for reaction yield, and take the resulting graph limit as the starting point for our study of the yield problem. More specifically, we indicate here the condition that must be imposed on an active vertex of the limit metric graph for it to represent what happens at an active *junction* in a network-shaped domain as in Figure 3.2.

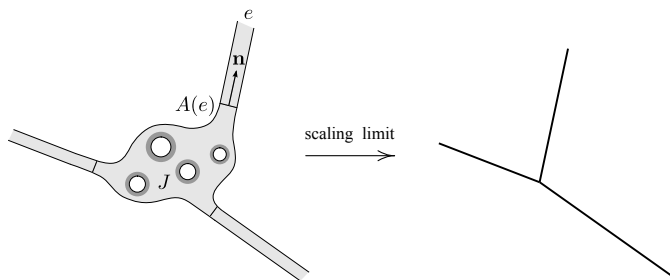


FIGURE 3.2. A neighborhood of an active site in a network-shaped domain and its limit to a neighborhood of a vertex in a metric graph. Here $A(e)$ represents the cross-section area associated to edge e and J represents a juncture. Only the cross sections of edges and junctures are scaled down, not edge lengths. The active region inside J , indicated in darker grey, is denoted R .

The network-shaped graph is taken to be a neighborhood in some Euclidean space \mathbb{R}^n of a graph whose edges are straight-line segments of finite length. The domain U is supposed to consist of solid cylinders smoothly connected to each other at neighborhoods of the vertices we call *junctures*. The chemically active region R is a subset of a juncture J , as shown in the figure. The boundary of J consists of the union of the cross sections of area $A(e)$ and the part of the reflecting boundary of U intersecting J . Let $\mathcal{D}(e)$ indicate the value of diffusivity, assumed to be constant along each edge cylinder e . (It will soon be assumed that \mathcal{D} is constant.) Denoting by A the sum of the areas of the interface cross-sections, we write $\bar{p}(e) := A(e)/A$.

Let u be a solution to the Feynman-Kac boundary value problem on the graph-like domain U and $(u'_e)_{\text{in}}(v) := \mathbf{n} \cdot \nabla u$ the value of the normal derivative of u on the cross-section boundary component of J into e . The unit normal vector to the cross-section pointing into the cylinder region is denoted \mathbf{n} and the derivative is assumed to be nearly constant along that cross section. The verification of this property, along the lines of [12], is a key step of a proof of the graph approximation. Then the time-independent Feynman-Kac equation takes the form

$$\nabla \cdot (\mathcal{D} \nabla u) - k \mathbb{1}_R u = 0.$$

Integrating over J , applying the divergence theorem, and assuming that the value of u in J does not differ significantly from its value at v when the graph is a small enough neighborhood of the skeleton graph (this, again, is shown as in [12]), we obtain the following approximate identity that will be used for the vertex condition in the graph limit:

$$(3.2) \quad \sum_{e \sim v} \mathcal{D}(e) \bar{p}_v(e) u'_e(v) = \kappa(v) u(v).$$

Here $e \sim v$ indicates that the sum is over all the edges incident to the vertex v associated to juncture J and $\kappa(v)$ is the limit of $k \text{Vol}(R)/A$, assumed to exist and to take on a finite non-zero value. The symbol $u'_e(v)$ indicates the derivative of u taken at the vertex v with respect to length parameter in the direction of e . Note that, as lengths near the vertex are scaled down to 0, the reaction constant k must increase in inverse proportion.

The quantity $\kappa(v)$ has the physical dimension of velocity. We write, somewhat arbitrarily, $\kappa(v) =: \kappa \delta(v)$, where κ is independent of v , having physical dimension 1/[time] and $\delta(v)$, which has dimension of distance, is intended to capture the geometric features of the neighborhood of the juncture that survive the limit process. Clearly, κ and $\delta(v)$ are uniquely defined only up to a constant independent of v .

3.3. Relationship between the PDE parameters and the stochastic ones.

We chose the letter $\bar{p}_v(e)$ for the quantities above because in the stochastic model of our problem, these numbers represent (speaking somewhat loosely) the probabilities that a process started at v transitions into the vertex e in the next instant. We explain this relationship later when considering diffusions on metric graphs. See proposition 4.3 and remark 4.4.

3.4. Metric graphs and the factorization formula. The data associated to the system on a general network-shaped domain that we retain for the formulation of the problem on graphs are the following:

- Junctures become elements of the vertex set \mathcal{V} . This includes the set \mathcal{V}_{bd} of terminal vertices, corresponding to open ends of tubes.

- To each edge e issuing from a vertex v is associated $\bar{p}_v(e) = A(e)/A$.
- To a vertex v is associated the length parameter $\delta(v)$.
- Lengths of the tubes are now parameters l_e associated to the edge e .
- The diffusion coefficient $\mathcal{D}(e)$ of a tube corresponding to edge e . This is assumed to be constant on tubes but may, for now, take on different values on different edges.
- The chemical reaction constant, κ , introduced above in subsection 3.2.

We denote by \mathcal{G} the compact metric graph with finite vertex set \mathcal{V} and finite (oriented) edge set \mathcal{E} . Active vertices comprise the set $\mathcal{C} \subset \mathcal{V}$ and terminal vertices the set $\mathcal{V}_{\text{bd}} \subset \mathcal{V}$. The space of functions on \mathcal{V} is taken to be the inner product space $L^2(\mathcal{V}, \delta)$ and the space of vector fields on \mathcal{G} is taken to be the inner product space $L^2(\mathcal{E}, \nu)$ with measure ν defined by $\nu(e) = |e|\bar{p}(e)$. Here $|e|$ is the length of e and $\bar{p}(e) = \bar{p}_v(e)$ for an edge e with initial vertex v . More details about these definitions will be given in subsection 6. From this we define the operation grad on $L^2(\mathcal{V}, \delta)$ and div on $L^2(\mathcal{E}, \nu)$ as described in 6. The generator of Brownian motion on edges is now the ordinary second derivative operator in terms of the arclength parameter on edges. Because harmonic functions on edges are affine, they are determined by their values on the set \mathcal{V} . The problem of finding the survival function on the graph will be shown to amount to the discrete boundary value problem

$$(3.3) \quad \text{div}(\mathcal{D} \text{grad} \psi) - \kappa \mathbb{1}_{\mathcal{C}} \psi = 0$$

where $\psi \in L^2(\mathcal{V}, \delta)$ has boundary values $\psi = 1$ on \mathcal{V}_{bd} . Aside from notation, the discrete Feynman-Kac's equation 3.3 is simply 3.2. Let \mathcal{L} denote the operation $\mathcal{L}f = \text{div}(\mathcal{D} \text{grad} f)$.

Theorem 3.1. *Let \mathcal{C} be the set of active vertices as described above. Then for each $v \in \mathcal{C}$ there is a degree $\leq |\mathcal{C}| - 1$ polynomial function of κ , written $\lambda_v(\kappa)$ whose coefficients depend only on v , \mathcal{C} and the geometry of \mathcal{G} , such that the following equation holds:*

$$\alpha(\mathbf{x}) = P(\mathbf{x}) - \sum_{v \in \mathcal{C}} P_v(\mathbf{x}) \frac{\lambda_v(\kappa)}{\lambda(\kappa)}$$

Here, $P(\mathbf{x})$ is the probability that the diffusion started at \mathbf{x} ever hits \mathcal{C} , $P_v(\mathbf{x})$ is the probability that the diffusion started at \mathbf{x} hits \mathcal{C} for the first time at v , and $\lambda(\kappa)$ is a non-zero polynomial function of degree $\leq |\mathcal{C}|$ whose coefficients depend only on \mathcal{C} and the geometry of \mathcal{G} . Furthermore, $\alpha(\mathbf{x})$ reduces to $P(\mathbf{x})$ when $\kappa \rightarrow \infty$.

We will say more later about how to calculate the coefficients in $\lambda_v(\kappa)$ and $\lambda(\kappa)$. For now it suffices to observe that, when $\mathcal{C} = \{v_c\}$, the probabilities $P(\mathbf{x})$ and $P_{v_c}(\mathbf{x})$ are the same, and the formula above simplifies as follows:

Corollary 3.2. *Suppose that the set of active vertices consists of a single element v_c . The probability of reaction, $P(x, v_c, \kappa)$, where x is the initial point of the process, satisfies*

$$P(x, v_c, \kappa) = P(x, v_c) \frac{\lambda \kappa}{1 + \lambda \kappa}$$

where $P(x, v_c)$ is the hitting probability of the set $\{v_c\}$ and λ is a parameter that only depends on the geometric configuration of the system and not on the reaction constant κ .

The factor $P(x, v_c)$ is well-known to be the solution of the discrete Dirichlet boundary value problem on \mathcal{V} with value 0 on \mathcal{V}_{bd} and 1 on $\{v_c\}$. We describe next the value of λ for a few examples of graphs.

3.5. Examples. In the following examples we assume that $\delta(v) = \delta$ and $\mathcal{D}(e) = \mathcal{D}$ are constant on vertices and edges, respectively, and that $p(e) = 1/\deg(v)$ where v is the initial vertex of oriented edge e and $\deg(v)$ is the degree of v . Let $\bar{\kappa} = \kappa\delta/\mathcal{D}$. Diagram definitions are explained in figure 3.3.

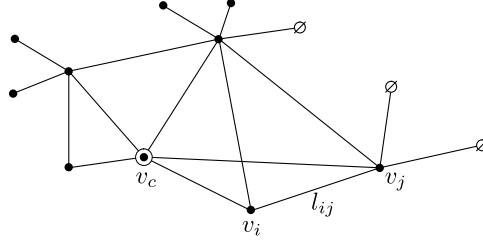


FIGURE 3.3. For the examples we let the edge probabilities be $\bar{p}_v(e) = 1/\deg(v)$. The active vertex, v_c , is indicated by \odot and the terminal vertices by \otimes . The latter constitute the boundary set \mathcal{V}_{bd} . The edge linking vertices v_i and v_j has length l_{ij} .

According to the factorization formula, the reaction probability for combinatorial graphs, is

$$P(x, v_c, \bar{\kappa}) = P(x, v_c) \frac{\lambda \bar{\kappa}}{1 + \lambda \bar{\kappa}}$$

where $P(x, v_c)$ is the hitting probability for random walk associated to the discrete Laplacian

$$(\Delta f)(v) = \sum_{e \in \mathcal{E}_v} |e|^{-1} (f(r(e)) - f(v)).$$

Since the hitting probability $P(x, v_c)$ is a standard quantity, we focus attention on the geometric parameter λ in the following examples. In each case, the objective is to calculate

$$1 - f(v_c) = \frac{\lambda \bar{\kappa}}{1 + \lambda \bar{\kappa}}$$

where $f(v)$ solves Equation 3.3 with boundary value 1 on the terminal vertices. Computations amount to solving elementary linear systems and will be omitted.

Figure 3.4 show three star-like graphs, with the terminal active vertices at different positions. The labels l_j indicate edge lengths.

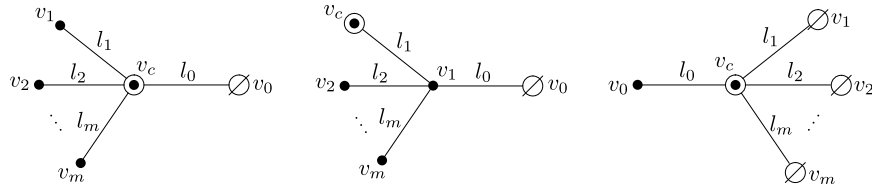


FIGURE 3.4. Star graphs with terminal vertices and the active vertex at different places.

For the leftmost graph of Figure 3.4, we have $\lambda = \deg(v_c)l_0$. It is interesting to observe that the edges with lengths l_1, \dots, l_m make a difference in the value of λ through the degree of the active vertex, but their lengths are immaterial. The value of λ for the middle graph of Figure 3.4 is

$$\lambda = l_0 + l_1.$$

In this case the edges with lengths l_2, \dots, l_m have no effect on the value of λ . For the rightmost graph we have

$$\lambda = \deg(v_c) \left(\frac{1}{l_1} + \dots + \frac{1}{l_m} \right)^{-1}.$$

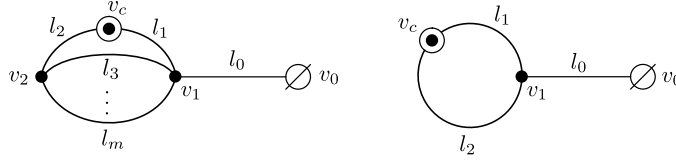


FIGURE 3.5. Graphs with loops.

We now turn to the graphs of Figure 3.5. Define $a := l_3^{-1} + \dots + l_m^{-1}$. Then for the graph on the left of Figure 3.5

$$\lambda = 2(l_0 + l_1) \frac{1 + al_2}{1 + (l_1 + l_2)a}.$$

For the graph on the right of Figure 3.5 we have

$$\lambda = 2l_0 \left(\frac{1}{l_0} + \frac{1}{l_1} + \frac{1}{l_2} \right) \left(\frac{1}{l_1} + \frac{1}{l_2} \right)^{-1}.$$

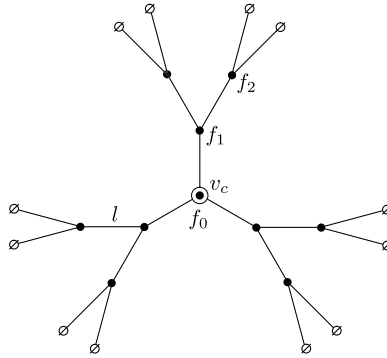


FIGURE 3.6. A tree graph.

Now consider the tree graph of Figure 3.6. More generally, let each vertex, except for the terminal ones, have degree $d = \deg(v_c)$ and assume that the diameter is nl , where l is the common length of the edge segments. Due to the symmetry of the

graph, the value of $f(v)$ only depends on the distance of the vertex to the root, indicated by f_j on the graph. Letting $a := (\deg(v_c) - 1)^{-1}$, we have

$$\lambda = (1 - a^n)(1 - a)^{-1}l.$$

4. METRIC GRAPHS, LOCAL TIMES AND VERTEX CONDITIONS

By a *metric graph* we mean an ordinary graph $\mathcal{G} = (\mathcal{V}, \mathcal{E})$ realized as a network of linear segments in \mathbb{R}^n that intersect only at their endpoints. Then \mathcal{G} has a natural metric defined by minimizing the length of a path between two points, with *length* being defined in the obvious way in terms of the ambient \mathbb{R}^n . Thus, a metric graph is a separable metric space rather than just an abstract collection of vertices and adjacency relations. Therefore it makes sense to consider differential operators on \mathcal{G} as well as their corresponding Markov processes. Everything works the same way as it does for intervals, except that in the graph case we must decide what to do about the vertices. We explain this issue briefly in section 4.1 using results borrowed from [6, 7]. Then in sections 4.2 and 4.3 we describe the generator of the killed diffusion modeling the TAP experiment. Knowing the generator reduces the problem of determining reaction probability to solving an ODE on the graph.

4.1. Diffusion processes on graphs. For each edge $e \in \mathcal{E}$ introduce a coordinate y_e parametrizing e by an interval $I_e = [0, l_e]$ (with $0 < l_e \leq \infty$) and a second-order elliptic differential operator

$$L_e f(x) = \frac{1}{2} \sigma_e^2(y_e) \frac{d^2 f}{dy_e^2}(y_e) + b_e(y_e) \frac{df}{dy_e}(y_e),$$

where $y_e = y_e(x)$ and the derivatives are understood to be one-sided if x is at an endpoint of e . The functions σ_e and b_e are in $C_b^2(e^\circ)$ (= functions on e whose order ≤ 2 derivatives are bounded and continuous in e) and the σ_e are strictly positive and bounded away from 0. By the classical theory espoused in, for example, [8] or [10], $(L_e, D(L_e))$ is the infinitesimal generator of a diffusion process X^e on e , for some appropriate domain $D(L_e)$. What is needed is a single process X on \mathcal{G} that coincides with X^e on e . This requires explaining the behavior of X when it reaches a vertex. Accordingly, we introduce parameters $\{\alpha_v; v \in \mathcal{V}\}$ and $\{\beta_v(e); v \in \mathcal{E}, e \sim v\}$ such that

$$(4.1) \quad \sum_{e:e \sim v} \beta_v(e) + \alpha_v > 0,$$

where $e : e \sim v$ indicates that the sum is over all the edges incident to the vertex v . Then we can define an operator A on $C_0(\mathcal{G})$ (the space of continuous functions on \mathcal{G} that vanish at ∞) as follows:

- (1) If $L_e F_e(x)$ exists for each $e \in \mathcal{E}$ and $x \in e^\circ$ (where F_e is the restriction of F to e), and if the one-sided limits $L_e F_e(v)$ exist and are equal for each $v \in \mathcal{V}$ and $e \sim v$, then we write AF for the function defined by $AF(x) = L_e F_e(x)$ for $x \in e^\circ$ and $AF(v) = L_e F_e(v)$ for $v \in \mathcal{V}$ and $e \sim v$. The point here is that we can make unambiguous sense of AF at v .
- (2) The domain $D(A)$ of A consists of all $F \in C_b^2(\mathcal{G})$ such that AF exists, is in $C_0(\mathcal{G})$, and satisfies the condition

$$\alpha_v AF(v) = \frac{1}{\sum_{e:e \sim v} \beta_v(e)} \sum_{e:e \sim v} \beta_v(e) \frac{dF}{dy_e}(v)$$

at each $v \in \mathcal{V}$.

With this setup, we have the following result:

Theorem 4.1 ([6] Theorem 3.1). *The operator $(A, D(A))$ defined above is the infinitesimal generator of a conservative (= infinite lifetime) diffusion process (X_t, \mathbb{P}^x) in \mathcal{G} . Furthermore:*

- (1) X coincides with X^e on e ;
- (2) If $\alpha_v = 0$, then v is instantaneously reflecting, i.e. X spends 0 time at v almost surely;
- (3) If $\alpha_v = 0$ for all $v \in \mathcal{V}$ then X has a density with respect to a measure m on \mathcal{G} , called the speed measure, that gives 0 mass to \mathcal{V} .

We need to understand how the parameters in 4.1 describe the behavior of X near a vertex. Since this is a local question, we may as well assume \mathcal{G} is a star-shaped graph consisting of a single vertex v with a finite number of incident edges homeomorphic to $[0, \infty)$. Then we can write $X_t = (x_t, e_t)$ where x_t is a continuous process on $[0, \infty)$ and e_t is a discrete process on \mathcal{E} . For simplicity, suppose further that we are in case (3) of the preceding Theorem, so that the $\beta_v(e)$ can be normalized by writing

$$p(e) = p_v(e) := \frac{\beta_v(e)}{\sum_{e: e \sim v} \beta_v(e)},$$

and then the vertex condition for $F \in D(A)$ reads:

$$\sum_e p(e) \frac{dF}{dy_e}(v) = 0.$$

In this case, the following result expresses x_t as a semimartingale, and gives an Ito-Tanaka formula for doing stochastic calculus on \mathcal{G} :

Theorem 4.2 (Stochastic calculus on a graph). *Let $X_t = (x_t, e_t)$ be defined as above. Then:*

- (1) *There exists a one-dimensional Brownian motion W_t and a continuous increasing process ℓ_t , both adapted to the filtration of X_t , such that the following stochastic equation holds:*

$$dx_t = \sigma_{e(t)}(x_t) dW_t + b_{e(t)}(x_t) dt + d\ell_t.$$

The process ℓ_t increases only on the set $\{t; X_t = v\} = \{t; x_t = 0\}$.

- (2) *For $F \in C_b^2(\mathcal{G})$, the following Itô-Tanaka formula holds:*

$$\begin{aligned} F(X_t) - F(X_0) &= \int_0^t \sigma_{e(s)}(x_s) \frac{dF_{e(s)}}{dx}(x_s) dW_s \\ &\quad + \int_0^t AF(x_s) ds + \left[\sum_e p_e \frac{dF_e}{dx}(v) \right] \ell_t. \end{aligned}$$

See Lemmas 2.1 and 2.2 of [7]. The process ℓ_t in (1) is called the *local time* at v , although we note from the equation that it has units of *length*. For some purposes, however, it is more natural to consider the *occupation time density* of X at v , which here takes the form

$$\bar{\ell}_t = \lim_{\delta \downarrow 0} \frac{1}{\delta} \int_0^t 1_{[0, \delta[}(x_s) ds.$$

This process has units of time per length, which we expect for a process representing occupation time density at a point. The apparent conflict reflects the linear

relationship between space and time for diffusion processes. Indeed, ℓ_t and $\bar{\ell}_t$ are related by the equation

$$(4.2) \quad \bar{\ell}_t = \left[\sum_e p_e \frac{2}{\sigma_e^2(v)} \right] \ell_t$$

This result comes from making a nice choice of F in theorem 4.2 and letting $\delta \downarrow 0$; see Remark 2.5 of [7]. Still another normalization of local time is relevant here. Let us write

$$(4.3) \quad L_t = \left[\sum_e \frac{p_e}{\sigma_e} \right] \ell_t$$

and observe that L is independent of the various diffusion constants. In other words, if we rescale by applying a space transformation to the process, thereby obtaining new p_e 's and σ_e 's, then L remains the same. See Lemma 3.1 and Remark 3.3 in [7].

Finally, we note the probabilistic significance of the parameters $p(e)$: with τ_δ denoting the first exit time of X from a symmetric δ -ball around v ,

$$(4.4) \quad \lim_{\delta \downarrow 0} \mathbb{P}^v [X(\tau_\delta) \in e] = p(e).$$

This result is a byproduct of the proof (1) as observed in Corollary 2.4 of [7]. In view of the (4.4), we call the parameters $p(e)$ the *dispersion parameters* at v .

4.2. Local times and vertex conditions. Now we use the results in Section (4.1) to explain condition (3.2) directly in terms of the diffusion process on the graph. Continue to assume \mathcal{G} is a star-shaped graph with a single vertex v , but now let $\sigma_e(x)$ be a positive constant $\sigma(e)$ on e . Setting $\mathcal{D}(e) = \frac{1}{2}\sigma^2(e)$, this means the associated diffusion X behaves like a Brownian motion on e with coefficient $\mathcal{D}(e)$.

The first thing we note is that we can rescale X to obtain an ordinary Walsh process with the same coefficient on each edge. Indeed, by setting

$$H(x, e) = H_e(x) = x/\sigma(e)$$

and then $Y_t = H_{e(t)}(X_t)$ we obtain a new continuous process on \mathcal{G} . It turns out that Y_t is the diffusion on \mathcal{G} generated by the operator $\frac{1}{2}d^2/dy_e^2$ together with the boundary condition

$$\sum_e q(e) \frac{dF}{dy_e}(v) = 0$$

where

$$q(e) = \frac{p(e)/\sigma(e)}{\sum_{e'} p(e')/\sigma(e')}.$$

Furthermore, if ℓ_t and L_t are the local times of X_t and Y_t (as defined in theorem 4.2) then

$$L_t = \left[\sum_e p(e)/\sigma(e) \right] \ell_t.$$

Thus, the local time of the Walsh process is the same as the “invariant” local time from 4.3. On the other hand,

$$\bar{\ell}_t = \left[\sum_e p(e)/\mathcal{D}(e) \right] \ell_t$$

is the symmetric local time defined as an occupation density. Therefore

$$\bar{\ell}_t = \left[\frac{\sum_e p(e)/\mathcal{D}(e)}{\sum_e p(e)/\sigma(e)} \right] L_t.$$

These facts are an application of the rescaling result of Lemma 3.1 of [7]. This Lemma in turn is an application of the Itô-Tanaka formula given in theorem 4.2.

Now, our modeling assumption for the reaction-diffusion experiment is that the irreversible first-order reaction $A \rightarrow B$ corresponds to killing the diffusion when its time spent near the catalyst exceeds an independent exponential random variable whose rate parameter defines the rate of the reaction. Here, it is most natural to use $\bar{\ell}_t$ as the definition of “time spent near the catalyst”. Thus, our object of interest is the process \hat{X} obtained by killing X when $\bar{\ell}_t$ exceeds an independent rate κ exponential random variable. From the relationships between ℓ , $\bar{\ell}$ and L , this is the same thing as killing X when L_t exceeds an independent rate $\bar{\kappa}$ random variable, where

$$\bar{\kappa} = \left[\frac{\sum_e p(e)/\mathcal{D}(e)}{\sum_e p(e)/\sigma(e)} \right] \kappa.$$

Write ξ for this variable. We can always enlarge the underlying probability space to support ξ . Then the new process \hat{X} has lifetime

$$\hat{\zeta} = \inf \{t > 0; L_t > \xi\}.$$

We need to determine what condition at v characterizes the killed process’s generator $(\hat{A}, D(\hat{A}))$. This is the content of the following:

Proposition 4.3. *The domain $D(\hat{A})$ of \hat{A} is characterized by the following vertex condition at v :*

$$(4.5) \quad \sum_e \mathcal{D}(e) \bar{p}(e) \frac{dF_e}{dy}(0) = \kappa F(v).$$

where $\bar{p}(e) = \frac{p(e)/\mathcal{D}(e)}{\sum_{e'} p(e')/\mathcal{D}(e')}$.

Proof. This is an application of Dynkin’s formula. Let $F \in D(\hat{A})$. Write $\hat{\mathbb{P}}^x$ for the laws of the killed diffusion \hat{X} and \mathbb{P}^x for the laws of the original conservative diffusion X . Then Dynkin’s formula applied at v reads:

$$\hat{A}F(v) = \lim_{\delta \downarrow 0} \frac{\hat{\mathbb{E}}^v [F(\hat{X}(\hat{\tau}_\delta))] - F(v)}{\hat{\mathbb{E}}^v [\hat{\tau}_\delta]}$$

where $\hat{\tau}_\delta$ is the first exit time of \hat{X} from U_δ and $\{U_\delta; \delta > 0\}$ is a family of neighborhoods shrinking down to v as $\delta \downarrow 0$. Here, we choose $U_\delta = H^{-1}(B_\delta(v))$, i.e. the inverse image of the symmetric ball δ -ball around v under the map H defined above. Thus, U_δ is a wheel-shaped set whose spokes have lengths $\sigma(e)\delta$. Also, $\hat{\tau}_\delta$ is the same thing as the first exit time of Y_t from $B_\delta(v)$.

Now the continuity of sample paths means that \hat{X} can leave U_δ only through one of the points $(\sigma(e)\delta, e)$ or by jumping to the dead state \dagger . Since any function is automatically zero at \dagger , we have, in view of 4.4:

$$\hat{\mathbb{E}}^v [F(\hat{X}(\hat{\tau}_\delta))] = \hat{\mathbb{P}}^v [\hat{\tau}_\delta < \hat{\zeta}] \sum_e q(e) F_e(\sigma(e)\delta)$$

But $(\hat{\tau}_\delta < \hat{\zeta})$ occurs iff L hasn’t exceeded ξ by time τ_δ , i.e. iff $(L(\tau_\delta) \leq \xi)$ occurs, where τ_δ is the exit time of the original conservative process X from U_δ ; equivalently,

to the exit time of Y_t from $B_\delta(v)$. But $L(\tau_\delta)$ is exponentially distributed with mean δ under \mathbb{P}^v . (This comes from the excursion decomposition of the Walsh Brownian motion.) Therefore we can compute

$$\hat{\mathbb{P}}^v [\hat{\tau}_\delta < \hat{\zeta}] = \mathbb{P}^v [L(\tau_v) \leq \xi] = \frac{1}{1 + \bar{\kappa}\delta}$$

On the other hand we can see easily that the expectation in the denominator of the expression for $\hat{A}F(v)$ is $\sim c\delta^2$. Putting it together, we have:

$$\hat{A}F(v) = \lim_{\delta \downarrow 0} \frac{1}{c\delta} \frac{1}{1 + \bar{\kappa}\delta} \left[\sum_e \sigma(e)q(e) \frac{F_e(\sigma(e)\delta) - F(v)}{\sigma(e)\delta} - \bar{\kappa}F(v) \right]$$

Since $1/\delta$ blows up as $\delta \downarrow 0$, the existence and finiteness of the whole limit entails that:

$$\sum_e \sigma(e)q(e) \frac{dF}{dy_e}(v) = \bar{\kappa}F(v).$$

From the definition of $q(e)$ and $\bar{\kappa}$ this last is

$$\sum_e p(e) \frac{dF}{dy_e}(v) = \left[\sum_e p(e)/\mathcal{D}(e) \right] \kappa F(v).$$

Then defining $\bar{p}(e) = \frac{p(e)/\mathcal{D}(e)}{\sum_{e'} p(e')/\mathcal{D}(e')}$, the condition takes the form

$$\sum_e \mathcal{D}(e)\bar{p}(e) \frac{dF}{dy_e}(v) = \kappa F(v)$$

as advertised in the beginning. \square

Remark 4.4. This clarifies the relationship mentioned before, between the probabilistic and PDE parameters. Also, note that killing the diffusion when $\bar{\ell}_t$ exceeds a rate κ exponential is the same thing as killing when $\kappa\bar{\ell}_t$ exceeds an independent rate 1 exponential. Remember that $\bar{\ell}$ has units 1/time, so we can think of $\kappa\bar{\ell}_t$ as a unitless normalized time.

4.3. Conversion function and ODE's on metric graphs. With the description of the generator given in section 4.2, we can relate the problem of determining reaction yield to boundary value problems involving \mathcal{G} . For the setup, we let \mathcal{G} be a metric graph with vertices \mathcal{V} and edges \mathcal{E} . This graph supports a diffusion process X which is characterized by diffusion coefficients $\mathcal{D}(e) = \frac{1}{2}\sigma^2(e)$ defined for each $e \in \mathcal{E}$ and dispersion parameters $p_v(e)$ defined for each $v \in \mathcal{V}$ and $e \sim v$. This diffusion process, whose generator was described in Theorem 4.1, models the diffusion in reaction-diffusion experiment introduced in section 2.

Now designate by \mathcal{V}_{bd} a set of vertices of degree 1 corresponding to the reactor exit; the rest will be called \mathcal{V}_{int} . Among the vertices in \mathcal{V}_{int} we specify a certain subset \mathcal{C} corresponding to catalytically active sites. Each $v \in \mathcal{C}$ has an associated geometric parameter $\delta(v)$ and then we write the kinetic parameter at v in the form $\kappa(v) = \kappa\delta(v)$. As explained above, we can model the reaction by killing X when

$$\ell_t(\mathcal{C}) = \sum_{v \in \mathcal{C}} \kappa\delta(v)\bar{\ell}_t(v)$$

exceeds an independent rate 1 exponential random variable. As before,

$$\bar{\ell}_t(v) = \left[\sum_{e: e \sim v} \frac{p_v(e)}{\mathcal{D}(e)} \right] \ell_t(v)$$

is the occupation time density of X at v and $\ell_t(v)$ is the local time at v as described in Theorem 4.2.

Theorem 4.5. *The generator of \hat{X} is characterized by the vertex conditions*

$$(4.6) \quad \sum_{e: e \sim v} p_v(e) \frac{dF}{dy_e}(v) = 0$$

at each $v \in \mathcal{V} \setminus \mathcal{C}$ and

$$(4.7) \quad \sum_{e: e \sim v} \mathcal{D}(e) \bar{p}_v(e) \frac{dF}{dy_e}(v) = \kappa \delta(v) F(v)$$

at each $v \in \mathcal{C}$.

Proof. This follows from the same sort of reasoning as in Proposition 4.3. Note that, in applying the Dynkin formula at $v \in \mathcal{C}$, $\ell_t(\mathcal{C})$ reduces to $\ell_t(v)$ because none of the other local times can contribute to the sum if X stays near v . \square

As a corollary, we can represent the solution to the boundary value problems on \mathcal{G} using the process X .

Corollary 4.6. *Let φ be a function on \mathcal{V}_{bd} . The solution to the BVP $Au = 0$ in \mathcal{G} with vertex conditions 4.7 on \mathcal{C} , $u = \varphi$ on \mathcal{V}_{bd} is:*

$$u(x) = \mathbb{E}^x \left[\exp \left\{ -\kappa \sum_{v \in \mathcal{C}} \delta(v) \bar{\ell}_T(v) \right\} \varphi(X_T) \right]$$

5. PROOF OF THE FACTORIZATION FORMULA FOR A SINGLE PARTICLE

Let $P(x, \mathcal{C}, \kappa)$ denote the probability that a Brownian particle starting at x in \mathcal{G} will undergo the reaction $A \rightarrow B$ before exit at time T . Here, as before, \mathcal{C} is the set of active vertices. We will soon assume that \mathcal{C} consists of a single point v_c . The Brownian process will be indicated by X_t . The first time X_t hits the catalyst set is

$$T_{\mathcal{C}} := \inf\{t > 0 : X_t \in \mathcal{C}\}$$

and $L_T^{\mathcal{C}}$ is the local time at \mathcal{C} . Since $L_T^{\mathcal{C}} = 0$ on the event $\{T_{\mathcal{C}} \geq T\}$ that X_t arrives at \mathcal{V}_{bd} without hitting \mathcal{C} , we have by the reaction model described above that

$$(5.1) \quad \begin{aligned} P(x, \mathcal{C}, \kappa) &= \mathbb{E}^x \left[\left(1 - \exp\{-\kappa L_T^{\mathcal{C}}\}\right) \mathbb{1}_{(T_{\mathcal{C}} < T)} \right] \\ &= P(x, \mathcal{C}) - \mathbb{E}^x \left[\exp\{-\kappa L_T^{\mathcal{C}}\} \mathbb{1}_{(T_{\mathcal{C}} < T)} \right] \end{aligned}$$

where $P(x, \mathcal{C})$ denotes the probability that X_t hits \mathcal{C} before arriving at \mathcal{V}_{bd} , that is, $P(x, \mathcal{C}) = \mathbb{E}^x[\mathbb{1}_{(T_{\mathcal{C}} < T)}]$. Note that, if we regard $\mathcal{C} \cup \mathcal{V}_{\text{bd}}$ as the boundary of \mathcal{G} , then $P(x, \mathcal{C})$ is the harmonic measure of \mathcal{C} at the point x for the process X_t . Also observe that the local time process $L_t^{\mathcal{C}}$ does not start increasing from 0 until the process hits \mathcal{C} . Expressed in terms of the shift operator $\theta_{T_{\mathcal{C}}}$ this means $L_T^{\mathcal{C}} = L_T^{\mathcal{C}} \circ \theta_{T_{\mathcal{C}}}$ on $\{T_{\mathcal{C}} < T\}$. Then, since $\{T_{\mathcal{C}} < T\} \in \mathcal{F}_{R_{\mathcal{C}}}$, the strong Markov property implies:

$$\mathbb{E}^x \left[\mathbb{E}^x \left[\exp\{-\kappa L_T^{\mathcal{C}}\} \circ \theta_{T_{\mathcal{C}}} \right] \mathbb{1}_{T_{\mathcal{C}} < T} \right] = \mathbb{E}^x \left[\mathbb{E}^{X_{T_{\mathcal{C}}}} \left[\exp\{-\kappa L_T^{\mathcal{C}}\} \right] \mathbb{1}_{(T_{\mathcal{C}} < T)} \right].$$

We now assume that $\mathcal{C} = \{v_c\}$ is a single point, in which case

$$\mathbb{E}^x \left[\mathbb{E}^{X_{T_{\mathcal{C}}}} \left[\exp\{-\kappa L_T^{\mathcal{C}}\} \right] \mathbb{1}_{(T_{\mathcal{C}} < T)} \right] = \mathbb{E}^{v_c} \left[\exp\{-\kappa L_T^{\mathcal{C}}\} \right] \mathbb{E}^x \left[\mathbb{1}_{(T_{\mathcal{C}} < T)} \right].$$

Therefore, using 5.1, and the definition of $P(x, \mathcal{C})$, we arrive at

$$(5.2) \quad P(x, \mathcal{C}, \kappa) = P(x, \mathcal{C}) \left(1 - \mathbb{E}^{v_c} \left[\exp\{-\kappa L_T^{\mathcal{C}}\} \right]\right).$$

Now observe that L_T^C must be exponentially distributed. To see this, first define the *inverse local time*

$$\tau(s) := \inf\{t > 0 : L_t^C > s\}.$$

By virtue of the additive property $L_{s+t}^C = L_t^C + L_s^C \circ \theta_t$ for all $s, t \geq 0$, we have

$$\tau(s+t) = \tau(s) + \tau(t) \circ \theta_{\tau(s)}.$$

Also note that the exit time T is a *terminal time*: $t < T \Rightarrow T = t + T \circ \theta_t$. From these observations we can compute:

$$\begin{aligned} \mathbb{P}^{v_c}(L_T^C > s+t) &= \mathbb{P}^{v_c}[\tau(s+t) < T] \\ &= \mathbb{P}^{v_c}[\tau(s) < T, \tau(s) + \tau(t) \circ \theta_{\tau(s)} < T] \\ &= \mathbb{P}^{v_c}[\tau(s) < T, \tau(t) \circ \theta_{\tau(s)} < T \circ \theta_{\tau(s)}]. \end{aligned}$$

Since $X_{\tau(s)} = v_c$ for any s , the strong Markov property implies that the last line equals

$$\begin{aligned} \mathbb{E}^{v_c}[\mathbb{1}_{(\tau(s) < T)} \mathbb{E}^{v_c}[\mathbb{1}_{(\tau(t) < T)} \circ \theta_{\tau(s)} | \mathcal{F}_{\tau(s)}]] &= \mathbb{E}^{v_c}[\mathbb{1}_{(\tau(s) < T)} \mathbb{E}^{X_{\tau(s)}}[\mathbb{1}_{(\tau(t) < T)}]] \\ &= \mathbb{P}^{v_c}(\tau(s) < T) \mathbb{P}^{v_c}(\tau(t) < T) \\ &= \mathbb{P}^{v_c}(L^{C_T} > s) \mathbb{P}^{v_c}(L^{C_T} > t). \end{aligned}$$

Therefore,

$$\mathbb{P}^{v_c}(L_T^C > s+t) = \mathbb{P}^{v_c}(L^{C_T} > s) \mathbb{P}^{v_c}(L^{C_T} > t),$$

which identifies L_T^C as exponentially distributed. Writing $\lambda := \mathbb{E}^{v_c}[L^{C_T}]$, the expression $\mathbb{E}^{v_c}[\exp\{-\kappa L_T^C\}]$ is simply the Laplace transform of a mean λ exponential random variable. Using the known formula

$$\mathbb{E}^{v_c}[\exp\{-\kappa L_T^C\}] = \frac{1}{1 + \lambda\kappa}$$

we obtain from 5.2 the desired result

$$P(x, \mathcal{C}, \kappa) = P(x, \mathcal{C}) \left(1 - \frac{1}{1 + \lambda\kappa}\right) = P(x, \mathcal{C}) \frac{\lambda\kappa}{1 + \lambda\kappa}.$$

5.1. Kac moment formula and multiple particles. This sort of reasoning works for any kind of Markov process for which it is possible to define local times. See the theory in [15], for example, which deals with “strongly symmetric Borel right processes with continuous α -potential densities.” Furthermore, this formula generalizes to more than one catalytically active site via the Kac moment formula, which we state in the following form:

Theorem. *Let X be a strong Markov process with continuous α -potential densities with respect to a reference measure m . Let $\ell = \{\ell_t^y\}$ be its family of local times, normalized by the condition*

$$\mathbb{E}^x \int_0^\infty e^{-\alpha t} d\ell_t^y = u^\alpha(x, y).$$

Given a terminal time T , let $\tilde{u}(x, y)$ be the 0-potential density of X killed at T ; that is, let

$$\tilde{u}(x, y) = \mathbb{E}^x \ell_T^y.$$

With these definitions, we have the following formula:

$$(5.3) \quad \mathbb{P}^x \left[\prod_{i=1}^n \ell_T^{y_i} \right] = \sum_{\pi} \tilde{u}(x, y_{\pi(1)}) \cdots \tilde{u}(y_{\pi(n-1)}, y_{\pi(n)})$$

where the sum runs over all permutations π of $\{1, 2, \dots, n\}$. In particular,

$$(5.4) \quad \mathbb{P}^x \left[(\ell_T^y)^n \right] = n! \tilde{u}(x, y) (\tilde{u}(y, y))^{n-1}.$$

Corollary. *The same things supposed, let $\tilde{\mathbf{U}}$ be the matrix whose (i, j) entry is $\mathbf{U}_{ij} = \tilde{u}(y_i, y_j)$, and $\mathbf{U}^{(r)}$ the matrix obtained from \mathbf{U} by subtracting its r -th row from every row:*

$$\mathbf{U}_{ij}^{(r)} = \mathbf{U}_{ij} - \tilde{\mathbf{U}}_{rj}$$

Finally, let $\mathbf{\Lambda}$ be the diagonal matrix whose (i, j) entry is $\mathbf{\Lambda}_{ij} = k_i \delta_{ij}$. Then, for all k_i sufficiently small,

$$(5.5) \quad \mathbb{P}^{y_r} \left[\exp \left\{ \sum_{i=1}^n k_i L_T^{y_i} \right\} \right] = \frac{\det(\mathbf{I} - \tilde{\mathbf{U}}^{(r)} \mathbf{\Lambda})}{\det(\mathbf{I} - \tilde{\mathbf{U}} \mathbf{\Lambda})}.$$

The above are essentially Theorem 3.10.1 and Lemma 3.10.2 of [15]. When there is more than one catalytically active site, the survival function now takes the form:

$$\alpha(x) = 1 - \mathbb{E}^x \exp \left\{ - \sum_{v \in \mathcal{C}} \kappa(v) \ell_T^v \right\}$$

The reasoning described in section 5 applies here, except that now we use the 5.5 to deal with an expression of the form

$$\mathbb{E}^u \exp \left\{ \sum_{v \in \mathcal{C}} \kappa(v) \ell_T^v \right\} \quad (u \in \mathcal{C}).$$

The result ends up being

$$(5.6) \quad \alpha(x) = P_0(x) - \sum_{v \in \mathcal{C}} P_v(x) \frac{\det(\mathbf{I} - \tilde{\mathbf{U}}^{(v)} \mathbf{\Lambda})}{\det(\mathbf{I} - \tilde{\mathbf{U}} \mathbf{\Lambda})}$$

Here, $P_0(x)$ is the probability of hitting \mathcal{C} at all starting from x , and $P_v(x)$ is the probability of starting from x and hitting \mathcal{C} for the first time at v . This equation says that yield is a rational function of k , with coefficients determined by the geometry of the graph and the parameters of the diffusion.

Remark. The expression 5.6 is hard to work with, but there are often reasons for simplifications to occur. For example, suppose \mathcal{G} consists of n segments placed end-to-end and that the diffusion X is just Brownian motion. Let x be in the left-most component of \mathcal{G} and take for T the first hitting time to the right-most endpoint. Then \mathcal{C} consists of some vertices $v_1 < \dots < v_n$ in between x and the right endpoint. Clearly, in this situation, the process can't escape without hitting \mathcal{C} , so $P_0(x) = 1$. Also, the first hit has to be at the left-most point of \mathcal{C} , so that $P_{v_1}(x) = 1$ and all the other $P_{v_k}(x)$'s are 0. Finally, it's clear enough that the amount of time you expect to spend at y is the same starting from any point to the left of y . So the matrix $\tilde{\mathbf{U}}$ is upper-triangular, which means that $\tilde{\mathbf{U}}^{(v)}$ has mostly 0's.

6. REDUCTION FROM METRIC TO ORDINARY GRAPHS

In section 4.3 we described how to reduce the problem of determining reaction probability to solving an ODE on a graph. Here, we'll reduce the problem still further, to a discrete one on the underlying combinatorial graph.

We assume that the diffusion coefficient is constant along edges and disregard the convection term in the differential operator, so that the differential equation on edges reduces to

$$(\mathcal{L}_e f)(x) := f_e''(x) = 0.$$

On the set of boundary vertices the function takes boundary value ϕ , and on the set of interior vertices we impose 3.2 at chemically active vertices, and that same condition with 0 right-hand side at inert vertices. The solution function is affine on each edge: $f_e(x) = ax + b$, where $b = f(s(e))$ and $a = f_e'(0)$.

At this point it is convenient to think in terms of the underlying combinatorial graph rather than the metric graph, since the solution function f is determined by its values on the set of vertices. A slight change in notation will be useful. We assume that \mathcal{G} contains the inversely oriented edge \bar{e} for each $e \in \mathcal{E}$. The derivative of a function at a vertex v , denoted above by $(f_e')_{\text{in}}(v)$, can then be written

$$f'(e) := \frac{f(r(e)) - f(s(e))}{|e|}.$$

Then $f_e(x) = f(s(e)) + xf'(e)$. The weight function will be written $p(e) := p_{s(v)}(e)$ and the vertex condition 3.2 becomes

$$(6.1) \quad \delta(v)\kappa q(v)f(v) = \sum_{e \in \mathcal{E}_v} \mathcal{D}(e)p(e)f'(e)$$

where now $q(v) = \mathbb{1}_{\mathcal{C}}$ is the indicator function of the set of active vertices.

Equation 6.1 may be regarded as the Feynman-Kac equation on the graph. A more suggestive expression is obtained by introducing the graph Laplacian, for which the following definitions are needed. Let $L^2(\mathcal{V}, \delta)$ be the inner-product space of functions on the vertex set \mathcal{V} with inner product

$$\langle f, g \rangle_{\mathcal{V}} := \sum_{v \in \mathcal{V}} f(v)\overline{g(v)}\delta(v).$$

A *vector field* on the graph is defined as a function X on \mathcal{E} such that $X(\bar{e}) = -X(e)$. The actual vector at e determined by X will be written $X(e)e/|e|$ where $e/|e|$ is regarded as a unit vector. In fact, we write the *dot-product* $e \cdot e := |e|^2$. Let $L^2(\mathcal{E}, \nu)$ be the inner-product space of vector fields with inner-product

$$\langle X, Y \rangle_{\mathcal{E}} := \frac{1}{2} \sum_{e \in \mathcal{E}} X(e) \cdot \overline{Y(e)} \nu(e)$$

where $\nu(e) := |e|p(e)$. The factor 1/2 is there because $X(\bar{e}) \cdot \overline{Y(\bar{e})} = X(e) \cdot \overline{Y(e)}$. The *gradient* of a function f is

$$\text{grad}f(e) = f'(e) \frac{e}{|e|}$$

and the *divergence* of a vector field is defined as the negative of the adjoint of the gradient with respect to the above inner products. Thus $-(\text{div}X, \varphi)_{\mathcal{V}} := \langle X, \text{grad}\varphi \rangle_{\mathcal{E}}$. It follows (by taking φ to be the indicator function of the set $\{v\}$) that

$$\text{div}(X)(v) = \frac{1}{\delta(v)} \sum_{e \in \mathcal{E}_v} p(e)X(e).$$

Therefore,

$$\text{div}(\mathcal{D} \text{grad}f) = \frac{1}{\delta(v)} \sum_{e \in \mathcal{E}_v} \mathcal{D}(e)p(e)f'(e)$$

and by 6.1

$$\operatorname{div}(\mathcal{D} \operatorname{grad} f) - \kappa q(v) f(v) = 0.$$

Thus we recover the Feynman-Kac boundary value problem, except that it now applies to functions on the vertex set \mathcal{V} with value ϕ on the boundary vertices.

For the examples described earlier, we assume that $q = \mathbb{1}_{\{v_c\}}$ and that $\mathcal{D}(e)$ and $\delta(v)$ are constant. Thus the boundary value problem for the survival function on the graph reduces to

$$(6.2) \quad \mathcal{D}\Delta\psi = \kappa \mathbb{1}_{\{v_c\}} \psi \text{ on } \mathcal{V}_{\text{in}} \text{ with boundary values } \psi = 1 \text{ on } \mathcal{V}_{\text{bd}}.$$

Here $\Delta = \operatorname{div} \operatorname{grad}$ is the graph Laplacian. Setting $\bar{\kappa} := \kappa \delta / \mathcal{D}$ and $p(e) = 1/d(s(e))$, where $d(v)$ is the degree of the vertex v and $\delta = \delta(v_c)$, this reduces to

$$(6.3) \quad \sum_{e \in \mathcal{E}_v} |e|^{-1} f(r(e)) = \left(\bar{\kappa} d(v) q(v) + \sum_{e \in \mathcal{E}_v} |e|^{-1} \right) f(v)$$

for $v \in \mathcal{V}_{\text{in}}$ and $f(v) = 1$ for $v \in \mathcal{V}_{\text{bd}}$.

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