

Reaction-diffusion on metric graphs: from 3D to 1D

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Abstract

We provide stochastic foundations for the analysis of a class of reaction-diffusion systems using as an example the known Temporal Analysis of Products (TAP) experiments, showing how to effectively obtain explicit solutions to the associated equations by approximating the 3-dimensional domain of diffusion U (the reactor) by 1-dimensional network models.

In a typical TAP experiment a pulse of reactant gas of species A is injected into U , which is filled with chemically inert material, permeable to gas diffusion. Particles of catalyst are placed amid this inert medium, forming active sites where the reaction $A \rightarrow B$ may occur. On part of the boundary of U designated as the exit, a mixture of A and B can escape. We study the problem of determining the (molar) fraction of product gas in the mixture after U is fully evacuated. This fraction is identified with the *reaction probability*—that is, the probability of a single diffusing molecule reacting before leaving U . Specifically, we are interested in how this probability depends on the reaction rate constant k .

After giving a stochastic formulation of the problem and the boundary value problem whose solution is this probability, we study a class of domains, called *fat graphs*, comprising a network of thin tubes with active sites at junctures. The main result of the paper is that in the limit, as the thin tubes approach curves in 3-dimensional space, reaction probability converges to functions of the point of gas injection that can be computed explicitly in terms of a rescaled parameter k . By this 3D to 1D reduction, the simpler processes on metric graphs can be used as model systems for more realistic 3-dimensional configurations. This is illustrated with analytic and numerical examples. One example, in particular, illustrates an important application of our method: finding the catalyst configuration that maximizes reaction probability at a given reaction rate constant.

Reaction-diffusion, metric graphs.

1 Introduction and main results

Reaction-diffusion systems are traditional subjects in physical chemistry and chemical engineering. A vast literature is devoted to different theoretical and applied aspects of these

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processes in non-porous and porous media covering such topics as the design of active materials and systems (catalysts, adsorbents, sensors, membranes, electrodes) [2, 19], precise kinetic characterization of catalytic materials [16, 22], and spatial optimization of chemical systems [24, 27, 7, 29], to mention a few. Typically, the 3-D and 2-D media in the chemical reactor include a set of elements, both chemically active and non-active (inert), e.g. catalytic particles and quartz particles, respectively. In chemical reactors, such elements may create active and non-active zones which are spatially separated.

Consequently, the following problems arise: how to design these ‘mixed’ reaction-diffusion systems in order to achieve the best activity and selectivity and to meet other technological requirements such as uniformity of flow and composition. Efficient computational procedures have been proposed to solve such mixed reaction-diffusion systems [27, 7, 29], but a rigorous mathematical foundation has so far been lacking.

The focus of this paper is on the determination of the fraction of reaction products, which we refer to as *conversion*, and the explicit dependence of conversion on the chemical rate constants for a type of reaction-diffusion systems of great current interest known as TAP (Temporal Analysis of Products). The essential features of a typical TAP system will be described shortly below. Some general theoretical results pertaining to the determination of conversion were given in our papers [10, 11] without a detailed explanation of the formal mathematical framework. This framework is developed here, along with a method of approximation based on the idea of approximating the domains of diffusion by 1-D networks. As will be seen below, this leads to explicit formulas for conversion in situations that can help us understand reaction-diffusion experiments in more realistic 3-D configurations. A very detailed study in which the theory developed in this paper is applied to realistic 3-dimensional TAP reactors is provided by [28]. We refer to [28] and the papers cited there for further explanations concerning the TAP technique, its theory, methodology, and practical applications.

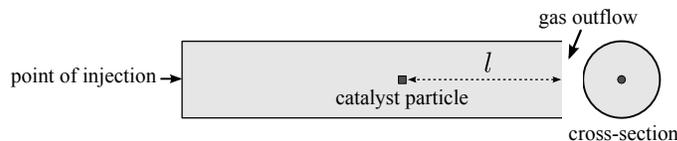


Figure 1: The reactor at the core in an actual TAP system in a simple but typical TAP experiment. See the explanations below. This configuration will be used below for a numerical example to illustrate our main 3D-to-1D approximation result.

As an illustrative TAP experiment, consider CO oxidation over platinum catalyst. The actual reactor at the core of the TAP system is depicted in Figure 1. It is a small cylinder in which CO gas is injected at the indicated point and product gases exit at the opposite side. The reactor’s interior is uniformly packed with non-porous small particles of quartz, creating a medium that can be assumed to have essentially constant diffusivity. Diffusion is assumed to proceed in the Knudsen regime, in which the mean free path of gas molecules is comparable or longer than the length scale of the small network of voids produced by the packing. It is thus natural to model the motion of gas molecules by mathematical Brownian motion, as this motion corresponds macroscopically to ordinary Fickian diffusion. The figure illustrates the

case of a single catalyst particle, of a given size and shape, placed at a well defined location inside the reactor amid the inert particles. The precise mechanism of the overall reaction $2\text{CO} + \text{O}_2 \rightarrow \text{CO}_2$ happening on the oxidized surface of the platinum catalyst may be very complex, but one is often justified in representing the kinetic dependence as a simple first order expression regarding CO. Therefore, from the kinetic point of view the overall reaction can be presented as $A \rightarrow B$. The quantity of our interest is the molar fraction of CO_2 in the total gas outflow.

Extracting the essential features of the experiment just described and allowing for more general domains and catalyst configurations, we are led to consider the system described schematically in Figure 2. The bounded domain $U \subset \mathbb{R}^d$ represents the chemical reactor packed with inert permeable material, which is characterized by its diffusivity constant \mathcal{D} . At the point $x \in U$, one injects a small pulse of gas molecules of species A . The pulse diffuses through U following the standard diffusion equation with coefficient \mathcal{D} before escaping at the reactor exit, marked in the figure with a dashed line and denoted ∂U_a .

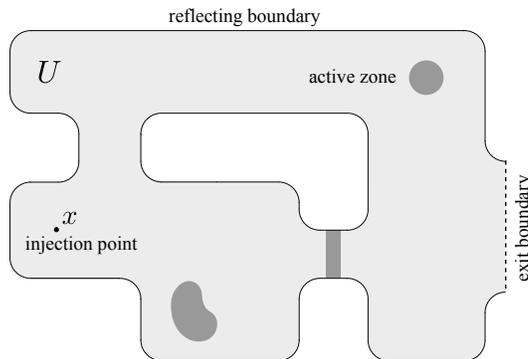


Figure 2: Schematic description of the chemical reactor. U is the domain of diffusion; the shaded regions represent active sites, whose union is denoted \mathcal{A} . The boundary of U is the union of a reflecting part ∂U_r and an absorbing part ∂U_a . The point x is where reactant gas of species A is injected. We are interested in the probability that a gas molecule starting at x and undergoing Brownian motion will react before reaching ∂U_a .

We suppose that a certain small subset \mathcal{A} of U contains a catalytically active material promoting the irreversible first-order reaction $A \rightarrow B$ with *rate constant* k . We call \mathcal{A} the *active zone*. A fraction of the molecules in the initial pulse may interact with \mathcal{A} and convert to B before exiting the reactor. This number is called the *fractional conversion*. Motivated by problems in heterogeneous catalysis (see [11, 10] and references therein) we seek to determine the fractional conversion in terms of the rate constant k , the diffusion coefficient \mathcal{D} and the geometric configuration of \mathcal{A} and U .

The practical concern is that k may be difficult to determine experimentally, because the reaction $A \rightarrow B$ may involve, at the microscopic level, a complex sequence of steps such as adsorption and surface reaction. On the other hand, measuring the fractional conversion is comparatively simple. Similarly, one can carefully control in a lab the size and shape of

the reactor, the size and shape of the active zone, and the nature of the particulate matter supporting the diffusion (hence the diffusion coefficient \mathcal{D}). Determining k in terms of these other variables is therefore of considerable interest.

We intend to set up a probabilistic model for determining k . Let us briefly describe what physical assumptions we impose for the model to work. First, we assume that the pressure within U is low enough, and the injected pulse is narrow enough, that the diffusion follows the *Knudsen regime*. In other words, the diffusion is driven at the microscopic level by tiny collisions between diffusing molecules and the particulate matter making up the reactor bed—not by collisions between molecules themselves. Second, we assume the pulse is small enough that any reactions occurring within U during the course of the experiment negligibly alter the composition of the active sites. These assumptions are physically reasonable and can in fact be arranged for in the lab; see [17] or [28] for more information.

With the set-up just described, write $\alpha(x)$ for the fractional conversion, or $\alpha_k(x)$ when necessary to emphasize dependence on the rate constant k . Because of our assumption about the Knudsenian character of the diffusion, we can identify $\alpha_k(x)$ with the *reaction probability*; that is, with the probability that a single molecule, entering the chamber at x and undergoing reflecting Brownian motion in U with diffusion coefficient \mathcal{D} , converts to B before hitting ∂U_a . This identification is possible because every molecule’s path in the reactor is independent of every other’s. Therefore a single pulse of N molecules is equivalent to N independent pulses of one molecule. For this reason, we can model the reaction $A \rightarrow B$ by killing a reflecting Brownian motion (RBM) in U with a rate function of the form $r = kq$ where k is the reaction rate and q is the indicator function on \mathcal{A} , or perhaps a smooth approximation thereof.

By RBM in U , we mean a diffusion process (X_t, \mathbb{P}_x) with sample paths in \bar{U} and satisfying the stochastic differential equation

$$X_t - X_0 = \sigma B_t + \int_0^t \nu(X_s) d\ell_s \quad (1)$$

where $\sigma = \sqrt{2\mathcal{D}}$, B_t is an ordinary d -dimensional Brownian motion, ν is the inward-pointing unit normal vector field on ∂U , and ℓ_s is a continuous increasing process (called the boundary local time) that increases only on $\{t : X_t \in \partial U\}$. The SDE (1) is called the *Skhorohod or semimartingale decomposition* of (X_t) . See, for example, [6, 9] for more information about RBM’s that have a semimartingale decomposition. As for killing a diffusion, see [25].

The existence of an RBM (X_t) in U with a decomposition (1) requires that ∂U satisfy certain modest smoothness conditions. For example, C^2 smoothness is more than sufficient to ensure that (1) has a pathwise unique solution; see [4, 5, 21, 21, 26]. See [18] for general notions about stochastic differential equations. Henceforth we shall assume ∂U is at least C^2 unless otherwise stated. Furthermore, we assume the first hitting time of (X_t) to ∂U_a is finite almost surely. As for \mathcal{A} , we assume for now that it’s a compact subset of U with a regular boundary, and impose further conditions when necessary.

It will be convenient to introduce the *survival function* $\psi_k(x)$, defined as the probability that Brownian motion starting at x reaches ∂U_a without being killed (that is, without reacting). We also write $\psi(x)$ when k is understood. Then the reaction probability we seek is $\alpha_k(x) =$

$1 - \psi_k(x)$. Our model for the reaction and diffusion within U entails that

$$\psi_k(x) = \mathbb{E}_x \left[\exp \left\{ - \int_0^T kq(X_s) ds \right\} \right] \quad (2)$$

where T is the first hitting time of (X_t) to ∂U_a , that is $T := \inf\{t > 0 : X_t \in \partial U_a\}$.

Functionals such as the right-hand side of (2) are well-known and have the following physical interpretation in terms of our catalysis problem: the probability that a gas molecule injected at x and following the sample path ω *hasn't* reacted decreases exponentially with the amount of time spent in the chemically active region \mathcal{A} , the reaction constant k being the exponential rate. Thus the expression $\exp \left\{ -k \int_0^{T(\omega)} q(X_s(\omega)) ds \right\}$ represents the probability, for that sample path, that the molecule does not react by the time it exits the reactor, and then $\psi_k(x)$ is the expected value of this probability.

It is also well-known in the theory of stochastic processes that $\psi_k(x)$ can be expressed as the solution to an elliptic boundary value problem in U . Our numerical examples below are based on this fact:

Theorem 1. *Suppose that u is a function which is bounded and continuous in \bar{U} , satisfies*

$$\mathcal{D}\Delta u - kqu = 0$$

in $U \setminus \partial\mathcal{A}$, together with the boundary conditions $\frac{\partial u}{\partial n} = 0$ on ∂U_r and $u = 1$ on ∂U_a . Suppose furthermore that $\partial\mathcal{A}$ is a set of zero potential for RBM (Reflecting Brownian Motion) in \bar{U} . Then $u = \psi$ within U .

Remark. For very fast reactions, it is meaningful to consider the limit $\psi_\infty(x)$ of $\psi_k(x)$ as k goes to infinity. It easily follows from the expression 2 that $P_h(x) := 1 - \psi_\infty(x)$ is the probability that RBM started at x hits \mathcal{A} before leaving U through ∂U_a . This probability can also be determined by solving a boundary value problem. Namely, if $v(x)$ solves Laplace's equation in $V := U \setminus \mathcal{A}$, together with the boundary conditions $v = 1$ on the boundary of \mathcal{A} , $v = 0$ on the adsorbing boundary ∂U_a , and the normal derivative of v vanishes on the complement in ∂V of the union of ∂U_a and $\partial\mathcal{A}$, then $v(x) = P_h(x)$.

Elsewhere below we will address the existence of solutions satisfying the conditions in Theorem 1. For now, we simply assume that a solution exists and can be approximated using the Finite Element (FE) method. This is not a serious defect since we only intend to use Theorem 1 to corroborate numerically the predicted form of $\alpha_k(x)$ in Theorem 2 below.

To understand what to expect, then, consider the case where U is a line or a metric graph, and $\mathcal{A} = \{a\}$, a single point. Then simple manipulations involving the strong Markov property (described in detail below) show that $\alpha_k(x)$ factors as $\alpha_k(x) = P_h(x)f(x, k)$ where $P_h(x)$ is the hitting probability for \mathcal{A} (described in the Remark under Proposition 1) and $f(x, k)$ is the reaction probability conditional on starting from a . Clearly $P_h(x)$ doesn't depend on k , so that $f(k, x)$ is the quantity of interest. In this case, $f(x, k)$ is simply equal to $\alpha_k(a)$, and it follows from basic properties of local times (described in detail below) that

$$f(x, k) = \frac{\lambda k}{1 + \lambda k} \quad (3)$$

where λ is a constant that doesn't depend on k . For this reason we regard formula (3) as “typical” behavior for situations where \mathcal{A} can reasonably be thought of as a single point in the state space. This involves some coarse-graining, because single points are polar for Brownian motion.

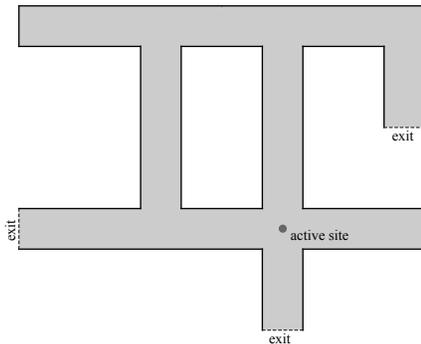


Figure 3: Example in dimension 2 of a reactor domain with a small active site.

To illustrate this behavior, consider the domain in Figure 3. Taking the length of the shortest side of the polygonal region as unit, the radius of the disc-shaped active site is 0.1. Here, \mathcal{A} is not a single point, but is nevertheless small enough relative to U that we can reasonably hope that a factorization of the form $\alpha_k(x) = P_h(x)f(x, k)$ holds. That is, if we define $f(x, k)$ by

$$f(x, k) := \frac{\alpha_k(x)}{P_h(x)} \quad (4)$$

and then compute the right-hand members of (4) using the boundary value problems determining $\alpha_k(x)$ and $P_h(x)$, then we expect to see the behavior described in (3).

To this end, we computed $f(x, k)$ as defined in (4) for a fixed x and 50 different equally-spaced values of $k \in [0, 100]$ using FEniCS, and then “solved for λ ” under the working assumption that (3) holds. That is, we defined

$$\lambda := \frac{1}{k} \frac{f(x, k)}{1 - f(x, k)} = \frac{1}{k} \frac{\psi_k(x)/P_h(x)}{1 - \psi_k(x)/P_h(x)}$$

and checked λ 's dependence on k . As expected, the resulting λ 's exhibited little dependence on k . Denoting by λ_{\max} and λ_{\min} the maximum and minimum values of λ over the range of k 's we looked at, we found $(\lambda_{\max} - \lambda_{\min})/\lambda_{\min} < 0.005$ with mean value $\lambda = 0.02342$.

It will be shown that the above expression (3) is indeed a typical approximation of $f(x, k)$ when the active region is a small single site. Roughly speaking, λ is the amount of time accumulated at a , starting from a , before departing through the reactor exit. In particular, λ depends only on the geometry of the reactor and the diffusion coefficient, and not k . For more general active site configurations, more complicated but related approximation formulas apply.

As another example, solving numerically the boundary value problem for the reactor configuration of the actual TAP system depicted in Figure 1 (the catalyst particle has the shape of a small cylinder and its position along the central axis of the reactor can vary) shows that Formula 3 is verified to good approximation. More precisely, this formula holds with $\lambda = 2l$ and $1.0 \leq k \leq 100.0$, and measure of error $(\lambda_{\max} - \lambda_{\min})/\lambda_{\min}$ less than 0.05. The error is significantly less for values of k that are not too small. It is not our intension here to go further into an analysis of actual TAP systems similar to figure 1; a detailed application of the present methods to a wide range of TAP configurations is the subject of [28].

Our main approximation result is given below in Theorem 2. We call the regions to which our main result applies *fat graphs*. These are graph-like domains comprising a number of thin tubes and junctures that converge, in an appropriate sense, to an underlying metric graph $\Gamma = (\mathcal{V}, \mathcal{E})$. Here, \mathcal{E} denotes the edges of Γ , and \mathcal{V} the vertices. Then each tube in the domain corresponds to an edge $e \in \mathcal{E}$, and each juncture corresponds to a vertex $v \in \mathcal{V}$. We assume that the active region \mathcal{A} is concentrated in the juncture regions. The precise definitions are given in section 2. For now, figure 4 conveys a rough idea.

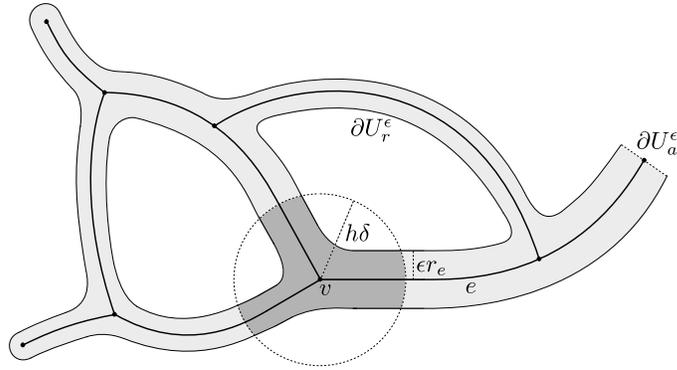


Figure 4: A fat graph in \mathbb{R}^d with its skeleton graph Γ . Edges have relative radii r_e and ϵ is a scaling parameter. Active sites, defined as regions where reaction can occur, have a relative radius δ with scaling parameter h . The reaction constant must also be scaled as $k^h = k/h$ as $h \downarrow 0$.

There are two scale parameters involved in the approximation: $\epsilon > 0$, which gives the thickness of the tubes in the domain, and $h > 0$, which gives the radius of the active zone around each active site. As $\epsilon \downarrow 0$, the domain collapses to the skeleton graph, and as $h \downarrow 0$, active sites collapse to vertices. At the same time, reaction activity, given by the rate constant $k^h = k/h$ must increase accordingly.

Thus let $f^{\epsilon, h}(x, k/h)$ denote the quantity introduced above that gives the dependence of the reaction probability on the rate constant. That is,

$$f^{\epsilon, h}(x, k/h) := \frac{\psi_k(x)}{P_h(x)}.$$

The main result is then the following.

Theorem 2 (3D to 1D reduction). *Let U^ϵ be a bounded fat graph whose skeleton metric graph Γ has finitely many vertices and edges. Let \mathcal{C} be the set of vertices corresponding to*

active sites of U^ϵ and δ the relative radius of the active sites. Define $\kappa := k\delta/\mathcal{D}$, where \mathcal{D} is the diffusion constant. Let $|\mathcal{C}|$ denote the number of active vertices. Then, under the hypotheses of Proposition 4 below,

$$\lim_{h \rightarrow 0} \lim_{\epsilon \rightarrow 0} f^{\epsilon, h}(x, k/h) = 1 - \sum_{v \in \mathcal{C}} p_v(x) \frac{\lambda_v(\kappa)}{\lambda(\kappa)},$$

where $p_v(x)$ is the probability that a diffusing particle starting from x hits \mathcal{C} for the first time at v , conditional on hitting \mathcal{C} at all, and $\lambda(\kappa)$, $\lambda_v(\kappa)$ are polynomials in κ of degree at most $|\mathcal{C}|$ and $|\mathcal{C}| - 1$, respectively. The coefficients of $\lambda(\kappa)$, $\lambda_v(\kappa)$ depend only on geometric properties of Γ : lengths of edges, degrees of vertices, location of exit and active vertices. When $\mathcal{C} = \{v\}$, this limit reduces to

$$\lim_{h \rightarrow 0} \lim_{\epsilon \rightarrow 0} f^{\epsilon, h}(x, k/h) = \frac{\lambda\kappa}{1 + \lambda\kappa}.$$

It would be interesting to find methods that could tell *a priori* how the coefficients of $\lambda(\kappa)$ and $\lambda_v(\kappa)$ can be expressed in terms of the geometry and topology of the graph, that is, as function of lengths, degrees, etc. A starting point would be to explore in a systematic way the properties of these polynomials for families of graphs. Here we are content with showing a few examples only.

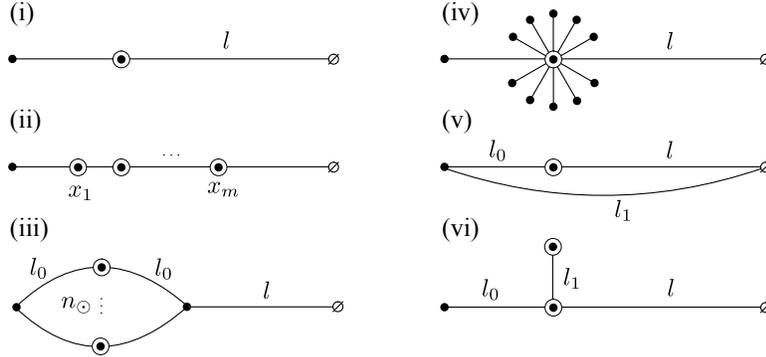


Figure 5: A few examples of graphs for which the reaction probability is easily computed. The vertex types are: \cdot = inert, \odot = active, \oslash = exit. The labels l_i indicate edge lengths and the x_i in graph (ii) are the coordinates of the active nodes. In graph (iii), n_\odot is the number of vertices of type \odot .

The reaction probability for the examples of figure 5 are easily obtained by solving the linear system of equations indicated in section 7. In all cases we assume that the point of gas injection is the left-most vertex. The results are as follows.

1. Graph (i):

$$\alpha(\kappa) = \frac{2l\kappa}{1 + 2l\kappa}.$$

Naturally, only the length of the edge between the active and exit vertices matters. On the other hand, if the initial edge is completely eliminated so that the starting point for Brownian motion is the active vertex, then the term $2l\kappa$ should be replaced with $l\kappa$.

2. Graph (ii): Let $l_j = x_j - x_{j-1}$. The value of $\alpha(\kappa)$ can be obtained recursively as follows. Set $g_1 = 1$ and $g_{j+1} = g_j + l_{j+1}(g_1 + \dots + g_j)(2\kappa)$ for $j = 2, \dots, m$. (The vertex \emptyset is at position x_{m+1} .) Then

$$\alpha(\kappa) = \frac{g_{m+1} - 1}{g_{m+1}}.$$

It is interesting to note the following property concerning optimal arrangement of active nodes: When κ is small,

$$\alpha(\kappa) = [(L - x_1) + \dots + (L - x_m)]\kappa + \text{higher order terms in } \kappa$$

where L is the total length of the graph. So if κ is small, one maximizes reaction probability by clustering all the active nodes near the entrance point. On the other hand, for large values of κ ,

$$\alpha(\kappa) = l_2 l_3 \dots l_{m+1} \kappa^m + \text{lower order terms in } \kappa.$$

One easily obtains that the coefficient of κ^m attains a maximum when the active vertices are equally spaced.

3. Graph (iii):

$$\alpha(\kappa) = \frac{2(l_0 + n_{\odot}l)\kappa}{1 + 2(l_0 + n_{\odot}l)\kappa}.$$

Despite having multiple active vertices, this system behaves, in its dependence on κ , like one with a single active vertex.

4. Graph (iv):

$$\alpha(\kappa) = \frac{\deg(v)l\kappa}{1 + \deg(v)l\kappa}$$

where $\deg(v)$ is the degree of the active vertex. As in the first example, only the length of the edge connecting the active vertex to the exit matters, but the number of shorter edges leading to inert vertices influences α , regardless of those edges' lengths, so long as their are greater than zero.

5. Graph (v):

$$\alpha(\kappa) = \alpha(\infty) \frac{\lambda\kappa}{1 + \lambda\kappa}$$

where $\alpha(\infty) = l_1/(l_0 + l_1)$ and $\lambda = 2l(l_0 + l_1)/(l_0 + l_1 + l)$.

6. Graph (vi):

$$\alpha(\kappa) = \frac{4l\kappa + 3ll_1\kappa^2}{1 + (4l + l_1)\kappa + 3ll_1\kappa^2}.$$

As expected for a system with two active vertices, this is the quotient of second degree polynomials in κ . Also note that, for l_1 large, $\alpha(\kappa) \approx \frac{3l\kappa}{1+3l\kappa}$, meaning that this graph behaves like graph (iv).

2 Metric graphs and fat-graph domains

The remainder of the paper is largely dedicated to proving the main results already stated above and explaining some of the computations involved in the graph examples above. We also indicate how the formulas for conversion of Theorem 2 relate to the so-called Kac's moment formula. We begin by introducing notation and terminology concerning *metric graphs*, together with an associated class of domains in \mathbb{R}^d we call *fat graphs*. Basically, a metric graph is an abstract graph realized as a collection of curvilinear segments; a fat graph is a neighborhood of Γ whose boundary satisfies some smoothness conditions.

More precisely, let $\mathcal{G} = (\mathcal{V}, \mathcal{E})$ be an abstract graph with vertex set \mathcal{V} and edge set \mathcal{E} . We assume the edges in \mathcal{E} are oriented, and denote by $s, t : \mathcal{E} \rightarrow \mathcal{V}$ the source and target vertex functions. For each edge $e \in \mathcal{E}$ let \bar{e} be the inverse of e , which is the same edge given the opposite orientation. Thus $s(\bar{e}) = t(e)$ and $t(\bar{e}) = s(e)$. We assume that \mathcal{E} is closed under the inverse operation. We also assume that $|\mathcal{E}|, |\mathcal{V}| < \infty$ where $|\cdot|$ indicates the cardinality.

Associate to each $v \in \mathcal{V}$ a point in \mathbb{R}^d , still denoted v (so that we now think of \mathcal{V} as a subset of the Euclidean space) and to each $e \in \mathcal{E}$ a smooth curve $\gamma_e : [0, l_e] \rightarrow \mathbb{R}^d$, parametrized by arclength, such that $\gamma_e(0) = s(e)$ and $\gamma_e(l_e) = t(e)$. Thus, l_e is the length of the curvilinear segment $E_e := \gamma_e([0, l_e])$. We assume that $\max_e l_e < \infty$ and write $l_e = |e| = |E_e|$. We also set $\gamma_{\bar{e}}(s) := \gamma_e(|e| - s)$.

The union $\Gamma := \bigcup_{e \in \mathcal{E}} E_e$ will be called a *metric graph*, denoted Γ . With slight notational abuse we also write Γ° for $\bigcup_{e \in \mathcal{E}} E_v^\circ$, where $E_v^\circ = \gamma_e((0, l_e))$. Thus, $\Gamma^\circ = \Gamma \setminus \mathcal{V}$. The word *metric* refers to the natural distance defined by minimizing a path between two points. This induced metric makes Γ into a separable metric space.

Each edge has a natural coordinate $y_e = \gamma_e^{-1} : E_e \rightarrow I_e$. By means of this coordinate we can identify functions on E_e with functions on $[0, l_e]$. Similarly, we can identify a function $f : \Gamma \rightarrow \mathbb{R}$ with a collection of functions on the various coordinate intervals $[0, l_e]$ by defining $f_e(s) = f(\gamma_e(s))$ for $s \in [0, l_e]$. Thus we have an obvious way of checking that f is continuous: each f_e must be continuous on $(0, l_e)$ in the ordinary sense, and the extensions to $[0, l_e]$ must agree at the vertices, in the sense that $f_{e_1}(l_{e_1}) = f_{e_2}(0)$ whenever $t(e_1) = s(e_2)$. The set of continuous functions on Γ is denoted $C(\Gamma)$.

Similarly, we can define the derivative of $f \in C(\Gamma)$ at a point $x = \gamma_e(s) \in E_v^\circ$ by $(f \circ \gamma_e)'(s)$, when this derivative exists in the ordinary sense. At a vertex v , we define the one-sided derivatives

$$(D_e f)(v) := \lim_{s \downarrow 0} \frac{f(\gamma_e(s)) - f(v)}{s}$$

when the limit exists. Thus $D_e f(v)$ is the directional derivative of f at v , pointing into e . Clearly this definition only makes sense for $e \in \mathcal{E}$ such that $s(e) = v$. Note that, in general, we do not require that the directional derivatives at v all agree.

We now define the fat graph U^ϵ as a union of certain ϵ -tubes U_e^ϵ (one for each $e \in \mathcal{E}$) together with ϵ -junctures J_v^ϵ (one for each $v \in \mathcal{V}$). Some care is required in formulating the definitions; however, Figure 4 should convey the right idea. The following conditions ensure

that the construction works properly:

1. If e, e' are any two edges such that $s(e) = s(e') = v$, then $\mathbf{T}_e(v) \neq \mathbf{T}_{e'}(v)$.
2. There exists a $r_0 > 0$ such that $\mathbf{T}'_e(s) = 0$ for $s \in [0, r_0]$ and all $e \in \mathcal{E}$.
3. The curves comprised by Γ do not intersect each other and have no self-intersection.
4. Each γ_e is C^3 .

Now fix an $\epsilon > 0$. We begin by defining the ϵ -tubes U_e^ϵ corresponding to the edges E_e in Γ . For each $e \in \mathcal{E}$, let there be given a *relative radius* $r_e > 0$; and then, for each $\epsilon > 0$ sufficiently small, let U_e^ϵ be a tubular neighborhood of E_e° with cross-sectional radius $r_e\epsilon$. According to [13], U_e^ϵ has the *nearest point property* with respect to E_e° , meaning each $x \in U_e^\epsilon$ has a unique point $\pi^\epsilon(x) \in E_e^\circ$ nearest to x , and the induced mapping $\pi^\epsilon : U_e^\epsilon \rightarrow E_e^\circ$ is a C^2 submersion. Furthermore, the distance function

$$x \mapsto d(x, E_e^\circ) := \inf\{y \in E_e^\circ : \|x - y\|\}$$

is C^3 near E_e° (because γ_e is C^3 —see [13]), so that the unit normal vector field, given by

$$\mathbf{n}^\epsilon(x) = \nabla d(x, E_e^\circ) / \|\nabla d(x, E_e^\circ)\|, \quad x \in \partial U_e^\epsilon,$$

is C^2 away from the ends of U_e^ϵ .

Now, the full U_e^ϵ 's may intersect near the vertices. For this reason, we use assumptions 2 and 3 from above to introduce constants $c_0 > 0$ and $\epsilon_0 > 0$ which depend only on Γ and have the following property: if each U_e^ϵ is shrunk by a length $c_0\epsilon$ at its ends, then $U_{e_1}^\epsilon \cap U_{e_2}^\epsilon = \emptyset$ whenever $e_1, e_2 \in \mathcal{E}$ are distinct and $\epsilon \leq \epsilon_0$. In summary, we have a family $\{U_e^\epsilon : e \in \mathcal{E}, \epsilon < \epsilon_0\}$ such that: (i) for fixed $\epsilon \leq \epsilon_0$ the U_e^ϵ 's are pairwise disjoint; (ii) $\bigcup_{e \in \mathcal{E}} U_e^\epsilon$ has the nearest point property with respect to Γ° , and the natural projection π^ϵ onto Γ° is C^2 ; (iii) $\bigcup_{e \in \mathcal{E}} U_e^\epsilon \downarrow \Gamma^\circ$ as $\epsilon \downarrow 0$.

Next, we define the juncture regions J_v^ϵ . For each $v \in \mathcal{V}$ let there be given a “template” region such that

$$J_v \cup \bigcup_{e:s(e)=v} U_e^{\epsilon_0}$$

is simply-connected and has a boundary smooth enough that the unit normal vector field is still C^2 away from the ends. In other words, J_v lines up smoothly with its incident ϵ_0 -tubes. It is clear that such a J_v exists. It is also clear that we can shrink or enlarge J_v so that $J_v \cap U_e^{\epsilon_0}$ is a cylindrical wafer of height $(r_0 - c_0)\epsilon_0 > 0$ and radius $r_e\epsilon_0$, for each $e \in \mathcal{E}$. Then J_v^ϵ is defined in an obvious way by scaling down homothetically:

$$J_v^\epsilon := \{x \in \mathbb{R}^d : v + \epsilon^{-1}(x - v) \in J_v\}.$$

Finally, with the ϵ -tubes and ϵ -junctures as above, we define the *fat graph* with fatness parameter ϵ and relative radii r_e as

$$U^\epsilon = \left[\bigcup_{v \in \mathcal{V}} J_v^\epsilon \right] \cup \left[\bigcup_{e \in \mathcal{E}} U_e^\epsilon \right].$$

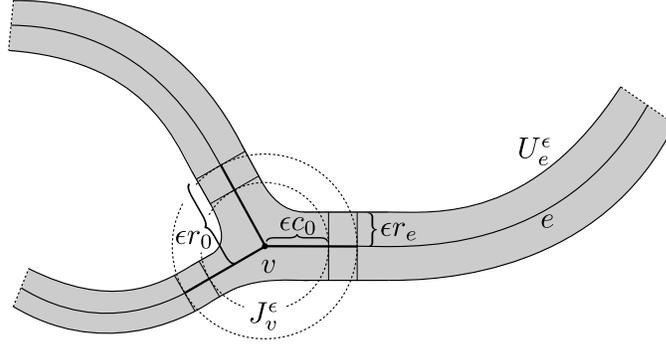


Figure 6: The ϵ -juncture J_v^ϵ at v in part of a fat graph domain U^ϵ with skeleton Γ . The r_e are the relative radii of the tube cross sections. Note that the part of the edge curve γ_e contained in J_v^ϵ is straight.

From the construction, the unit normal vector field on ∂U^ϵ is C^2 , and $U^\epsilon \downarrow \Gamma$ as $\epsilon \downarrow 0$. It is also clear that we can extend the projections π^ϵ to be defined inside the J_v^ϵ 's in such a way that $\pi^\epsilon : U^\epsilon \rightarrow \Gamma$ is continuous, and

$$\sup_{v \in \mathcal{V}} \sup_{x \in J_v^\epsilon} \|\pi^\epsilon(x) - v\| = O(\epsilon).$$

Furthermore, we have that

$$\sup_{x \in U^\epsilon} \|\pi^\epsilon(x) - x\| = O(\epsilon) \tag{5}$$

uniformly in $x \in U^\epsilon$.

3 Limit of diffusions from the fat graph to its graph skeleton

In this section we review some background material related to diffusions on fat-graph domains and their limits as the fat graphs shrink down to their underlying metric graphs. The main result quoted here comes from [1], which extends the earlier work [15], with modifications required for our needs.

Let Γ be a metric graph in \mathbb{R}^d , and U^ϵ a family of fat graphs with skeleton Γ , fatness parameter $\epsilon > 0$, and relative radii r_e ($e \in \mathcal{E}$) as defined in Section 2. Let $a = (a^{ij}(x))$ be a $d \times d$ matrix-valued function on \mathbb{R}^d and $b = (b^i(x))$ a vector field in \mathbb{R}^d . We assume that a is uniformly positive definite, and that a and b are both bounded and Lipschitz continuous in \mathbb{R}^d . Define the differential operator

$$L = \frac{1}{2} \sum_{i,j} a^{ij}(x) D_i D_j + \sum_i b^i(x) D_i,$$

where D_i is partial differentiation in x_i .

Writing $a(x) = \sigma(x)\sigma^t(x)$, with σ assumed positive-definite and Lipschitz continuous, consider the stochastic differential equation

$$X_t^\epsilon - X_0^\epsilon = \int_0^t \sigma(X_s^\epsilon) dW_s + \int_0^t b(X_s^\epsilon) ds + \int_0^t \mathbf{n}^\epsilon(X_s^\epsilon) d\ell_s^\epsilon, \quad (6)$$

in which W is a d -dimensional Brownian motion, \mathbf{n} is the inward pointing unit normal vector field on ∂U^ϵ and (ℓ_t^ϵ) is a continuous increasing process adapted to the filtration of X and increasing only on the set $\{t : X_t \in \partial U^\epsilon\}$. Since \mathbf{n}^ϵ is C^2 , the geometric conditions in [26] are clearly met. Therefore (6) admits a strong solution, in the sense of [18].

Let us describe the behavior of (X_t^ϵ) as $\epsilon \downarrow 0$. First, define an operator on $C(\Gamma)$ as follows. For each $e \in \mathcal{E}$, let $C_b^2(E_e^\circ)$ denote the space of functions on E_e° with two bounded and continuous derivatives; and then let L_e act on $f \in C_b^2(E_e^\circ)$ as

$$(L_e f)(x) = \frac{1}{2} \|\sigma^t(x) \mathbf{T}_e(x)\|^2 f_e''(s) + [\langle b(x), \mathbf{T}_e(x) \rangle + \langle a(x) \mathbf{T}_e'(x), \mathbf{T}_e(x) \rangle] f_e'(s),$$

where $x = \gamma_e(s)$, $\mathbf{T}_e'(x) = (\mathbf{T}_e \circ \gamma_e)'(s)$ and $\langle \cdot, \cdot \rangle$ is the ordinary Euclidean inner product. To “paste together” the L_e 's, we must specify what happens at the vertices. Thus, we define $\mathcal{D}(L_\Gamma)$ to contain those functions $f \in C(\Gamma)$ for which:

1. $f_e \in C_b^2(E_e^\circ)$ for each $e \in \mathcal{E}$;
2. for each $v \in \mathcal{V}$, and $e \in \mathcal{E}$ such that $v = s(e)$, the one-sided limits $\lim_{s \downarrow 0} (L_e f)(\gamma_e(s))$ exist and have a common value, denoted $(L f)(v)$;
3. for each $v \in \mathcal{V}$,

$$\sum_{e: s(e)=v} p_v(e) (D_e f)(v) = 0 \quad (7)$$

where the numbers $p_v(e)$ are defined by

$$p_v(e) := \frac{r_e^{d-1}}{\sum_{e': s(e')=v} r_{e'}^{d-1}}. \quad (8)$$

Then, for $f \in \mathcal{D}(L_\Gamma)$ as above, we define $L_\Gamma f$ by

$$(L_\Gamma)(x) = \begin{cases} (L_e f_e)(y_e(x)) & \text{if } x \in E_e^\circ \\ \lim_{y \rightarrow x} (L_e f)(y) & \text{if } x \in \mathcal{V}. \end{cases}$$

According to Theorem 3.1 in [15], there is a diffusion process (X_t) on Γ generated by $(L_\Gamma, \mathcal{D}(L_\Gamma))$. On the other hand, Theorem 4.2 in [1] says that (X_t^ϵ) converges in distribution to (X_t) as $\epsilon \downarrow 0$ if X_0^ϵ converges in distribution to a Γ -valued random variable. Since pathwise uniqueness holds for (6) under our assumptions, “in distribution” can be replaced by “almost sure” in the preceding sentence. In particular, this is true if the starting point X_0^ϵ is a point $x \in \Gamma$ for all $\epsilon > 0$.

Theorem 3. *Let U^ϵ be a fat graph with skeleton Γ . Assume that $X_0^\epsilon = x$ for all $\epsilon > 0$ and some $x \in \Gamma$. Then X^ϵ converges in distribution to X with initial value $X_0 = x$. If pathwise uniqueness holds in (6), then X^ϵ converges a.s. to X .*

Remark. The coefficients $p_v(e)$ appearing above have the following probabilistic significance: if τ_δ is the first exit time of X_t from a ball of radius δ at v , then $p_v(e) = \lim_{\delta \downarrow 0} \mathbb{P}_v[X(\tau_\delta) \in E_e]$.

4 Diffusions with killing

Let U^ϵ be a fat-graph domain with skeleton Γ . The terminology and assumptions of Sections 2 and 3 remain in force.

We introduce a function $r(x)$ which represents the *rate of killing* of a diffusion in U^ϵ or in Γ . This function is assumed to depend on a parameter $h > 0$ whose role will become clear later; roughly, r^h will “collapse” to a vertex condition when h goes to 0. But for the moment we suppress h in order to simplify the notation.

Thus, let $r : \mathbb{R}^d \rightarrow [0, \infty)$ be a non-negative measurable function, representing the chemical reaction rate. We are interested in processes obtained from X^ϵ on U^ϵ (resp. X on Γ) by killing using the rate function r . Loosely, killing with rate r means forming new processes Y^ϵ (resp. Y) which behave like X^ϵ (resp. X) until $\int_0^t r(X_s^\epsilon) ds$ (resp. $\int_0^t r(X_s) ds$) exceed an independent exponential random time; after this time, they are sent to a cemetery state Δ . In this situation, the Feynman-Kac formula says that Y^ϵ and Y have extended generators

$$L^r f = Lf - r(x)f \quad \text{and} \quad L_\Gamma^r f = L_\Gamma f - r(x)f,$$

respectively, where L and L_Γ are as defined in section 3 and the domains are the same. Furthermore, the semigroup of Y^ϵ acts on functions as

$$P_t^\epsilon f(x) = \mathbb{E}_x \left[\exp \left\{ - \int_0^t r(X_s^\epsilon) ds \right\} f(X_t^\epsilon) \right]$$

with a similar statement holding for Y . In particular, $P_t^\epsilon 1(x) = \mathbb{E}_x \left[\exp \left\{ - \int_0^t r(X_s^\epsilon) ds \right\} \right]$ is the probability that Y^ϵ is still in U^ϵ , i.e. still “alive” at time t . With this in mind, we define the *survival function* of the process at $x \in U^\epsilon$ as

$$\psi^\epsilon(x) := \mathbb{E}_x \left[\exp \left\{ - \int_0^{T_a^\epsilon} r(X_s^\epsilon) ds \right\} \right]. \quad (9)$$

Here, T_a^ϵ is a random time which can be thought of as the time that X^ϵ is absorbed at the reactor, as we now explain.

Let there be given a certain subset $\mathcal{V}_a = \{a_j\} \subset \mathcal{V}$ of degree 1 vertices in Γ to be regarded as the reactor exit. Write (with abuse of notation) ∂U_a^ϵ for the closure of the union of the corresponding juncture regions in U^ϵ , and ∂U_r^ϵ for the rest of the boundary of U^ϵ . We call ∂U_a^ϵ the *absorbing* part of the boundary and ∂U_r^ϵ the *reflecting* part. Then $\partial U_a^\epsilon \downarrow \mathcal{V}_a$ as $\epsilon \downarrow 0$. (See Figure 7.) Let T_a^ϵ be the first hitting time of X^ϵ to ∂U_a^ϵ , and T_a the first hitting time of X to \mathcal{V}_a . For now, we *assume* that T_a^ϵ and T_a are finite a.s., and that $T^\epsilon \rightarrow T$ a.s. Under these circumstances, we have the following:

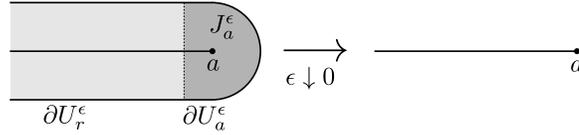


Figure 7: A portion of the absorbing part of the boundary of U^ϵ and its limit in Γ . The process X^ϵ in U^ϵ is killed when it reaches the dotted line separating the regions indicated in light and dark shading. The limiting process X on Γ is killed when it reaches a .

Proposition 4. *Suppose that T_a^ϵ and T are a.s. finite and that $T_a^\epsilon \rightarrow T_a$ a.s. If $x \in \Gamma$ then*

$$\psi^{\epsilon,h}(x) \rightarrow \mathbb{E}_x \left[\exp \left\{ - \int_0^{T_a} r^h(X_s) ds \right\} \right]$$

as $\epsilon \downarrow 0$, where T_a is the hitting time to \mathcal{V}_a of the limiting process X .

With some additional smoothness on r^h , this conclusion can also be recast as a boundary value problem, which will be useful for computations. The following conclusion is standard. See, for example, [3].

Corollary 5. *Suppose that u is a bounded and continuous function on $\overline{U^\epsilon}$ that solves the equation $Lu - r^h u = 0$ in U^ϵ , together with the boundary conditions*

$$\frac{\partial u}{\partial n} = 0 \text{ on } \partial U_r^\epsilon \text{ and } u = 1 \text{ on } \partial U_a^\epsilon.$$

Then $u = \psi^{\epsilon,h}$, with $\psi^{\epsilon,h}$ defined as in (9), and

$$\psi^{\epsilon,h}(x) \rightarrow \psi^h(x)$$

for every $x \in \Gamma$, where ψ^h is the solution to the corresponding ordinary differential equation on the graph Γ , namely: $L_\Gamma u - r^h u = 0$ with boundary condition $u = 1$ on \mathcal{V}_a .

5 Collapsing active zones towards vertices of Γ

In the previous sections we described a conservative diffusion $X = (X_t)$ on a metric graph Γ generated by an operator L_Γ acting on a domain characterized by the vertex condition (7). This X was obtained by collapsing the conservative diffusion X^ϵ on the fat graph U^ϵ down to Γ as $\epsilon \downarrow 0$. We also described a nonconservative process $Y^h = (Y_t^h)$ obtained by killing X using the rate function r^h . The killed process Y^h has generator $L_\Gamma - r^h$ acting on the same domain. The function r^h represents the rate of chemical activity on the active zones.

Now, we wish to collapse the active zones, i.e. the regions in Γ where r^h is positive, to a collection of vertices, as $h \downarrow 0$. We have in mind that all the chemical activity is concentrated on the active vertices as $h \downarrow 0$, while the killing rate is increased towards ∞ in such a way that the overall effect is the same in the limit.

For concreteness, we assume that the operator L_Γ acts as $\mathcal{D} \frac{d^2}{dy^2}$ on each edge E_e , where \mathcal{D} is the diffusion coefficient; also, that the active regions are balls $B(v, h\delta)$ centered at some of the vertices with radius $h\delta$, where $\delta > 0$ is a fixed number with the units of distance, and $h > 0$ is a dimensionless parameter. Thus, each $B(v, h\delta)$ is a star-shaped neighborhood of v consisting of v and a union of segments of edges of length $h\delta$ for each edge issuing from v . The killing rate function $r^h(x)$ will then be assumed to have the form

$$r^h(x) = \sum_{v \in \mathcal{V}} \frac{k_v}{h} \mathbb{1}_{B(v, h\delta)}(x) \quad (10)$$

where k_v is either k or 0 depending on whether that vertex is to be considered active or not. It is known (as explained in Remark 2.5 of [14]) that, as $h \downarrow 0$,

$$\mathbb{E}_x \left[\exp \left\{ - \int_0^{T_a} r^h(X_s) ds \right\} \right] \rightarrow \mathbb{E}_x \left[\exp \left\{ - \sum_{v \in \mathcal{V}} \kappa_v \ell_v(T_a) \right\} \right],$$

where $\kappa_v = k_v \delta / \mathcal{D}$ and $\ell_v(T_a)$ is the semimartingale local time (as defined in [14]) at v evaluated at the hitting time T_a .

Write \mathcal{C} for the set of active vertices in \mathcal{V} , and let $\ell_{\mathcal{C}}(t)$ denote the local time accumulated at \mathcal{C} up to time t . In other words, $\ell_{\mathcal{C}}(t)$ is the sum of the $\ell_v(t)$ for which k_v is not zero. Then the limit in the above expression becomes $\mathbb{E}_x [\exp \{-\kappa \ell_{\mathcal{C}}(T_a)\}]$ where $\kappa = k\delta / \mathcal{D}$. Also, the killed processes Y^h converge to a process Y which is obtained from X as follows: run X until $\kappa \ell_{\mathcal{C}}(t)$ exceeds an independent rate 1 exponential; after this time, send X to the cemetery state Δ . In other words, kill X using the local time $\ell_{\mathcal{C}}(t)$ rather than the integral $\int_0^t r^h(X_s) ds$. Then the new process Y has a generator which is defined in the same way as L_Γ for functions on Γ° . However, the domain of Y 's generator is characterized by a different vertex condition, as explained in the following:

Proposition 6. *Let $r^{\epsilon, h}(x)$ be positive bounded functions on U^ϵ with the property that*

$$\lim_{\epsilon \downarrow 0} r^{\epsilon, h}(x) = r^h(x)$$

for all $x \in \Gamma$, where $r^h(x)$ is defined at (10). Let $\psi^{\epsilon, h}(x)$ and $\psi(x)$ be the survival functions associated with $Y^{\epsilon, h}$ and Y , respectively; that is,

$$\begin{aligned} \psi^{\epsilon, h}(x) &= \mathbb{E}_x \left[\exp \left\{ -\kappa \int_0^{T_a^\epsilon} r^{h, \epsilon}(X_s^\epsilon) ds \right\} \right], \\ \psi(x) &= \mathbb{E}_x [\exp \{-\kappa \ell_{\mathcal{C}}(T_a)\}]. \end{aligned}$$

If the conditions of Proposition 4 are met, then

$$\psi(x) = \lim_{h \rightarrow 0} \lim_{\epsilon \rightarrow 0} \psi^{\epsilon, h}(x)$$

where $\kappa = k\delta / \mathcal{D}$, as defined above. Furthermore, the generator of the limiting process has a domain characterized by the vertex condition

$$\sum_{e: s(e)=v} p_v(e) (D_e u)(v) = \kappa_v u(v) \quad (11)$$

where $\kappa_v = \kappa$ if $v \in \mathcal{C}$ and $\kappa_v = 0$ if $v \in \mathcal{V} \setminus \mathcal{C}$.

Sketch of proof. The limit statement has already been discussed. As for the vertex condition, we will show that a function in the domain of Y 's generator must satisfy (11). Thus, let $(\hat{L}, D(\hat{L}))$ be the generator of Y . Fix an active vertex $v \in \mathcal{C}$. Let $U_\delta = B(v, \delta)$ and $\hat{\tau}_\delta$ the first exit time of Y_t from U_δ . Also, write $\hat{\mathbb{E}}_v$ for the law of Y_t started at v . If $F \in D(\hat{L})$ then Dynkin's formula (see [25] Ch. 3) reads:

$$(\hat{L}F)(v) = \lim_{\delta \downarrow 0} \frac{\hat{\mathbb{E}}_v[F(Y(\hat{\tau}_\delta))] - F(v)}{\hat{\mathbb{E}}_v[\hat{\tau}_\delta]}$$

Let \mathbf{e} be an independent rate 1 exponential (we can always enlarge the probability space to accommodate such a variable) and then $\hat{\zeta} = \inf\{t > 0 : \kappa \ell_{\mathcal{C}}(t) > \mathbf{e}\}$. Thus, $\hat{\zeta}$ is the time that Y_t jumps from Γ to the cemetery state Δ . Evidently $\hat{\tau}_v = \tau_\delta \wedge \hat{\zeta}$ where τ_δ is the first exit time of X_t from U_δ . In the denominator, then, we have

$$\hat{\mathbb{E}}_v[\hat{\tau}_v] \sim \mathbb{E}_v[\tau_\delta] = \frac{\delta^2}{2\mathcal{D}}$$

as $\delta \downarrow 0$. On the other hand, Y_t leaves U_δ either through a point (δ, e) (using local coordinates) if $\tau_\delta < \hat{\zeta}$ or by a jump to Δ if $\hat{\zeta} \leq \tau_\delta$. Since $F(\Delta) = 0$ in the latter case, we have in the numerator, in view of the Remark under Theorem 3,

$$\begin{aligned} \hat{\mathbb{E}}_v[F(Y(\hat{\tau}_\delta))] - F(v) &= \sum_e F_e(\delta) \mathbb{P}_v[\tau_\delta < \hat{\zeta}] - F(v) \\ &= \sum_e F_e(\delta) p_v(e) \mathbb{P}_v[\tau_\delta < \hat{\zeta}] - F(v) + o(\delta) \end{aligned}$$

Now $(\tau_\delta < \hat{\zeta}) = (\kappa \ell_{\mathcal{C}}(\tau_\delta) \leq \mathbf{e}) = (\kappa \ell_{\mathcal{C}}(\tau_\delta) \leq \mathbf{e})$ \mathbb{P}_v -a.s., because starting from v , only the local time at v can contribute to $\ell_{\mathcal{C}}(t)$ before τ_δ . Also, $\ell_v(\tau_\delta)$ has an exponential distribution under \mathbb{P}_v , as explained below; we can compute its \mathbb{E}_v -mean as $\mathbb{E}_v[\tau_\delta] = \delta$ using the methods in Section 7. Therefore $\mathbb{P}_v[\kappa \ell_v(\tau_\delta) \leq \mathbf{e}]$ is the probability that a mean $\kappa\delta$ exponential is less than an independent mean 1 exponential; this is easily found to be $\frac{1}{1+\kappa\delta}$. Therefore the numerator equals

$$\begin{aligned} \frac{1}{1+\kappa\delta} \sum_e F_e(\delta) p_v(e) - F(v) + o(\delta) &= \frac{1}{1+\kappa\delta} \sum_e p_v(e) [F_e(\delta) - F(v) - \kappa\delta F(v)] \\ &= \frac{1}{1+\kappa\delta} \sum_e p_v(e) [D_e F(v) - \kappa F(v)] \delta + o(\delta) \end{aligned}$$

Existence and finiteness of the limit in Dynkin's formula therefore requires that $\sum_e (D_e F)(v) - \kappa F(v) = 0$ if $F \in D(\hat{L})$. Similar reasoning away from the vertex shows that \hat{L} has to act as L there. For the rest of the details see [20]. \square

Remark. The upshot of these considerations is that, in the limit as $h \downarrow 0$ and then $\epsilon \downarrow 0$, we obtain an expression $\mathbb{E}_x[\exp\{-\kappa \ell_{\mathcal{C}}(T_a)\}]$ for the survival probability. Therefore the problem of finding explicit formulas for reaction probabilities reduces to the problem of evaluating \mathbb{E}_x -moments of $\ell_{\mathcal{C}}(T_a)$. There is a method for dealing with this issue in considerable generality, called Kac's moment formula, which we explain in the next section.

6 Explicit formulas for reaction probability

We now focus on the dependence on κ of the conversion probability $\alpha_\kappa(x) = 1 - \psi_\kappa(x)$ for the reaction-diffusion process on a metric graph Γ , where the active sites consist of a set of vertices $\mathcal{C} \subset \mathcal{V}$. In this case, it is possible to obtain reasonably explicit formulas for $\alpha_\kappa(x)$ by simple arguments using the strong Markov property. First we consider the case where \mathcal{C} is a single vertex:

Proposition 7. *Suppose $\mathcal{C} = \{c\}$ and $T_a = \inf\{t > 0 : X_t \in \mathcal{V}_a\}$. Set $\lambda := \mathbb{E}_c[\ell_c(T_a)] =$ the expected local time accumulated at c up to time T , starting from c . Then*

$$\alpha_\kappa(x) = \alpha_\infty(x) \frac{\lambda\kappa}{1 + \lambda\kappa}. \quad (12)$$

Proof. Write $T_c := \inf\{t : X_t = c\}$, the first time that X_t hits the active vertex. Since $\ell_c(T_a) = 0$ on the event $(T_c \geq T_a)$, we have

$$\begin{aligned} \alpha_\kappa(x) &= \mathbb{E}_x \left[(1 - \exp\{-\kappa\ell_c(T_a)\}) \mathbb{1}_{(T_c < T_a)} \right] \\ &= \alpha_\infty(x) - \mathbb{E}_x \left[\exp\{-\kappa\ell_c(T_a)\} \mathbb{1}_{(T_c < T_a)} \right] \end{aligned} \quad (13)$$

where $\alpha_\infty(x) = \mathbb{E}_x[\mathbb{1}_{(T_c < T_a)}]$ is the probability that X_t hits c before \mathcal{V}_a . Also, since $\ell_c(t)$ does not start increasing until T_c , we have that $\ell_c(T_a) = \ell_c(T_a) \circ \theta_{T_c}$ on $(T_c < T_a)$. Using the strong Markov property, and then the fact that $X(T_c) = c$ a.s., we find that the right-most term in the second line of (13) equals:

$$\begin{aligned} \mathbb{E}_x \left[\exp\{-\kappa\ell_c(T_a) \circ \theta_{T_c}\} \mathbb{1}_{(T_c < T_a)} \right] &= \mathbb{E}_x \left[\mathbb{E}_{X(T_c)}[\exp\{-\kappa\ell_c(T_a)\}] \mathbb{1}_{(T_c < T_a)} \right] \\ &= \mathbb{E}_c[\exp\{-\kappa\ell_c(T_a)\}] \mathbb{E}_x[\mathbb{1}_{(T_c < T_a)}] \end{aligned}$$

We arrive at

$$\alpha_\kappa(x) = \alpha_\infty(x) (1 - \mathbb{E}_c[\exp\{-\kappa\ell_c(T_a)\}]). \quad (14)$$

Now, we use the fact that $\ell_c(T_a)$ must have an exponential distribution under \mathbb{P}_c . This follows from a simple argument which can be found on p. 106 of [23]. Writing $\lambda := \mathbb{E}_c[\ell_c(T_a)]$ for the mean, and then explicitly computing the Laplace transform, we obtain the result

$$\mathbb{E}_c[\exp\{-\kappa\ell_c(T_a)\}] = \frac{1}{1 + \lambda\kappa}.$$

Inserting this last expression into (14) establishes (12). \square

When \mathcal{C} consists of more than one point, the survival function takes the form

$$\psi_\kappa(x) = \mathbb{E}_x \left[\exp \left\{ -\kappa \sum_{c \in \mathcal{C}} \ell_c(T_a) \right\} \right]$$

where $\ell_c(T_a)$ is the local time at the vertex c up to the exit time T_a . In this case, it is still possible to obtain an explicit formula for $\psi_\kappa(x)$ (hence $\alpha_\kappa(x)$) because Kac's moment formula can be used to evaluate the expectation appearing in $\psi_\kappa(x)$.

Specifically, we can use the following corollary of Kac's moment formula, which can be found in Section 6 of [12]:

Proposition 8. Write $\mathcal{C} = \{c_j\}_{j=1}^C$ with $C = \#\mathcal{C}$ and define the Green's function by

$$G_{ij} := g(c_i, c_j) = \mathbb{E}_{c_i}[\ell_{c_j}(T_a)].$$

Let $\kappa_i = \kappa(c_i)$ be a positive function on \mathcal{C} . Then the function

$$\psi_\kappa(c_i) := \mathbb{E}_{c_i} \left[\exp \left\{ - \sum_{j=1}^C \kappa_j \ell_{c_j}(T_a) \right\} \right]$$

is the unique solution to the system of equations

$$\psi(c_i) = 1 - \sum_{j=1}^C G_{ij} \kappa_j \psi(c_j).$$

In other words, if M_κ is the diagonal matrix with the entries of κ_j along the main diagonal, then

$$\psi_\kappa = (I + GM_\kappa)^{-1} \mathbb{1}_{\mathcal{C}}. \quad (15)$$

Remark. The expression (15) for the survival function on \mathcal{C} can be recast as a formula involving determinants by using Cramer's rule. To wit, let $G^{(j)}$ denote the matrix obtained from G by subtracting row j from every row. (So, $G^{(j)}$ has a row of 0's in the j -th row.) Then

$$\psi_\kappa(c_j) = \frac{\det(I + G^{(j)} M_\kappa)}{\det(I + GM_\kappa)}. \quad (16)$$

See [23] Ch. 2 for additional details about (16).

Now we can repeat the same argument that was given in Proposition 7, replacing the single point c with the set \mathcal{C} , so that T_c becomes $T_{\mathcal{C}} = \inf\{t > 0 : X_t \in \mathcal{C}\}$. Then (13) takes the form

$$\alpha_\kappa(x) = \alpha_\infty(x) - \mathbb{E}_x \left[\exp \{ -\kappa \ell_{\mathcal{C}}(T_a) \} \circ \theta_{T_{\mathcal{C}}} \mathbb{1}_{(T_{\mathcal{C}} < T_a)} \right]$$

where we abbreviate $\sum_{j=1}^C \ell_{c_j}(T_a)$ as $\ell_{\mathcal{C}}(T_a)$. To deal with the expectation in the last display, split the event $(T_{\mathcal{C}} < T_a)$ as $\bigcup_{j=1}^C (X(T_{\mathcal{C}}) = c_j, T_{\mathcal{C}} < T_a)$, and then write

$$p_j(x) = \mathbb{P}_x[X(T_{\mathcal{C}}) = c_j | T_{\mathcal{C}} < T_a].$$

Thus, $p_j(x)$ is the probability of starting from x and first hitting \mathcal{C} at c_j , conditional on hitting \mathcal{C} at all. We get

$$\begin{aligned} \mathbb{E}_x \left[\exp \{ -\kappa \ell_{\mathcal{C}}(T_a) \} \circ \theta_{T_{\mathcal{C}}} \mathbb{1}_{(T_{\mathcal{C}} < T_a)} \right] &= \sum_{j=1}^C \mathbb{P}_x[X(T_{\mathcal{C}}) = c_j, T_{\mathcal{C}} < T_a] \mathbb{E}_{c_j} \left[\exp \{ -\kappa \ell_{\mathcal{C}}(T_a) \} \right] \\ &= \sum_{j=1}^C p_j(x) \mathbb{P}_x[T_{\mathcal{C}} < T_a] \mathbb{E}_{c_j} \left[\exp \{ -\kappa \ell_{\mathcal{C}}(T_a) \} \right] \end{aligned}$$

Since $\mathbb{P}_x[T_{\mathcal{C}} < T_a] = \alpha_\infty(x)$, we can apply (16) with $\kappa(c_j)$ all being the same constant κ to express this last equation in the simple form

$$\alpha_\kappa(x) = \alpha_\infty(x) \left[1 - \sum_{j=1}^C p_j(x) \frac{\det(I + \kappa G^{(j)})}{\det(I + \kappa G)} \right]. \quad (17)$$

In the numerator, the determinant is a polynomial with degree $\leq C - 1$, because κ appears in only $C - 1$ rows of the matrix. On the other hand the denominator is a polynomial with degree $\leq C$. Furthermore the coefficients depend only on the G_{ij} , which in turn depend only on the geometric properties of Γ . This explains the claim made in Theorem 2.

7 Remark concerning the examples

In this section we present two slightly different approaches to computing the reaction probabilities. In both subsections, we let $X = (X_t)$ be a diffusion process on Γ as described in section 2. For simplicity, we'll assume that X is a Brownian motion with coefficient \mathcal{D} , so that the operator L_Γ acts as $L_\Gamma f(x) = \mathcal{D} \frac{d}{dx^2} f_e(x)$ for $x \in E_e^\circ$. This X is a conservative diffusion process (i.e. without killing) which corresponds to the limit of a conservative diffusion process on U^ϵ as $\epsilon \downarrow 0$.

7.1 First method

Previously, we explained how Kac's moment formula can be used to express the reaction probabilities in terms of certain polynomials involving the coefficients $G_{ij} = \mathbb{E}_{c_i}[\ell_{c_j}(T_a)]$. What remains, then, is to compute the G_{ij} 's from the graph and diffusion coefficients. To this end we apply the graph stochastic calculus from [14].

Recall that $\ell_v(t)$ is a process which is adapted to the filtration of X , continuous, increasing, and increases only on $\{t : X_t \in v\}$. Any multiple of a $\ell_v(t)$ retains these properties; for concreteness, we specify $\ell_v(t)$ as $1/\mathcal{D}$ times the occupation density at v :

$$\ell_v(t) = \frac{1}{\mathcal{D}} \lim_{h \downarrow 0} \frac{1}{h} \int_0^t \mathbb{1}_{B(v,h)}(X_s) ds$$

where $B(v, h)$ is a ball around v of radius h .

A version of the Ito-Tanaka formula holds for these local times. To state it, let $C_b^2(\Gamma)$ be the set of $F \in C(\Gamma)$ with two continuous derivatives in Γ° . (The derivatives do not necessarily extend to be continuous at the vertices.) Then [14] gives the following:

Theorem 9. *Let F be a function in $C_b^2(\Gamma)$. Define, for each $v \in \mathcal{V}$,*

$$\rho_v(F) = \sum_{e \in \mathcal{E}: s(e)=v} p_v(e) (D_e F)(v).$$

Then

$$F(X_t) - F(X_0) = M_t + \int_0^t (L_\Gamma F)(X_s) ds + \sum_{v \in \mathcal{V}} \rho_v(F) \ell_v(t)$$

where M_t is a continuous local martingale.

Ito's formula is all we need to find the G_{ij} . Namely, to find $\mathbb{E}_{c_i}[\ell_{c_j}(T_a)]$, we must find a function $F \in C_b^2(\Gamma)$ for which (i) $L_\Gamma F = 0$ on Γ° , (ii) $F(v) = 0$ for $v \in \mathcal{V}_a$, and (iii) $\rho_v(F) = 0$ except for $v = c_j$.

In the present case, (i) means that F is affine on each edge, so that $F_e(y) = a_e y + b_e$ for certain constants a_e and b_e and $0 \leq y \leq |e|$, where we abbreviate $|E_e| = |e|$ for the length of the segment E_e . Choosing an orientation arbitrarily for each e , this gives a total of $2E$ constants, with $E = \#\mathcal{E}$, which must be determined compatibly with (i)-(iii). This reduces the problem to a discrete one on the underlying combinatorial graph.

This method is best illustrated by working a few examples. In the examples, when it is not necessary to give names to the edges, we write $[v_1, v_2]$ for the edge with $s(e) = v_1$ and $t(e) = v_2$.

Example 1. Consider the graph shown in the upper right of Figure 5. Write c for the active vertex in the middle, a for the absorbing vertex at the far end, and v_1, \dots, v_n for the remaining inert vertices. For simplicity, we assume that the $p_c([c, v_j])$'s are all equal to $\frac{1}{n}$, i.e. that the relative radii in U^ϵ were all equal. Starting from any v_j , the probability of hitting c before a is 1. So the conversion will have the form

$$\alpha_\kappa(v_j) = \frac{\lambda\kappa}{1 + \lambda\kappa}$$

where $\lambda = \mathbb{E}_c[\ell_c(T_a)]$. Orient the various edges so that c is the origin. Then we seek a function F which is linear on each segment and continuous on Γ . The condition $\rho_{v_j}(F) = 0$ forces F to be constant on the $[c, v_j]$'s, and we can choose this constant to be l , the length of $[c, a]$. Then $F(a) = 0$ implies that F is linear with slope -1 on $[c, a]$. Thus, $\rho_c(F) = \frac{-1}{n}$. Taking expectations in Ito's formula,

$$0 - l = 0 + \frac{-1}{n} \cdot \lambda \quad \Rightarrow \quad \lambda = nl.$$

From this we obtain the formula given in item 2 in the list of examples after Theorem 2:

$$\alpha_\kappa(v_j) = \frac{nl\kappa}{1 + nl\kappa}.$$

Example 2. In a similar spirit, consider the second figure in the left column of Figure 5. Let v be the inactive vertex at the left, and c_1, \dots, c_m the active vertices, and a the absorbing vertex at the right. Starting from v , X hits \mathcal{C} with probability 1, and with probability 1 this first hit occurs at c_1 . Thus $p_1(v) = 1$ and $p_j(v) = 0$ for the other c_j and formula (17) simplifies to

$$\alpha_\kappa(v) = 1 - \frac{\det(I + \kappa G^{(1)})}{\det(I + \kappa G)}.$$

To simplify, we again assume that $p_{[c_j, c_k]}(e) = 1/2$ for adjacent c_j, c_k and $p_v([v, c_1]) = 1$. Now, to compute G_{ij} , first write l_j for the length of the segment to the right of c_j . Then set $L_j = \sum_{i=j}^m l_i$. Thus, L_k is the sum of the lengths of all the segments to the right of c_k . Regarding Γ as a single straight line, take F to be the function which is constantly L_j on $[0, c_j]$ and then decreases linearly with slope -1 on $[c_j, a]$, so that $F(a) = 0$ and $\rho_{c_j}(F) = -1/2$. Using this F in Ito's formula shows that: if $c_i \leq c_j$ then $G_{ij} = 2L_j$, and if $c_i > c_j$ then $G_{ij} = 2L_i$. In particular, the matrix $G^{(1)}$ must be strictly triangular, so that the determinant in the numerator of $\alpha_\kappa(v)$ is 1. Therefore we can write

$$\alpha_\kappa(v) = \frac{\det(I + \kappa G) - 1}{\det(I + \kappa G)}.$$

An induction argument shows that this formula is equivalent to the one given in the Introduction.

Example 3. Consider the figure in the bottom right of Figure 5. Write v for the inert vertex at the far left, a for the absorbing vertex at the far right, and c_1, c_2 for the upper and lower active vertices. Assume $p_c(e) = 1/3$ for all e incident to c . Choose a function F which is constantly l on $[a, c_2]$ and $[c_1, c_2]$, and which decreases from l to 0 on $[c_2, a]$. Then $\rho_v(F) = \rho_{c_1}(F) = 0$ and $\rho_{c_2}(F) = -1/3$. Using Ito's formula with this F , one can check that $G_{12} = G_{22} = 3l$.

Next, choose a different F with $F(c_1) = l_1 + l$, $F(a) = F(c_2) = l$ and $F(v) = 0$. Then $\rho_{c_1}(F) = -1$ and $\rho_v(F) = \rho_{c_2}(F) = 0$. Applying Ito's formula with this F shows that $G_{11} = l_1 + l$ and $G_{21} = l$. We find that:

$$G = \begin{bmatrix} l + l_1 & 3l \\ l & 3l \end{bmatrix}$$

The determinants in (17) simplify, and one can easily check that

$$\alpha_\kappa(v) = \frac{4l\kappa + 3ll_1\kappa^2}{1 + (4l + l_1)\kappa + 3ll_1\kappa^2}.$$

The remaining graphs in Figure 5 can be handled in a similar way, by making appropriate choices of F to determine the coefficients G_{ij} .

7.2 Second method

A different approach is to work instead with the process $Y = (Y_t)$ obtained from X by sending it to Δ at ζ , the first time that $\kappa\ell_c(t)$ exceeds an independent rate 1 exponential. This new process Y is a non-conservative diffusion whose generator still acts as L_Γ , but whose domain now consists of functions $F \in C^2(\Gamma)$ satisfying these vertex conditions:

$$\begin{aligned} \sum_{e:s(e)=c} p_v(e)(D_e F)(c) &= \kappa F(c) & c \in \mathcal{C} \\ \sum_{e:s(e)=v} p_v(e)(D_e F)(v) &= 0 & v \in \mathcal{V} \setminus [\mathcal{C} \cup \mathcal{V}_a] \end{aligned} \tag{18}$$

It follows that if $F \in C_b^2(\Gamma)$ satisfies $L_\Gamma F(x) = 0$ in Γ° , $F(a) = 1$ for $a \in \mathcal{V}_a$, together with the vertex conditions (18), then $F(Y_t)$ is a martingale. By optional stopping,

$$F(v) = \mathbb{E}_v[F(Y(T_a))] = \mathbb{P}_v[T_a < \zeta]$$

which means that $F(v) = \psi_\kappa(v)$, i.e. the survival function evaluated at v .

Again we assume that $p_v(e) = 1/\deg(v)$ whenever $v = s(e)$; equivalently, that all r_e 's are equal. Since F must be affine on each edge, it is determined by its values on \mathcal{V} , and its derivative DF can be regarded as a function on \mathcal{E} :

$$DF(e) = \frac{F(t(e)) - F(s(e))}{|e|}.$$

Therefore we can couch the problem of determining F as a kind of discrete boundary problem on the combinatorial graph \mathcal{G} rather than on the metric graph Γ . For this purpose, regard the vertices in \mathcal{V}_a as the *boundary* of \mathcal{G} , and the remaining vertices as the *interior* of \mathcal{G} . Then F is determined by the equations

$$\sum_{e:s(e)=v} |e|^{-1} F(r(e)) = \left(\deg(v)\kappa_v + \sum_{e:s(e)=v} |e|^{-1} \right) F(v) \quad (19)$$

for interior vertices and $f(v) = 1$ for exit vertices, $v \in \mathcal{V}_a$. Reaction probability for the examples given in the introduction can be obtained by solving the above system of linear equations to obtain ψ_κ and then setting $\alpha_\kappa = 1 - \psi_\kappa$.

Remark. Equation (19) can be regarded as a kind of discrete Feynman-Kac equation involving the discrete Laplacian on \mathcal{G} . See [8] for more information.

8 Conclusions

We investigate a class of reaction-diffusion systems involving the first order reaction $A \rightarrow B$; we assume that this reaction can occur at well-localized catalytic (active) sites placed inside a chemical reactor amid an inert diffusion medium. More specifically, we model mathematically the so-called TAP (Temporal Analysis of Products) systems, a type of pulse-response experiment being used primarily in heterogeneous catalysis involving gases and complex solid materials.

In addition to giving a stochastic processes foundation for the analysis of TAP systems, we obtain a 3D to 1D reduction that allows us to gain information about 3-dimensional (or 2-dimensional) reactor shapes in terms of 1-dimensional network models, which are much easier to solve and analyze. Our main focus is on the determination of *conversion*, which we define as the molar fraction of the product gas B in the total gas outflow from the TAP reactor. We wish in particular to obtain the precise dependence of conversion on the reaction rate constant k . Conversion is naturally interpreted microscopically as the probability that a molecule of gas of species A will have reacted and given rise to a molecule of species B by the time it exits the reactor, under the natural assumption that molecular motion is described by mathematical Brownian motion. The main results and conclusions are as follows.

- **Direct method for obtaining conversion.** Conversion as a function of the point of gas injection is obtained directly by solving a boundary value problem for the Feynman-Kac operator with mixed boundary conditions. This is the content of Theorem 1. We solve this boundary value problem numerically in two representative examples to illustrate the graph-approximation method for fat-graph domains.
- **Reduction from 3D to 1D.** The core result is the 3D to 1D reduction theorem (Theorem 2). When the domain of diffusion (the reactor) corresponds to a fat-graph (defined in section 2), which roughly corresponds to a system of tubes whose junctions may be catalytically active, we obtain approximate explicit formulas for conversion as functions

of the reaction rate constant k . This is in essence the meaning of the limit in Theorem 2. These approximate functions are the exact solutions of the same problem for the limit (skeleton) graphs associated to a given fat-graph domain. The 1D conversion problem is much easier to solve.

- **Explicit formulas for conversion.** We show how explicit formulas for conversion on graphs are easily obtained by solving a system of linear equations that exactly corresponds to a Feynman-Kac difference equation. This is equation 19.
- **Optimizing catalyst configuration.** The graph examples reveal a few notable properties of the conversion function. A particularly striking property comes from an analysis of graph (ii) in figure 5, which shows that the configuration of active sites maximizing conversion depends strongly on the rate constant k : for small values of k the optimal arrangement of catalyst sites is obtained by bunching them together near the point of gas injection whereas for large values of k the optimal configuration is obtained by arranging the sites in evenly spaced intervals. This point is further studied in [28]. The problem of optimizing catalyst arrangement for a given amount of metal catalyst is a practical problem for which our methods are especially well-suited. We plan to investigate this point in future work for typical spatial structures known in catalytic chemistry.

References

- [1] Sergio Albeverio and Seiichiro Kusuoka. Diffusion processes in thin tubes and their limits on graphs. *Ann. Probab.*, 40(5):2131–2167, 2012.
- [2] R. Aris. *The mathematical theory of diffusion and reaction in permeable catalysis: the theory of the steady state*. Oxford University Press (1975).
- [3] Richard F. Bass. *Diffusions and elliptic operators*. Probability and its Applications (New York). Springer-Verlag, New York, 1998.
- [4] Richard F. Bass and Krzysztof Burdzy. Pathwise uniqueness for reflecting Brownian motion in certain planar Lipschitz domains. *Electron. Comm. Probab.*, 11:178–181 (electronic), 2006.
- [5] Richard F. Bass and Krzysztof Burdzy. On pathwise uniqueness for reflecting Brownian motion in $C^{1+\gamma}$ domains. *Ann. Probab.*, 36(6):2311–2331, 2008.
- [6] Richard F. Bass and Pei Hsu. Some potential theory for reflecting Brownian motion in Hölder and Lipschitz domains. *Ann. Probab.*, 19(2):486–508, 1991.
- [7] M.P. Bendsoe, O. Sigmund. *Topological optimization, methods and applications*. 2nd Edition Heidelberg, Springer (2004) Berlin, Germany.
- [8] Gregory Berkolaiko and Peter Kuchment. *Introduction to quantum graphs*, volume 186 of *Mathematical Surveys and Monographs*. American Mathematical Society, Providence, RI, 2013.

- [9] Zhen Qing Chen. On reflecting diffusion processes and Skorokhod decompositions. *Probab. Theory Related Fields*, 94(3):281–315, 1993.
- [10] R. Feres, A. Cloninger, G.S. Yablonsky, and J.T. Gleaves. A general formula for reactant conversion over a single catalyst particle in tap pulse experiments. *Chemical Engineering Science*, 64(21):4319–4460, 2009.
- [11] R. Feres, G.S. Yablonsky, A. Mueller, A. Baernstein, X. Zheng, and J.T. Gleaves. Probabilistic analysis of transport-reaction processes over catalytic particles: Theory and experimental testing. *Chemical Engineering Science*, 64(3):568 – 581, 2009.
- [12] P. J. Fitzsimmons and Jim Pitman. Kac’s moment formula and the Feynman-Kac formula for additive functionals of a Markov process. *Stochastic Process. Appl.*, 79(1):117–134, 1999.
- [13] Robert L. Foote. Regularity of the distance function. *Proc. Amer. Math. Soc.*, 92(1):153–155, 1984.
- [14] Mark Freidlin and Shuenn-Jyi Sheu. Diffusion processes on graphs: stochastic differential equations, large deviation principle. *Probab. Theory Related Fields*, 116(2):181–220, 2000.
- [15] Mark I. Freidlin and Alexander D. Wentzell. Diffusion processes on graphs and the averaging principle. *Ann. Probab.*, 21(4):2215–2245, 1993.
- [16] John T. Gleaves, J.R. Ebner, T.C. Kuechler. *Temporal analysis of products (TAP)—a unique catalyst evaluation system with millisecond time resolution*. Catal. Rev. Sci. Eng. 30 (1988) 49-116.
- [17] John T. Gleaves, Gregory Yablonsky, Xiaolin Zheng, Rebecca Fushimi, and Patrick L. Mills. Temporal analysis of products (TAP) – recent advances in technology for kinetic analysis of multi-component catalysts. *Journal of Molecular Catalysis A: Chemical*, 315(2):108 – 134, 2010. In memory of M.I. Temkin.
- [18] Nobuyuki Ikeda and Shinzo Watanabe. *Stochastic differential equations and diffusion processes*, volume 24 of *North-Holland Mathematical Library*. North-Holland Publishing Co., Amsterdam; Kodansha, Ltd., Tokyo, second edition, 1989.
- [19] J. Karger and D.M. Ruthven. *Diffusion in zeolites and other microporous solids*. John Wiley, New York, USA (1992), 605 pp.
- [20] Vadim Kostykin, Jürgen Potthoff, and Robert Schrader. Brownian motions on metric graphs. *J. Math. Phys.*, 53(9):095206, 36, 2012.
- [21] P.-L. Lions and A.-S. Sznitman. Stochastic differential equations with reflecting boundary conditions. *Comm. Pure Appl. Math.*, 37(4):511–537, 1984.
- [22] G.B. Marin, G. Yablonsky. *Kinetics of chemical reactions: decoding complexity*. Wiley-VCH, Weinheim (2011).

- [23] Michael B. Marcus and Jay Rosen. *Markov processes, Gaussian processes, and local times*, volume 100 of *Cambridge Studies in Advanced Mathematics*. Cambridge University Press, Cambridge, 2006.
- [24] E.B. Nauman. *Chemical reactor design, optimization, and scale-up*. 2nd Edition Wiley (2008) 656 pp.
- [25] L. C. G. Rogers and David Williams. *Diffusions, Markov processes, and martingales. Vol. 1: Foundations*. Cambridge Mathematical Library. Cambridge University Press, Cambridge, 2000. Reprint of the second (1994) edition.
- [26] Yasumasa Saisho. Stochastic differential equations for multidimensional domain with reflecting boundary. *Probab. Theory Related Fields*, 74(3):455–477, 1987.
- [27] P. Trogadas, M.M. Nigra, and M.-O. Coppens. *Nature-inspired optimization of hierarchical porous media for catalyst and separation processes*. *New J. Chem.*, 40 (2016) 4016-4026.
- [28] M. Wallace, R. Feres, G. Yablonsky, A. Stern. Explicit formulas for reaction probability in reaction-diffusion experiments. preprint 2016.
- [29] Y.M. Xi and G.P. Steven. *A simple evolutionary procedure for structural optimization*. *Computers and Structures*, 49(5), 1993, 885-886.