

Reactant conversion in a simple reaction-diffusion system

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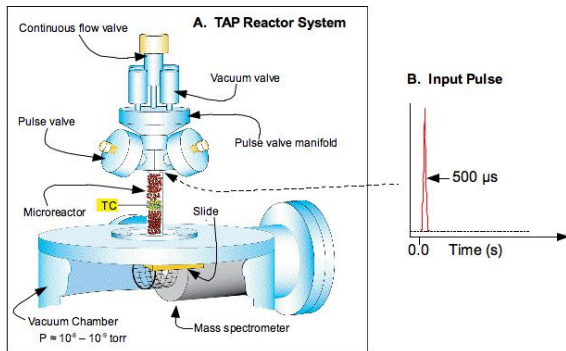
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Acknowledgment

This talk is based on two undergraduate honors thesis by Washington University mathematics majors:

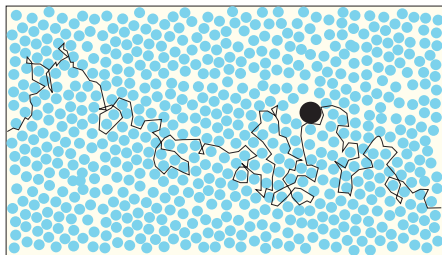
- ALEX MUELLER (class of 2007, currently a graduate student of mathematics at Michigan State University)
- ALEX CLONINGER (class of 2009, currently a graduate student of applied mathematics at University of Maryland)

The T.A.P. (Temporal Analysis of Products) apparatus



New type of chemical reactor invented by John Gleaves (Washington U., Chem. Eng. Dept.) Controlled pulse of reactant gas is injected into small cylindrical reactor. Gas diffuses through a packed bed containing inert and catalytic solid material permeable to the gas. Composition of the outflow of products is measured by a mass spectrometer.

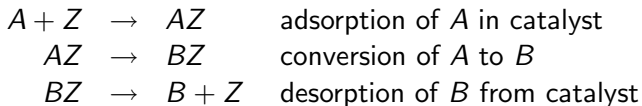
Reaction-diffusion in a T.A.P. system



A pulse of gas A (say, CO , carbon monoxide) is released into the reactor and collected as it leaves through the right-end open side. The black circle represents a particle of catalyst Z (say, platinum covered with oxygen). It is surrounded by a chemically inert material, permeable to the gas mixture, represented by the smaller light colored dots (say, silica). As molecules of species A hit the catalyst particle, a chemical reaction takes place that converts A into another kind of molecule, B (say, CO_2 , carbon dioxide).

How much of B is produced?

Assume a simple first order reaction mechanism:



The gas collected at the open end of the reactor consists of a mixture of two types. If N_A and N_B are the numbers of molecules of types A and B in the gas outflow, we define the conversion fraction, or yield, by

$$\alpha = \frac{N_B}{N_A + N_B}.$$

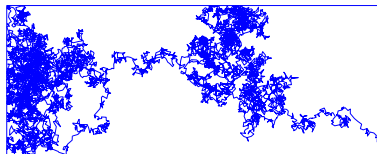
How to calculate α ?

Mathematical model of molecular motion

In the **Knudsen regime** of long mean free paths (low concentration of gases), gas molecules are assumed to collide infrequently with each other. Random motion due to collision with the inert solid material can be modeled by Brownian motion (Wiener process) W_t :

- W_t is continuous (no instantaneous jumps);
- $\Delta W_t = W_{t+h} - W_t$ is statistically independent of W_s , $s \leq t$;
- ΔW_t is normally distributed with mean 0 and variance $\mathcal{D}h$.

The constant \mathcal{D} is the diffusion constant characteristic of the medium and depends on the packing properties of the reactor bed.



First: the case of infinite reaction constant

As a first (but reasonable) approximation, assume that the reaction constant for the overall reaction



is very large. So A **will convert to B upon colliding with catalyst**. Thus we assume:

$$\alpha = \text{probability of hitting catalyst}$$

That is, the yield fraction α is equated with the probability that a random trajectory of the Wiener process (Brownian motion) starting at a position vector \mathbf{x} hits the catalyst before leaving.

Problem: calculate α given the position and shape of the catalyst and the shape of the reactor.

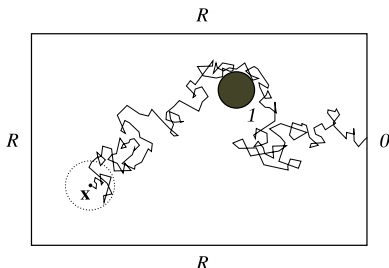
Brownian motion and harmonic functions

Therefore, $\alpha(\mathbf{x})$, is a **harmonic function of the initial position \mathbf{x}** , i.e.,

$$\nabla^2 \alpha = 0,$$

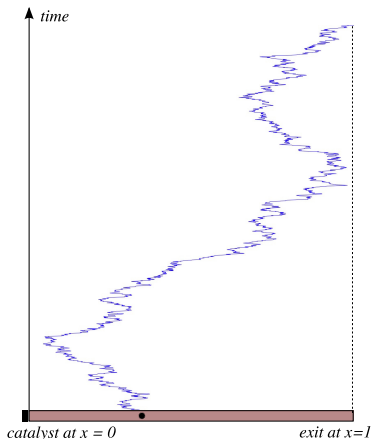
such that:

- $\alpha = 0$ on the exit boundary;
- $\alpha = 1$ on the surface of the catalyst;



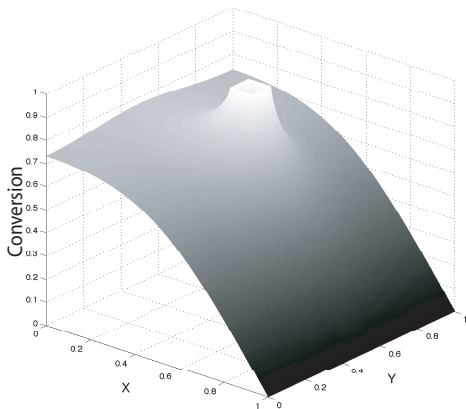
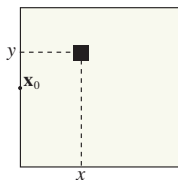
On other sides (R) assume reflecting boundary conditions $\partial\alpha/\partial\mathbf{n} = 0$.

A one-dimensional example



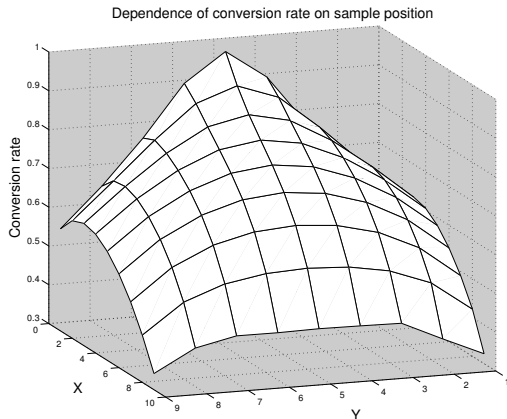
Molecule starts at x and leaves the reactor at $x = 1$. Catalyst at $x = 0$.
Then $\alpha(x) = 1 - x$ is the solution of $\alpha''(x) = 0$, $\alpha(0) = 1$, $\alpha(1) = 0$.

Numerical results by Alex Mueller



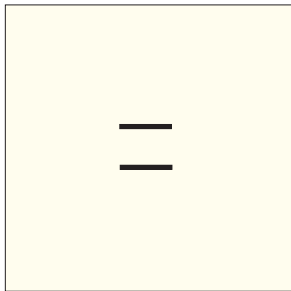
Hitting probability as function of the current position of a single molecule of type A for a square reactor with a small square catalyst its center.

Dependence of α on position of catalyst



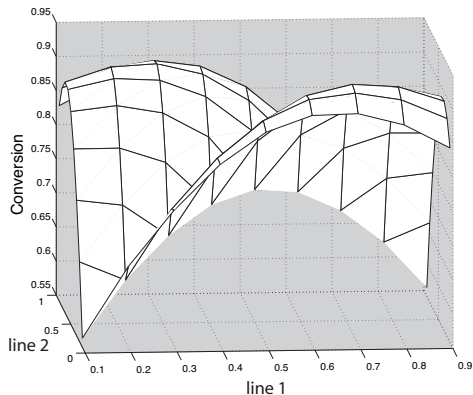
Conversion probability as function of the center of square catalyst. Gas molecule starts at the middle point of the back-side.

Pair of lines



A pair of lines placed along the reactor axis. The position of both line segments can be changed.

Conversion for a pair of lines



Conversion probability as a function of the heights of both catalyst lines. Maximum value when lines are approximately 0.4 apart symmetrically positioned.

The hero of our story so far



Shizuo Kakutani as a young man. Was first to clearly make the connection between harmonic functions and Brownian motion, in a paper published in 1944. Born in Osaka, Japan, in 1911, he was a mathematics professor at Yale until retirement in 1982. He died in 2004 in New Haven, Connecticut.

Finite reaction constant—work of Alex Cloninger

Need a probabilistic model of reaction: the probability that a single molecule, following a particular random trajectory, does not react is

$$p = e^{-k\tau}$$

where

- k is the reaction constant and
- τ is the total time the molecule spends near the catalyst before leaving the reactor.

Then reaction non-conversion ($1 - \alpha$), assuming that initial point is \mathbf{x} , is the expected (i.e., the mean) value

$$\psi(\mathbf{x}) = E_{\mathbf{x}}[e^{-k\tau}]$$

over all the possible histories (trajectories) that the molecule can conceivably follow. Call ψ the **survival function**.

A quantity of interest: local times

Let p_0, p be two locations in the reactor, $\delta > 0$, and define:

- T = random time a gas molecule leaves the reactor;
- $\mathcal{O}_{p_0}(p, \delta, T)$ = total amount of time a random molecular trajectory starting at p_0 at time $t = 0$ spends in a small spherical region of radius δ centered at p . Time is counted until the molecule leaves the reactor;
- $V(p, \delta)$ = volume of that spherical region;

We define the **occupation time density** (or **local time** in probability theory) as the random variable:

$$\tau(p_0, p, T) = \lim_{\delta \rightarrow 0} \frac{\mathcal{O}_{p_0}(p, \delta, T)}{V(p, \delta)}.$$

The **occupation time** in some region U in the reactor is defined by volume integration of the above density.

The Feynman-Kac equation

The survival function satisfies the equation:

$$\mathcal{D}\nabla^2\psi - kV(\mathbf{x})\psi = 0$$

where $V(\mathbf{x})$ indicates proximity to the catalyst, \mathcal{D} is the diffusion constant, and k is the reaction constant.

For an active zone U , then $V = \chi_U$, the indicator function of U . From definition of α (regarded as function of k) the occupation time in U is

$$\tau = \alpha'(0).$$

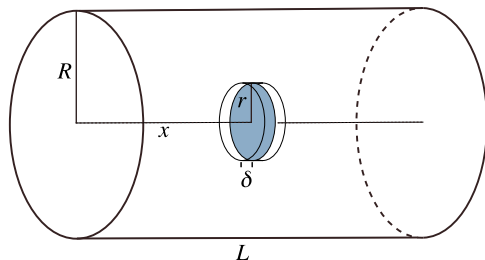
If the active zone is a thin zone near the surface of the solid catalyst, use

$$\nabla^2\psi = 0$$

with boundary condition

$$\frac{\partial\psi}{\partial\mathbf{n}} = \frac{\delta k}{\mathcal{D}}\psi$$

A realistic situation



A cylindrical reactor of radius R and length L contains a circular catalytic metal foil of radius r at position x along the reactor axis. It is filled with an inert material that is permeable to gas transport. The back (or left) wall is closed except for a small passage at the center where a pulse of gas can be injected into the reactor; the front (or right) side is open to gas moving out of the reactor. The case $R = r$ is also of interest when the circular foil is replaced by a permeable catalyst **thin zone**. V is the indicator function of the foil δ -neighborhood.

Special case in dimension-one: thin-zones



Active layers of catalyst, permeable to gas diffusion. Layer at position x_j has thickness δ_j . Gas is injected into the reactor at position $x = 0$. The reactor end at $l_2 = l$ is open to gas flow, whereas the end at $l_1 = 0$ is closed. Outside the thin zones, equation reduces to

$$\psi'' = 0,$$

and crossing a zone incurs discontinuity of ψ'

$$\psi'(x_j^+) - \psi'(x_j^-) = (k\delta_j/\mathcal{D})\psi(x_j).$$

For the case of a single zone at $x_1 = z$:

$$\alpha(k) = \frac{k\tau}{1 + k\tau}, \quad \tau = \alpha'(0) = \frac{(l - z)\delta}{\mathcal{D}} = \text{time spent in thin-zone}$$

Main result: a factorization formula

Suppose that on the active zone (say, catalyst surface)

the occupation time density is nearly constant.

Then reactant conversion is given by

$$\alpha = P_H \times \frac{\tau_H k}{1 + \tau_H k}$$

where

- τ_H is the expected time spent near the catalyst, given that molecule collides with catalyst (**conditional occupation time**);
- P_H is the probability of collision, calculated by means of the method developed with Alex Mueller.

Proof of the factorization formula—Part I

Express α in terms an average over a large independent sample values of τ :

$$\alpha(k) = 1 - E_{x_0}[e^{-k\tau}] = 1 - \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N e^{-k\tau_j}.$$

Of N independent trials, suppose

- $N_0 = \#$ of random trajectories that miss the catalyst (so $\tau_j = 0$);
- $N_1 = N - N_0$.

Then

$$\alpha(k) = \frac{N_1}{N} \left(1 - \frac{1}{N_1} \sum_{j=1}^{N_1} e^{-k\tau_j} \right) = P_H \alpha(k|\text{Hit}).$$

Since $\alpha(\infty|\text{Hit}) = 1$, then $P_H = \alpha(\infty)$, i.e., conversion for fast reactions equals the hitting probability.

Proof of the factorization formula—Part II

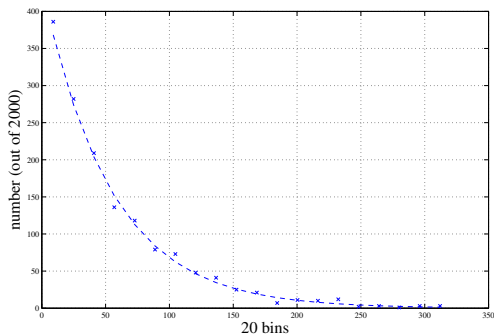
Let $\langle \tau^n | \text{Hit} \rangle =$ conditional expectation of τ if mol. hits catalyst. Then

$$\langle \tau^n | \text{Hit} \rangle = (-1)^{n+1} \alpha^{(n)}(0 | \text{Hit}).$$

In fact,

$$\begin{aligned} \alpha^{(n)}(0 | \text{Hit}) &= \frac{d^n}{dk^n} \left(1 - \lim_{N_1 \rightarrow \infty} \frac{1}{N_1} \sum_{j=1}^{N_1} e^{-k\tau_j} \right)_{k=0} \\ &= (-1)^{n+1} \lim_{N_1 \rightarrow \infty} \frac{1}{N_1} \sum_{j=1}^{N_1} \tau_j^n \\ &= (-1)^{n+1} \langle \tau^n | \text{Hit} \rangle. \end{aligned}$$

But the conditional occupation time is exponential



Histogram for the occupation time in thin neighborhood (represented by crosses) compared to an exponential distribution whose parameter is the observed sample mean. Drawn from 2000 observations, approximately 70% of which are trajectories hitting the catalyst. So the total number of data points in the histogram is approximately 1400.

Proof of the factorization formula—Part III

A property of exponential random variables:

$$\langle \tau^n | \text{Hit} \rangle = n! \langle \tau | \text{Hit} \rangle^n.$$

From this (and a little faith) we get:

$$\begin{aligned} \alpha(k | \text{Hit}) &= \sum_{n=1}^{\infty} \frac{\alpha^{(n)}(0 | \text{Hit})}{n!} k^n \\ &= \sum_{n=1}^{\infty} (-1)^{n+1} \frac{\langle \tau^n | \text{Hit} \rangle}{n!} k^n \\ &= \sum_{n=1}^{\infty} (-1)^{n+1} \langle \tau | \text{Hit} \rangle^n k^n \\ &= \frac{\langle \tau | \text{Hit} \rangle k}{1 + \langle \tau | \text{Hit} \rangle k} \end{aligned}$$

Can we smell the shape of a catalyst?

The one-dimensional case: Let the unknown density of catalyst be given by

$$\rho : [0, l] \rightarrow [0, \infty)$$

where $[0, l]$ represents the one-dimensional reactor of length l . Gas injection at 0 and exit at l . We are allowed to vary k (say, by changing the temperature).

Can we recover the function $\rho(x)$ from the conversion function $\alpha(k)$?

Special case: suppose there are n active thin-zones of thickness δ . Can we find their positions in $[0, l]$ from knowledge of $\alpha(k)$?

Some positive evidence

Suppose there are m thin zones located at x_1, x_2, \dots, x_m . Then

$$\alpha(k) = \frac{f(k)}{1 + f(k)}$$

where $f(k)$ is a polynomial of degree m in $\kappa = \frac{k\delta}{D}$ whose coefficients are functions of x_1, x_2, \dots, x_m, l . Let $K = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} = K_m K_{m-1} \dots K_1$,

where

$$K_j = \begin{pmatrix} 1 + \frac{\kappa}{m}(x_j - x_{j-1}) & \frac{\kappa}{m} \\ x_j - x_{j-1} & 1 \end{pmatrix}.$$

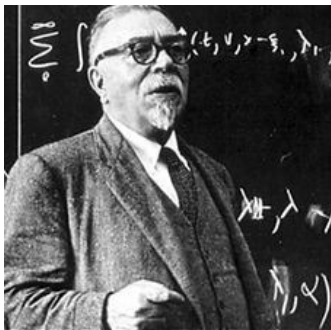
Then

$$f(k) = (l - x_m)a_{12} + a_{22} - 1 + \frac{\kappa}{m}((l - x_m)a_{11} + a_{21}).$$



Marian Smolukowski in Viena (Austria-Hungary, 1872-1917). He (1906) and A. Einstein (1905) were the first to describe the phenomenon of Brownian motion on the basis of statistical physics.

Norbert Wiener



Norbert Wiener (1894-1964, Columbia, Missouri). Shown here at MIT. He developed the mathematical foundations to the theory of Brownian motion in a series of papers from 1920-1924.



Mark Kac (Poland, USA, 1914-1984) Probabilist; taught at Cornell University (1939-1961), then the Rockefeller University in New York City, and after 20 years there, he moved to the University of Southern California. He is also famous for the central question in spectral geometry: “Can we hear the shape of a drum?”

Richard Feynman



Richard Philips Feynman (1918-1988, born in Queens, New York.) Photo of ID badge while working on the Manhattan Project (1942-1946) to develop first atomic bomb. Physicist, best known for his work on quantum electrodynamics. Was a professor at Caltech.