The Diffusion Equation
A Multi-dimensional Tutorial

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Background

This tutorial is meant to acquaint readers from various backgrounds with many of the common ideas surrounding diffusion. The diffusion equation, most generally stated

$$\frac{\partial}{\partial t} c(\bar{x}, t) = D \nabla^2 c(\bar{x}, t), \tag{1}$$

has multiple historical origins each building upon a unique physical interpretation. This partial differential equation (PDE) also encompasses many ideas about probability and stochasticity and its solution will require that we delve into some challenging mathematics. The most common applications are particle diffusion, where c is interpreted as a concentration and D as a diffusion coefficient; and heat diffusion where c is the temperature and D is the thermal conductivity. It has also found use in finance and population dynamics, and is closely related to Schrodinger's Equation for a free particle.

But before delving into those fascinating details, what is it that the diffusion equation is actually trying to describe? It allows us to talk about the statistics of randomly moving particles in n dimensions. By random, we mean the movement at one moment in time cannot be correlated movement at any other moment in time, or in other words, there is no deterministic/predictive power over the exact motion of the particle. Already this means we must abandon Newtonian

mechanics and the notion of inertia, in favor of a system that directly responds to fluctuations in the surrounding environment.

It is then inherent (almost by definition) that diffusion takes place in an environment where viscous forces dominate (*i.e.* very low Reynolds Number). Given a group of *non-interacting* particles immersed in a fluctuating (Brownian) environment, the movement of each individual particle is *not* governed by the diffusion equation. However, many identical particles each obeying the same boundary and initial conditions share statistical properties of their spatial and temporal evolution. It is the evolution of the probability distribution underlying these statistical properties that the diffusion equation captures. The function $c(\bar{x}, t)$ is a distribution that gives the probability of finding a perfectly average particle in the small vicinity of the point $\bar{x}$ at time t. The evolution of some systems does follow the diffusion equation outright: for instance, when you put a drop of dye in a beaker of water, there are millions of dye molecules each exhibiting the random movements of Brownian motion, but as a group they exhibit the smooth, well-behaved statistical features of the diffusion equation.

In this tutorial we will briefly discuss the equations of motion at low Reynolds number that underly diffusion. We then derive the diffusion equation from two perspectives: 1) the continuum limit using potentials, forces and fluxes, 2) from a microscopic point of view where the individual probabilistic motions of particles lead to diffusion. Finally we explore the diffusion equation using the Fourier Transform to find a general solution for the case of diffusion in an infinite n-dimensional space.

A Continuum View of Diffusion

Unlike our macroscopic experiences, where objects move at constant speeds, with a well-defined momentum in a straight line, the life of a small particle is dominated by fast time scales, short distances, and collisions with neighboring particles that yield a very erratic (or even ergodic) motion. In some sense, the apparent disparity between macro- and micro-scopic life is really an issue of scale, that is to say, our normal observations are very very slow (on the order of seconds) compared to molecular collisions (on the order $10^{-12}s$) and our distances are very very large (on the order of a 10^0 m) compared to molecular mean free paths (on the order of $10^{-10} - 10^{-9}$ m). Thus the ideas of viscosity and random walk are in place only to allow us to ignore the massive complexity of such a small, fast system, to yield a more tractable problem.

The Reynolds number is a dimensionless measure of the ratio of inertial forces to viscous forces in a fluid, hence if viscous forces dominate in diffusion, we would expect a very low Reynolds number. The Reynolds Number of a particle with characteristic size r is given by

$$R = \frac{\rho v_s r}{\eta} \tag{2}$$

where ρ is fluid density, η is absolute viscosity, and v_s is the characteristic speed at which the particle moves through the fluid. In the thermal setting, equipartition gives a measure of $\langle v_s \rangle$ by

$$\langle v_s \rangle = \sqrt{\frac{k_B T}{m}}, \tag{3}$$

where m is the particle mass. For example, a particle with radius $10\,\text{nm}$ and density comparable to water, at room temperature $v_s \sim 1\,\text{m/s}$. Then given the density $(1000\,\text{kg/m}^3)$ and viscosity $(0.001\,\text{Ns/m}^2)$ of water, $R \simeq 10^{-2}$. At this low Reynolds number, viscous effects dictate that a

particle moves at a velocity proportional to the force applied

$$\bar{v} = \sigma \bar{F}, \tag{4}$$

where the constant of proportionality (σ) is called the mobility. Such a strange equation of motion arises because energy is dissipated very quickly at high viscosity. Let us consider quasi-spherical particles, where it makes sense that the mobility should decrease both with increasing particle size (more fluid to move out of the way) and fluid viscosity (each unit volume of fluid is harder to move out of the way), where by dimensional analysis

$$\sigma \propto \frac{1}{r\eta}. \tag{5}$$

By definition, a flux is a movement of particles (or other quantities) through a unit measure (point, length, area) per unit time. In the case of diffusion, we are concerned with a probability flux (very similar to a concentration flux) and hence

$$\bar{J}(\bar{x}, t) = c(\bar{x}, t)\bar{v}(\bar{x}, t). \tag{6}$$

From statistical mechanics we know that the chemical potential (with units of energy) for an ensemble of non-interacting particles is related to local probability density (or local concentration) by

$$\mu = \mu_o + k_B T \ln(c/c_o), \tag{7}$$

where μ_o and c_o are constants. If the probability density varies in space, then the chemical potential also varies in space, effectively generating a force on the particles, given by

$$\bar{F} = -\nabla\mu = -\frac{k_B T}{c}\nabla c. \tag{8}$$

Putting this altogether, this means the flux in the system is

$$\bar{J} = -k_B T \sigma \nabla c. \tag{9}$$

For spherical particles the mobility is the inverse of the Stokes drag

$$\sigma = \frac{1}{6\pi\eta r}, \tag{10}$$

and thus the diffusion coefficient is defined as

$$D = \frac{k_B T}{6\pi\eta r}. \tag{11}$$

Finally, we recover Fick's First Law

$$\bar{J} = -D\nabla c. \tag{12}$$

For a normal diffusion process, particles cannot be created or destroyed, which means the flux of particles into one region must be the sum of particle flux flowing out of the surrounding regions. This can be captured mathematically by the continuity equation

$$\frac{\partial}{\partial t}c + \nabla \cdot \bar{J} = 0, \tag{13}$$

which upon substitution yields the diffusion equation

$$\frac{\partial}{\partial t}c = \nabla \cdot (D\nabla c). \tag{14}$$

If the diffusion coefficient is constant in space, then

$$\frac{\partial}{\partial t}c = D\nabla^2 c. \tag{15}$$

We should note that c and D take on different meanings in different situations: in heat conduction $c \propto T$ and $D = \kappa$ is the thermal conductivity, and in the movement of material, c is interpreted as a concentration.

A Microscopic View of Diffusion

The continuum view of diffusion appeals to our intuition about forces and fluxes, but gives little understanding of how the erratic motion of particles and the probabilistic nature of motion on this scale gives rise to diffuse behavior. In one of his landmark papers in 1905, Einstein derived a more general version of the diffusion equation using a microscopic perspective. We will roughly follow that derivation here.

Imagine you are a small particle in a fluctuating environment. Standing at position $\bar{x}$ you are bombarded by particles whose energy is distributed according to $e^{-E/k_B T}$. During a time Δt you are impacted by some number of particles such that there is a probability ϕ that you have been moved to a new position $\bar{x} + \bar{\epsilon}$. In isotropic diffusion, the rate at which you are bombarded by particles is not dependent on direction, and hence on average your position does not change much. This defines a 'jump' distribution

$$\phi(\bar{x}, \bar{\epsilon}, \Delta t), \tag{16}$$

which is interpreted as the probability that during a time Δt, you will be jostled by your neighbors such that you move from $\bar{x} \rightarrow \bar{x} + \bar{\epsilon}$. We impose the obvious constraint that regardless of position or size of the time step, you must jump somewhere ($\bar{\epsilon} = 0$ is somewhere), or mathematically

$$\int_{\mathcal{M}} \phi(\bar{x}, \bar{\epsilon}, \Delta t)\mathrm{d}\bar{\epsilon} = 1, \tag{17}$$

where $\mathcal{M}$ is the set of all possible jumps. Now we construct a so-called 'master equation', which dictates how probability flows from one state to another in a system. Consider the probability density at position $\bar{x}$ and time $t + \Delta t$; this can be written as the sum of all probability density which flows from an arbitrary position into this position in a time Δt. Whatever probability density was originally at $\bar{x}$ has a probability $(1 - \phi(\bar{x}, 0, \Delta t)\mathrm{d}\bar{\epsilon})$ of moving from $\bar{x}$, hence it will always moves. This is written as the Einstein Master Equation

$$c(\bar{x}, t + \Delta t) = \int_{\mathcal{M}} c(\bar{x} - \bar{\epsilon}, t)\phi(\bar{x} - \bar{\epsilon}, \bar{\epsilon}, \Delta t)\mathrm{d}\bar{\epsilon}. \tag{18}$$

More pedantically, let us read this as a (long) sentence: the probability density at position $\bar{x}$ and forward time step $t + \Delta t$ is increased by the flow of probability from a point $\bar{x} - \bar{\epsilon}$. There was a probability $\phi(\bar{x} - \bar{\epsilon}, \bar{\epsilon}, \Delta t)$ that the *all* the probability density at $\bar{x} - \bar{\epsilon}$ (*i.e.* $c(\bar{x} - \bar{\epsilon}, \Delta t)$) made a jump $\bar{\epsilon}$ to reach $\bar{x}$. During that same small time step, whatever probability density

was originally at $\bar{x}$ made any number of jumps $\bar{\epsilon} \in \mathcal{M}$ to move *all* of the original probability density at $\bar{x}$ to some new point (that is of no consequence). We then go around and add the contributions from all possible jumps. The truly amazing thing here is that *all* of the probability density at a point moves in the same direction. For instance, why doesn't half of the probability density go one way, and half another? The success of this theoretical construct demands that we consider the probability density as being defined by an ensemble average of many identical, quantized particles (as opposed to the flow of some completely continuous field). This is why it has been said that Einstein's analysis of diffusion helped solidify the idea of atoms and molecules as real physical objects. One could also interpret this as a nascent prediction of the existence of the particles that carry heat, called phonons.

Examining the left-hand side in a Taylor series for small time step we find

$$c(\bar{x}, t + \Delta t) = c(\bar{x}, t) + \frac{\partial}{\partial t} c(\bar{x}, t) \Delta t + O(\Delta t^2). \tag{19}$$

To proceed we need to make one assumption, which is that during an arbitrarily small time step, the nominal distance traversed by particles is small so that we can expand about $\bar{x} = \bar{x} + \bar{\epsilon}$. This is very rational, in that it demands that particles cannot just 'poof' from one distant point to another in an arbitrary time step. Examining the right-hand side near the point $\bar{x} + \bar{\epsilon}$, we write the Taylor series of

$$\int_{\mathcal{M}} c(\bar{x} - \bar{\epsilon}, t) \phi(\bar{x} - \bar{\epsilon}, \bar{\epsilon}, \Delta t) d\bar{\epsilon} \tag{20}$$

term by term. The first term is simply

$$\int_{\mathcal{M}} [c(\bar{x} - \bar{\epsilon}, t) \phi(\bar{x} - \bar{\epsilon}, \bar{\epsilon}, \Delta t)] |_{\bar{x} = \bar{x} + \bar{\epsilon}} \, d\bar{\epsilon} = \int_{\mathcal{M}} c(\bar{x}, t) \phi(\bar{x}, \bar{\epsilon}, \Delta t) d\bar{\epsilon} = c(\bar{x}, t). \tag{21}$$

The second term is

$$\int_{\mathcal{M}} (-\bar{\epsilon} \cdot \nabla) [c(\bar{x} - \bar{\epsilon}, t) \phi(\bar{x} - \bar{\epsilon}, \bar{\epsilon}, \Delta t)] |_{\bar{x} = \bar{x} + \bar{\epsilon}} \, d\bar{\epsilon} = -\nabla \cdot \left[c(\bar{x}, t) \int_{\mathcal{M}} \bar{\epsilon} \phi(\bar{x}, \bar{\epsilon}, \Delta t) d\bar{\epsilon} \right] \tag{22}$$

Finally, the third term is

$$\frac{1}{2} \int_{\mathcal{M}} (\bar{\epsilon} \cdot \nabla)^2 [c(\bar{x} - \bar{\epsilon}, t) \phi(\bar{x} - \bar{\epsilon}, \bar{\epsilon}, \Delta t)] |_{\bar{x} = \bar{x} + \bar{\epsilon}} d\bar{\epsilon} = \nabla \cdot \left[\nabla [c(\bar{x}, t)] \frac{1}{2} \int_{\mathcal{M}} \phi(\bar{x}, \bar{\epsilon}, \Delta t) |\bar{\epsilon}|^2 \, d\bar{\epsilon} \right]. \tag{23}$$

To study diffusion as a continuous process, we let $\Delta t \to 0$ (and hence terms $O(\Delta t^2) = 0$). Combining the Taylor series for the right and left hand sides and canceling a common factor of $c(\bar{x}, t)$, we have

$$\frac{\partial}{\partial t} c(\bar{x}, t) = -\nabla \cdot \left[c(\bar{x}, t) \lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_{\mathcal{M}} \bar{\epsilon} \phi(\bar{x}, \bar{\epsilon}, \Delta t) d\bar{\epsilon} \right] \tag{24}$$

$$+ \nabla \cdot \left[\nabla [c(\bar{x}, t)] \lim_{\Delta t \to 0} \frac{1}{2\Delta t} \int_{\mathcal{M}} \phi(\bar{x}, \bar{\epsilon}, \Delta t) |\bar{\epsilon}|^2 \, d\bar{\epsilon} \right].$$

In some sense, this is the most general statement of the diffusion equation, however, the moments of ϕ have far more intuitive meanings than are embodied by their integral representation. Let us examine those more closely - the first moment is the average distance a particle travels in a time Δt, hence

$$\lim_{\Delta t \to 0} \frac{1}{\Delta t} \int_{\mathcal{M}} \bar{\epsilon} \phi(\bar{x}, \bar{\epsilon}, \Delta t) d\bar{\epsilon} = \bar{v}(\bar{x}), \tag{25}$$

defines an average particle velocity $\bar{v}$, but what is this velocity? Recall that in this low Reynolds number environment, there is a linear relationship between force and velocity ($\bar{v} = \sigma \bar{F}$) and further recall that all (conservative) forces can be thought of as the gradient of a potential $V(\bar{x})$ ($\bar{F} = -\nabla V$). Then this is the average velocity of particles due to forces generated by an external energy landscape

$$\bar{v} = -\sigma \nabla V, \tag{26}$$

where $\sigma = D/k_B T$ (there is also a rigorous derivation of this relationship from statistical mechanics). For instance, in electrophoresis, a species with charge q in an electrostatic potential Φ, moves with an average velocity $\bar{v} = -\mu q \nabla \Phi$, essentially showing us the origin of Ohm's Law, where the mobility is related to the temperature and the mean free path. The second moment measures the variance of a particle's movement and is the microscopic definition of the diffusion constant

$$\lim_{\Delta t \to 0} \frac{1}{2\Delta t} \int_{\mathcal{M}} \phi(\bar{x}, \bar{\epsilon}, \Delta t) |\bar{\epsilon}|^2 \, d\bar{\epsilon} = D. \tag{27}$$

Putting this altogether yields a more general version of the diffusion equation, often called a *Fokker-Planck* equation

$$\frac{\partial}{\partial t} c(\bar{x}, t) = \nabla \cdot D \left[\frac{c(\bar{x}, t)}{k_B T} \nabla V + \nabla c(\bar{x}, t) \right], \tag{28}$$

and defines a more general kind of particle flux

$$\bar{J} = -D \left[\frac{c(\bar{x}, t)}{k_B T} \nabla V + \nabla c(\bar{x}, t) \right]. \tag{29}$$

This equation holds even under conditions of non-conservative forces, *i.e.* $\nabla \times \nabla V \neq 0$. If the forces are conservative, *i.e.* $\nabla \times \nabla V = 0$, then we know the Boltzmann distribution must be a stationary solution of the diffusion equation,

$$c(\bar{x}, t \to \infty) \propto e^{-V(\bar{x})/k_B T}. \tag{30}$$

For instance, Ohm's Law is the case where electron concentration is constant and hence $\bar{J} = -\sigma c q \bar{E}$. Additionally, we can add all kinds of terms to the right-hand side to create, destroy or modify probability, leading to so-called 'reaction-diffusion' equations, however, we will end our derivation here. If the diffusion coefficient does not vary in space then

$$\frac{\partial}{\partial t} c(\bar{x}, t) = D \nabla \cdot \left[\frac{c(\bar{x}, t)}{k_B T} \nabla V + \nabla c(\bar{x}, t) \right], \tag{31}$$

and if no external potential is applied, we retrieve the canonical diffusion equation

$$\frac{\partial}{\partial t} c(\bar{x}, t) = D \nabla^2 c(\bar{x}, t). \tag{32}$$

Solutions to the Diffusion Equation

Thus far, we have spent a lot of time discussing the physical origins and implications of diffusion, but still do not know how to actually solve this equation explicitly for the evolution of a diffuse system. As we will see, there are other physical concepts buried within the diffusion

equation that only become apparent upon solution. As a mathematical entity, the diffusion equation has two very important features: it is a 'linear' equation, and it is 'separable' (in most useful coordinate systems).

The equation being separable means that we can decompose the original equation into a set of uncoupled equations for the evolution of c in each dimension (including time). This means that whatever solution one finds for c, it can be represented as the multiplication of separate solutions, for instance, in two dimensions

$$c(\bar{x}, t) = X(x) \cdot Y(y) \cdot T(t). \tag{33}$$

This fact will also prove quite useful when we consider how dimensionality affects diffusion. Explicitly, in two dimensions the diffusion equation is

$$\frac{\partial}{\partial t} c = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right), \tag{34}$$

where if we substitute the separable form of c we have

$$\frac{1}{DT} \frac{\partial T}{\partial t} = \frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2}. \tag{35}$$

The only way that an equation strictly in time (lhs) can be equal to an equation strictly in space (rhs) is if they are both equal to a constant, that is

$$\frac{1}{DT} \frac{\partial T}{\partial t} = -(m_1^2 + m_2^2), \tag{36}$$

and

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} = -(m_1^2 + m_2^2), \tag{37}$$

where we have defined the peculiar constant $m_1^2 + m_2^2$, which will make more sense when compared to the actual solution. Likewise, we can rearrange the spatial equation to read

$$\frac{1}{X} \frac{\partial^2 X}{\partial x^2} + m_1^2 = - \left(\frac{1}{Y} \frac{\partial^2 Y}{\partial y^2} + m_2^2 \right). \tag{38}$$

In order for two completely independent equations of precisely the same form, and opposite sign, to be equal, they must both equal zero, that is

$$\frac{\partial^2 X}{\partial x^2} + m_1^2 X = 0 \tag{39}$$

and

$$\frac{\partial^2 Y}{\partial y^2} + m_2^2 Y = 0. \tag{40}$$

We garner a few important facts from this. First, regardless of the dimensionality, we can always split the diffusion equation into uncoupled dimensionally independent equations, using a constant of the form $\sum_{i=1}^{n} m_i^2$, where n is the number of spatial dimensions. In other coordinate systems, the number of constants does not change, but their construction should be modified (e.g. in spherical coordinates one uses constants of the form $l(l+1)$). Second we learn that the solutions for the time component will have a form

$$T(t) \propto e^{-D\left(\sum_{i=1}^{n} m_i^2\right)t} \tag{41}$$

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while the spatial components will have solutions

$$X_j(x_j) \propto e^{im_j x_j}. \tag{42}$$

Being a linear equation means the equation itself has no powers or complicated functions of the function c (*i.e.* there are no terms like c^2, e^c, etc). This means we can think of the equation as a so-called 'linear differential operator' acting on the function c

$$\mathcal{L}[c] = 0 \ \text{ with } \ \mathcal{L} = \frac{\partial}{\partial t} - D\nabla^2. \tag{43}$$

This is arguably one of the most profound ideas in all of mathematical physics. If a differential equation is linear, and has more than one solution, new solutions can be constructed by adding together other solutions. This means that if

$$\mathcal{L}[c_k] = 0 \tag{44}$$

for some solution c_k, then the weighted sum of solutions

$$\mathcal{L}\left[\sum_k a_k c_k\right] = 0 \tag{45}$$

for any arbitrary constants a_k. By completeness and orthonormality of the Fourier modes, we know that $c(\bar{x}, t)$ can be represented by its Fourier Transform

$$c(\bar{x}, t) = \int A_k(t) e^{-i\bar{k}\cdot\bar{x}} \mathrm{d}\bar{k} \tag{46}$$

with no loss of generality, and this representation can be used to simultaneously discuss any level of dimensionality. Using the linearity of the diffusion equation, if one Fourier mode solves the diffusion equation, a general solution can be built by adding together many such modes at different frequencies with the right 'strength' $A_k(t)$. First we note that

$$c(\bar{x}, t) = \int c_k(\bar{x}, t) \mathrm{d}\bar{k} \ \text{ where } \ c_k(\bar{x}, t) = A_k(t) e^{-i\bar{k}\cdot\bar{x}}. \tag{47}$$

Taking the time derivative of a single mode gives

$$\frac{\partial}{\partial t} c_k = e^{-i\bar{k}\cdot\bar{x}} \frac{\partial}{\partial t} A_k, \tag{48}$$

and taking the spatial derivative gives

$$\nabla^2 c_k = -A_k(\bar{k} \cdot \bar{k}) e^{-i\bar{k}\cdot\bar{x}}. \tag{49}$$

Thus the linear operator $\mathcal{L}$ acting on c_k gives a differential equation for the coefficient A_k

$$\mathcal{L}[c_k(t)] = e^{-i\bar{k}\cdot\bar{x}} \frac{\partial}{\partial t} A_k + DA_k |k|^2 e^{-i\bar{k}\cdot\bar{x}} = 0, \tag{50}$$

which simplifies to

$$\frac{\partial}{\partial t} A_k + DA_k |k|^2 = 0. \tag{51}$$

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This first-order differential equation in time is easily solved, yielding

$$A_k(t) = A_k(0)e^{-D|k|^2 t} \tag{52}$$

where $A_k(0)$ is an initial condition that we will address momentarily. The first interesting fact emerges here, that higher frequencies are damped quadratically, hence any sharp variations in probability density 'smooth out' very quickly, while longer wavelength variations persist on a longer time-scale. Using $A_k(t)$ we construct the general solution as

$$c(\bar{x}, t) = \int A_k(0)e^{-D|k|^2 t}e^{-i\bar{k}\cdot\bar{x}}\,\mathrm{d}\bar{k}, \tag{53}$$

but still need to find the $A_k(0)$'s using the initial condition $c(\bar{x}, 0)$. The first way to proceed is simply by taking the Fourier Transform on the initial condition, namely

$$A_k(0) = \frac{1}{(2\pi)^n} \int c(\bar{x}, 0)e^{i\bar{k}\cdot\bar{x}}\,\mathrm{d}\bar{x}, \tag{54}$$

where n is the number of dimensions. In some sense, this is the answer, but a more useful result can be had if we study the impulse initial condition $c(\bar{x}, 0) = \delta(\bar{x} - \bar{x}')$, where

$$A_k(0) = \frac{1}{(2\pi)^n} \int \delta(\bar{x} - \bar{x}')e^{i\bar{k}\cdot\bar{x}}\,\mathrm{d}\bar{x} = \frac{1}{(2\pi)^n}e^{i\bar{k}\cdot\bar{x}'}. \tag{55}$$

We create a solution to the PDE known as the *Green's Function*, by studying the response to this initial δ-function impulse

$$G(\bar{x}, \bar{x}', t) = \frac{1}{(2\pi)^n} \int e^{-D|k|^2 t}e^{-i\bar{k}\cdot(\bar{x}-\bar{x}')}\,\mathrm{d}\bar{k}. \tag{56}$$

The Green's Function tells us how a single point of probability density initially at $\bar{x}'$ evolves in time and space. Thus the evolution of the system from any initial condition can be found simply by adding up the right *amount* of probability density at the right points in space, given by

$$c(\bar{x}, t) = \int G(\bar{x}, \bar{x}', t)c(\bar{x}', 0)\,\mathrm{d}\bar{x}', \tag{57}$$

because each point of probability density evolves in space and time independently. It behooves us to mention one caveat, that this method becomes very difficult to employ when the evolution of the probability density depends on the current (or past) state of the probability distribution, so-called 'non-linear field' problems.

In the case of diffusion in Cartesian coordinates, the Green's Function is quite easy to determine from the integral representation. Consider that we are working in n dimensions, such that

$$G(\bar{x}, \bar{x}', t) = \frac{1}{(2\pi)^n} \int e^{\left(-Dt\sum_{j=1}^{n}|k_j|^2\right)}e^{-i\sum_{j=1}^{n}k_j(x_j-x_j')} \prod_{j=1}^{n} \mathrm{d}k_j. \tag{58}$$

At first this looks quite messy, but upon inspection one notices that it can be reorganized to

$$G(\bar{x}, \bar{x}', t) = \left(\frac{1}{2\pi} \int e^{-Dk^2 t}e^{-ik(x-x')}\,\mathrm{d}k\right)^n. \tag{59}$$

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This striking result tells us diffusion is happening in precisely the same way, independently in all dimensions. In other words, diffusion in 3D is really just diffusion in 1D happening simultaneously on three orthogonal axes - this is the result of 'separability' of the PDE. Performing the integral gives the n-dimensional Green's function of infinite extent

$$G(\bar{x}, \bar{x}', t) = \frac{e^{-\frac{|\bar{x}-\bar{x}'|^2}{4Dt}}}{(4\pi Dt)^{n/2}}, \tag{60}$$

with the proper normalization

$$\int G(\bar{x}, \bar{x}', t) \mathrm{d}\bar{x} = 1. \tag{61}$$

It is important to realize that the Green's Function depends on the precise boundary conditions applied, for instance a fixed flux boundary condition $J(\bar{x}(s), t) = J_o$ or fixed probability-density boundary condition $c(\bar{x}(s), t) = c_o$ results in a very different Green's Function (where s is a variable that parameterizes spatial location of a boundary condition).

Finally, we can use this the Green's Function to study the ensemble dynamics of a diffusing particle. The average position of a particle is given

$$\langle \bar{x} \rangle (t) = \int G(\bar{x}, \bar{x}', t) \bar{x} \mathrm{d}\bar{x} = \bar{x}', \tag{62}$$

or in other words, on average the particle remains where it was initially located at $t = 0$. The more exciting calculation is what happens to the root-mean-square position of the particle? The mean-square position is a measure of the degree of fluctuation in the particle's position, given by the second moment

$$\langle \bar{x}^2 \rangle (t) = \int G(\bar{x}, \bar{x}', t)(\bar{x} \cdot \bar{x}) \mathrm{d}\bar{x}. \tag{63}$$

Again, let us appeal to the full dimensional notation

$$\langle \bar{x}^2 \rangle (t) = \frac{1}{(4\pi Dt)^{n/2}} \int e^{-\frac{\sum_{j=1}^{n}(x_j-x_j')^2}{4Dt}} \left(\sum_{j=1}^{n} x_j^2 \right) \prod_{j=1}^{n} \mathrm{d}x_j. \tag{64}$$

This can be rewritten

$$\langle \bar{x}^2 \rangle (t) = n \cdot \left(\int \frac{e^{-\frac{(x-x')^2}{4Dt}}}{(4\pi Dt)^{1/2}} \mathrm{d}x \right)^{(n-1)} \cdot \int \frac{e^{-\frac{(x-x')^2}{4Dt}}}{(4\pi Dt)^{1/2}} x^2 \mathrm{d}x. \tag{65}$$

and quickly simplifies to

$$\langle \bar{x}^2 \rangle (t) = n \cdot \int \frac{e^{-\frac{(x-x')^2}{4Dt}}}{(4\pi Dt)^{1/2}} x^2 \mathrm{d}x. \tag{66}$$

and finally

$$\langle \bar{x}^2 \rangle (t) = |\bar{x}'|^2 + 2nDt. \tag{67}$$

The the mean-square motion has independent contributions, of strength $2Dt$, from each dimension. Finally, the root-mean-square motion is given by

$$\sqrt{\langle \bar{x}^2 \rangle - \langle \bar{x} \rangle^2} = \sqrt{2nDt}, \tag{68}$$

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essentially saying that all diffuse particles move in a way proportional to $\sqrt{Dt}$, independent of dimensionality. There are certain important features of diffusion which do depend on dimensionality, for instance the probability that a particle is found in a neighborhood $|\bar{r}|$ around its initial point scales as $(r/\sqrt{Dt})^n$.

One final, curious property of diffusion is that it has a deep connection on many levels to quantum mechanics and Schrodinger's Wave Equation. One brief parallel is the following, recall from elementary quantum mechanics that upon measurement of a particle's position, the wave function and hence corresponding probability distribution collapses to a δ-function. In much the same way, a measurement of a diffusing particle's position at $\bar{x}'$ effectively collapses the probability distribution to a δ-function, and resets time to $t = 0$, given by $c(\bar{x}, 0) = \delta(\bar{x} - \bar{x}')$.

Application of Boundary Conditions using Images

In some rare but informative cases, boundary conditions can be applied simply by the right addition of two or more Green's functions to create a new Green's function. The most common types of boundary conditions are the so-called *Dirichlet* and *Neumann* boundary conditions, which correspond to specifying either a constant probability density, c, or a constant flux, $\bar{J} \propto \nabla c$, at some boundary, respectively.

In the first case, let us presume we want to study diffusion with complete absorption, *i.e.* $c = 0$, at some boundary. We examine the 2D version of this problem, with the absorbing boundary at the $x = 0$ line. Consider what happens if we add one Green's function at a position $\bar{x} = (x = x', y)$ and subtract a Green's function at $\bar{x} = (x = -x', y)$. At $x = 0$ the values will completely cancel all along the y-axis for all time. Thus on the half-plane defined by $x \geq 0$ the $x = 0$ line acts like a perfect absorbing boundary, regardless of where we put $\bar{x}'$. Thus the new Green's function for this scenario is given by

$$G_D(x \geq 0, y, x' \geq 0, y', t) = G(x, y, x', y', t) - G(x, y, -x', y', t), \tag{69}$$

and one can see how this generalizes to many dimensions. The general solution for any initial condition $c(\bar{x}, 0)$ is then

$$c(\bar{x}, t) = \int G_D(\bar{x}, \bar{x}', t)c(\bar{x}', 0)\mathrm{d}\bar{x}' \tag{70}$$

for all $(x, x') \geq 0$. Figure 1c shows a time series with the $x = 0$ line at the top. Alternatively, we can construct a simple Neumann boundary condition, where we do not allow any flux through the $x = 0$ line, *i.e.* $J(x = 0, y, t) = 0$, which is the same a reflecting boundary condition. Consider what happens if we add one Green's function at a position $\bar{x} = (x = x', y)$ and another at $\bar{x} = (x = -x', y)$. Whatever flux passes through the $x = 0$ line from the particle whose position is $x > 0$ is exactly replaced by the image flux from the particle with $x < 0$, thus $x = 0$ acts like a perfect reflecting boundary. The new Green's function for this scenario is given by

$$G_N(x \geq 0, y, x' \geq 0, y', t) = G(x, y, x', y', t) + G(x, y, -x', y', t), \tag{71}$$

and one can see how this generalizes to many dimensions. The general solution for any initial condition $c(\bar{x}, 0)$ is then

$$c(\bar{x}, t) = \int G_N(\bar{x}, \bar{x}', t)c(\bar{x}', 0)\mathrm{d}\bar{x}' \tag{72}$$

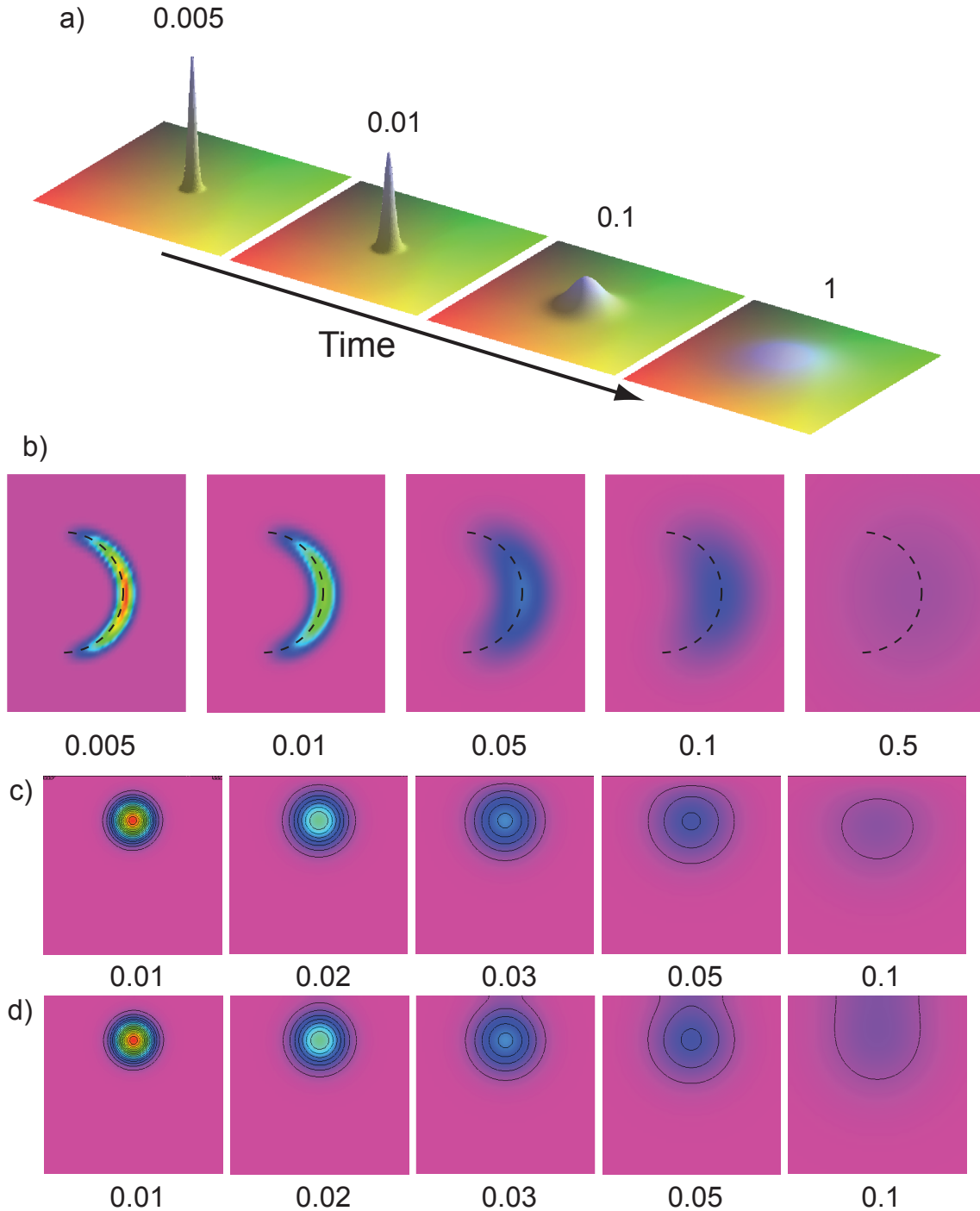for all $(x, x') \geq 0$. Figure 1d shows a time series with the $x = 0$ line at the top.

Figure 1: Diffusion in two dimensions. a) The evolution of a δ-function impulse is shown at four different scaled times, in units of Dt. The peak height of the distribution decays as $(Dt)^{-n/2}$. b) Evolution of semi-circle geometry (as indicated by the dashed line) created using the Green's function, shown at five scaled times, in units of Dt. c) Time series of the Green's function for the case where $c(x, y, t)|_{x=0} = 0$ in time units of Dt. d) Time series of the Green's function for the case where $\partial c(x, y, t)/\partial x|_{x=0} = 0$ in time units of Dt.

The reader can then imagine how other interesting scenarios could be constructed in n dimensions using the idea of images.

First Passage Times using Images

The combination of Green's functions and images is a powerful tool for exploring other dynamic aspects of diffusion. A classic problem is to determine the rate of arrival of particles to a certain portion of physical space, and in many interesting instances, a specific area of 'phase space.' For instance, say you wanted to know how long it would take a particle that starts at some position $\bar{x}'$ to reach some region $\delta\Gamma$ (where everything that is not $\delta\Gamma$ we just call Γ)? Since diffusion is not a deterministic process, the result will be a distribution of arrival times for a given set of identical particles all obeying the same boundary and initial conditions. In some instances that distribution is amenable to calculating a mean rate of arrival, or the 'mean first passage time', and in other cases the distribution is amenable to calculating the median rate of arrival, in which case we call this the 'median first passage time.'

Probably the easiest way to conceptualize this problem is to consider all the individual trajectories a particle might take that lead to $\delta\Gamma$ from $\bar{x}'$ and take a time t, taken with their relative probabilities of occurence. For instance, there are higher probability paths starting from $\bar{x}'$ that lead relatively directly to the region $\delta\Gamma$, while other less likely paths might travel far from the starting point before coming back to $\delta\Gamma$, as schematically shown in Fig. 2a. This defines a so-called 'path integral', where one would sum all the (infinite) paths that lead to $\delta\Gamma$ in a time t. The challenge with this route is that it is tremendously difficult to enumerate all of these paths in a way that is easy to manipulate. However, this is precisely how one would setup a stochastic simulation to measure the distribution of arrival times, that is, one would simulate the paths of many identical particles and simply measure what fraction of particle trajectories arriving in $\delta\Gamma$ between t and $t + \Delta t$. Toward the end of this section, we will show computed results as compared to our analytical calculation for a tractable example problem. But first, let's discuss the problem in more general terms.

Recall that the solution to the diffusion equation, $c(\bar{x}, t)$, is the probability of finding a particle in a spatial region near $\bar{x}$ at a particular point in time, which is *not* the same as asking for the probability that the particle will enter the region near $\bar{x}$ for the *first* time at a particular point in time. The probability one calculates in $c(\bar{x}, t)$ encompasses all the phase-space trajectories that lead to the region near $\bar{x}$ at that time, including all trajectories that entered that same spatial region at earlier times and then returned again. Thus the local probability around $\bar{x}$ is made up of a mixture of trajectories; some arriving there for the first time, and other trajectories that have been to that region any number of times before. Let us assume that the boundary between our region of interest, $\delta\Gamma$, and the rest of space, Γ, is defined by the parametric equation $\bar{\gamma}(\bar{s})$, as shown in Fig. 2b. If we are working in a space with n dimensions, the boundary of $\delta\Gamma$ is parameterized by $\bar{s}$ with $n-1$ dimensions (e.g. a 1D line defines a bounded area in 2D space, a 2D surface defines a bounded volume in 3D space, and so on). Considering that the probability density $c(\bar{x}, t)$ is the result of all the possible trajectories that lead to a certain region at a certain time, calculating the fraction of trajectories that first enter the region $\delta\Gamma$ at a time t requires that trajectories entering the region be immediately removed from the pool of all possible trajectories (so that those trajectories do not re-enter at later times). In terms of $c(\bar{x}, t)$, that amounts to removing any probability that enters the region $\delta\Gamma$ with an absorbing boundary condition along $\bar{\gamma}(\bar{s})$. Then the distribution of first arrival times is the rate of arrival of trajectories that enter $\delta\Gamma$ and never leave, or simply the flux into $\delta\Gamma$ at the boundary

$\bar{\gamma}(\bar{s})$.

If we denote $G(\bar{x}, \bar{x}', t)$ as the Green's function for diffusion in the region $\Gamma + \delta\Gamma$, then the challenge to calculating the first passage time distribution is to find the Green's function that corresponds to the solution with all appropriate boundary conditions in Γ, but now with the additional boundary condition that

$$G_\Gamma(\bar{x}, \bar{x}', t)\big|_{\bar{x}=\bar{\gamma}(\bar{s})} = 0, \tag{73}$$

where we denote this new Green's function by G_Γ. This Green's function can be subject to any number of other distinct boundary conditions, and may even exist on a potential energy landscape where particles collect or drift to certain locations. Recall that the flux for diffusion is

$$\bar{J} = -D\nabla G_\Gamma, \tag{74}$$

and in this case we want to integrate around the boundary that fraction of the flux that crosses the boundary and enters $\delta\Gamma$. The fraction of the flux that enters $\delta\Gamma$ flows perpandicular to the boundary. Mathematically, that is the dot product of the flux (a vector field) and the unit normal of the parametric curve describing the boundary, integrated around the boundary, which can be written as

$$P(t, \bar{x}') = -D \int_{\bar{\gamma}(\bar{s})} \left[\left(\nabla G_\Gamma(\bar{x}, \bar{x}', t)\right)\big|_{\bar{x}=\bar{\gamma}(\bar{s})} \cdot \hat{n}(\bar{s}) \right] \mathrm{d}\bar{s}. \tag{75}$$

The function $P(t, \bar{x}')$ is then the probability density for a particle starting at $\bar{x}'$ to reach $\delta\Gamma$ for the first time at a time t. Said differently, the probability that the particle will first enter $\delta\Gamma$ between t and $t + \Delta t$ is the integral of $P(t, \bar{x}')$ from t to $t + \Delta t$. While it is certainly most informative to know the distribution of arrival times, often we simply want to know on average, how long must we wait for a particle to arrive, given by

$$\int_0^\infty (P(t, \bar{x}') \cdot t)\mathrm{d}t = \tau_1(\bar{x}'). \tag{76}$$

However, if the tail of $P(\bar{x}', t)$ decays with a power of t^{-2} or slower, the average time for arrival will diverge, and hence the mean first passage time is infinite. Despite this possible complication, the distribution will always have a most likely time of arrival (or possibly more than one), and even more informatively, all distributions will have a median time of arrival, as defined by the implicit equation

$$\int_0^{\tau_{1/2}} P(t, \bar{x}')\mathrm{d}t = \frac{1}{2}. \tag{77}$$

The median time of arrival is the time it will take half the particles that will enter $\delta\Gamma$ to enter $\delta\Gamma$, keeping in mind that depending on the G_Γ and the boundary conditions, not all particles necessarily arrive at $\delta\Gamma$.

One can also calculate the distribution of first passage times going from one region (not just a point) to another region. For instance, if the initial particle starts off with a (properly normalized) spatial probability distribution function $c(\bar{x}', 0)$ that resides in Γ, then due to the linearity of the diffusion equation, we know that this can be written as the weighted sum over all the possible single particle first passage time distributions, given by

$$P_\Gamma(t) = \int_\Gamma c(\bar{x}', 0)P(\bar{x}', t)\mathrm{d}\bar{x}'. \tag{78}$$

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To see these concepts in action, let us consider a fairly simple 2D example. Consider a particle that is placed at a position $\bar{x}' = (x', y')$, and let us assume that the particle starts in the left half plane with $x' < 0$. For a given $\bar{x}'$, what is the distribution of arrival times to the right half plane, where $x > 0$? We already know from eqn. 60 that the Green's function for *free* diffusion on a plane is

$$G(\bar{x}, \bar{x}', t) = \frac{e^{-\frac{|\bar{x} - \bar{x}'|^2}{4Dt}}}{4\pi Dt}. \tag{79}$$

As discussed above, we need to calculate the flux across the boundary of interest – in this case the $x = 0$ line – and hence we need to find a Green's function that has the property that $G(x = 0, y, x' < 0, y', t) = 0$. As we saw in the previous section on images, this situation can be constructed by combining two free-diffusion Green's function into the form

$$G_\Gamma(\bar{x}, \bar{x}', t) = \frac{e^{-\frac{|\bar{x} - \bar{x}'|^2}{4Dt}} - e^{-\frac{|\bar{x} + \bar{x}'|^2}{4Dt}}}{4\pi Dt}. \tag{80}$$

The boundary of interest is simply the y-axis, hence $\bar{\gamma}(s) = (0, s)$ and the unit normal to that boundary is $\hat{n}(s) = (-1, 0)$. Then using the eqn. 75, the first passage time distribution is calculated from

$$P(t, \bar{x}') = D \int_{-\infty}^{\infty} \frac{\partial}{\partial x} G_\Gamma(x, y, x', y', t) \bigg|_{x=0} \mathrm{d}y, \tag{81}$$

which can be solved explicitly to find

$$P(t, \bar{x}') = \frac{x'}{t^{3/2}} \frac{e^{-\frac{x'^2}{4Dt}}}{\sqrt{4\pi D}}. \tag{82}$$

This example has a combination of interesting properties. First note that the integral

$$\int_0^\infty P(t, \bar{x}') \mathrm{d}t = 1, \tag{83}$$

which means that given enough time, every particle will eventually cross over the $x = 0$ line. Second, notice that for long times, the distribution takes the asymptotic form $P(x', t) \propto \frac{x'}{t^{3/2}\sqrt{D}}$, meaning there is no finite *mean* first passage time, however, the *median* first passage time is given by the implicit equation

$$\mathrm{erf}\left[\frac{x'}{\sqrt{4D\tau_{1/2}}}\right] = -\frac{1}{2}, \tag{84}$$

which can be approximated by

$$\tau_{1/2} \simeq \frac{4x'^2}{\pi D}. \tag{85}$$

It is also interesting to note that, in general, we can find the expected, first-order *fluctuations* in the arrival time distribution. Consider that if we have N particles, the expected number of particle arrivals in Δt is

$$\langle n(t, \Delta t) \rangle = N \int_t^{t + \Delta t} P(\bar{x}', t) \mathrm{d}t. \tag{86}$$

For a small time window, Δt, the expected number of arrivals is small and by our definition, the expected number of arrivals does not depend on the number of previous arrivals, hence we can view the arrival of particles to the region of interest as a Poisson process. Thus within a time
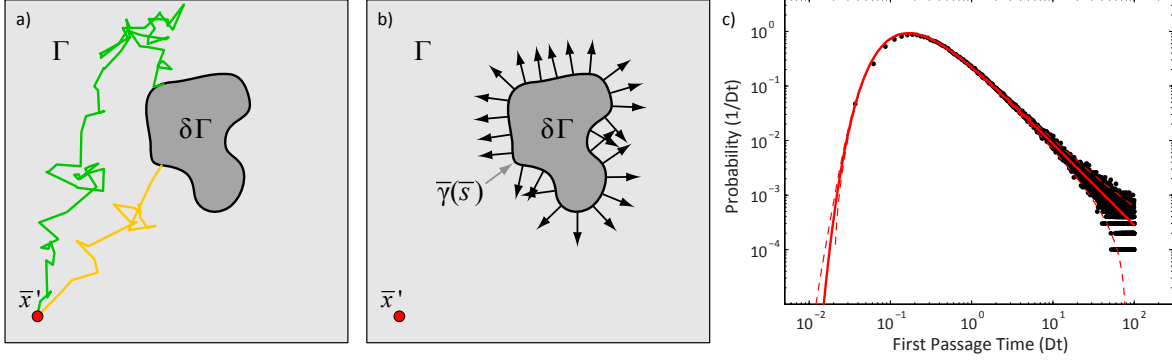
Figure 2: Distribution of first passage times. a) A schematic showing the starting point of a particle, $\bar{x}'$, with two possible Brownian paths terminating in the region of interest $\delta\Gamma$. The orange path is takes less time than the green path to reach $\delta\Gamma$. b) A schematic defining the boundary $\bar{\gamma}(\bar{s})$ with the unit normal vectors to the boundary used to calculate the flux across the boundary. c) Plot of the first passage time distribution where $\delta\Gamma$ is the half-space in n dimensions. The solid red line is the analytical result from eqn. 82, while the black dots are the results from a stochastic simulation of the first passage time into the half-space. The red dashed lines are plus and minus two standard deviations of the expected fluctuation in the arrival rate of particles into $\delta\Gamma$.

window Δt, we expect the fluctuation about the mean to be approximately $\sqrt{\langle n \rangle}$, as shown in Fig. 2c.

Finally, it is also interesting to note that the solution to this example problem is valid for any half-space in any number of dimensions, yet another result from the separability of the original diffusion equation.