COMPUTATIONAL EXPERIMENTS IN MODERN PHYSICS

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MODERN PHYSICS LABORATORY - PHYSICS 155

Computational Studies of Diffusion and Reactions in One Dimension

I. Introduction

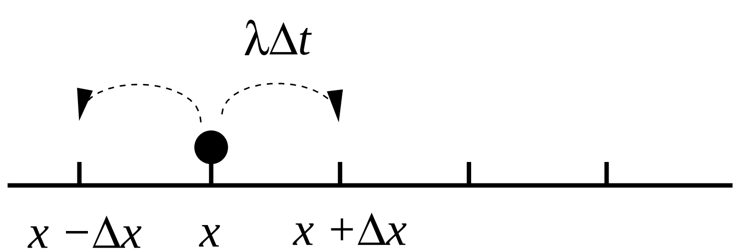
In this laboratory you will perform computational investigations of diffusing particles and reactions between diffusing particles. This lab is really a numerical *experiment* on particles undergoing Brownian motion. As such, many of the same considerations apply here as do in a physics laboratory: The experimental apparatus needs to be constructed and tested (the computer program has to be written and tested on known cases); if the program is a simulation, you must determine what are the relevant quantities to measure, how to measure them and how to quantify your uncertainties.

II. Studies of Single Particle Diffusion

A. Analytical Investigation of the Probability Distribution.

Consider a small particle that is placed in a solvent. If the particle is light enough, the random motions of the colliding solvent molecules will produce a small random motion (Brownian motion) of the particle. Let us first consider such motion confined to one dimension. In the one dimensional version of Brownian motion, the particle is bumped randomly to the left or right by a random amount, at random time intervals.

Let us now consider a simplified model: At each fixed time interval Δt, the particle hops randomly to the left or right a distance Δx with some probability to a neighboring site or remains fixed at its initial site. Let λ be the probability per unit time of a hop in either direction. For example, the probability for a hop to the right in time Δt is then $\lambda \Delta t$.



Let $P(x,t)$ be the *probability* that the particle is found on site x at time t. We will write down an equation for P rather than for the position of the particle, x. The probability $P(x, t + \Delta t)$ that the particle is found at x at time $t + \Delta t$ is now the sum of two parts:

the probability that it remains at x plus the probability that it hops onto x from one of the neighboring sites to the left or right. Therefore,

$$P(x,t+\Delta t) = (1-\lambda\Delta t)P(x,t) + \frac{1}{2}\lambda\Delta t(P(x+\Delta x,t) + P(x-\Delta x,t))$$

In the theory of stochastic processes, this equation is sometimes called a *master equation*. Moving the first term on the right hand side to the left hand side, we recognize this combination as,

$$P(x,t+\Delta t) - P(x,t) \approx \Delta t\frac{\partial P}{\partial t}$$

Now look at the spatial part of the equation. We iterate the discrete formula for first derivatives

$$\frac{df}{dx} \approx \frac{f(x+\Delta x) - f(x)}{\Delta x}$$

to obtain an expression for second derivatives:

$$\frac{d^2 f}{dx^2} \approx \frac{d}{dx}[\frac{f(x+\Delta x) - f(x)}{\Delta x}] \approx \frac{f(x+2\Delta x) - 2f(x+\Delta x) + f(x)}{\Delta x^2}$$

The equation for P now reads:

$$\Delta t\frac{\partial P}{\partial t} = \frac{1}{2}\lambda\Delta t\Delta x^2\frac{\partial^2 P}{\partial x^2} \quad \text{or} \quad \frac{\partial P}{\partial t} = D\frac{\partial^2 P}{\partial x^2} \tag{1}$$

where D, the diffusion constant has been defined as $D = \frac{1}{2}\lambda\Delta x^2$. The second of the two equations above is called the diffusion equation. The solution to this partial differential equation, $P(x,t)$, expresses the *probability distribution* for a free brownian particle. Roughly speaking, $P(x,t)\Delta x$ is the probability that the particle is found between x and $x+\Delta x$ at time t. The probability that the particle is found in the interval $[a,b]$ is $\int_a^b P(x,t)dx$.

i. Show that $t^{-1/2}e^{-x^2/4Dt}$ satisfies the diffusion equation (Equation (1)).

ii. Show that

$$P(x,t) = (\frac{1}{4\pi Dt})^{1/2}e^{-x^2/4Dt}$$

is a properly *normalized* solution. That is, the total probability of finding the particle somewhere, at any time, is one. i.e. $\int_{-\infty}^{\infty} P(x,t)dx = 1$. This particular solution describes the subsequent behavior of a particle located at $x=0$ when $t=0$.

iii. Show that the average distance squared that a particle moves from zero is $\langle x^2\rangle = \int_{-\infty}^{\infty} x^2 P(x,t)dx = 2Dt$.

Notice that we quickly rephrased the description of the motion of a single brownian particle into a description of the particle's probability distribution. You may ask: "Is there any description of the particle that resembles our old equations of motion?"

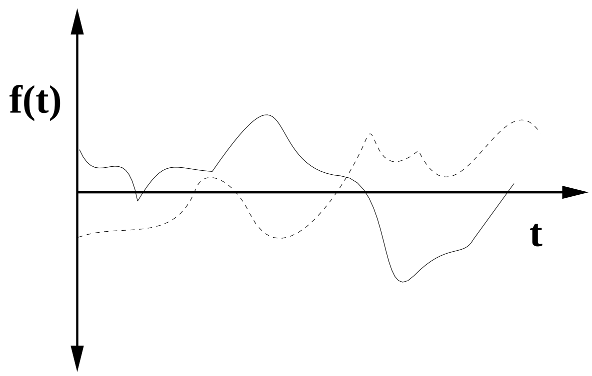
B. Analytical Investigation of the Brownian Trajectory.

The equation of motion for a brownian particle is simply Newton's second law of motion but with a special force term.

$$m\frac{d^2x}{dt^2} = -\gamma\frac{dx}{dt} + f(t) \tag{2}$$

The first term on the right hand side corresponds to frictional (velocity dependent) damping of the brownian particle motion. The second term is an external time-dependent force corresponding to the random influence of the solvent bath that pushes the brownian particle around. $f(t)$ is therefore a *random* function and the differential equation above is called a *stochastic differential equation* or *Langevin equation*.

What is meant by a "random function?" Roughly speaking, it is a function whose value at one instant in time is unrelated to its value a short time later or before. Depicted below are some examples of plausible random functions.



To summarize: the ingredients of brownian motion are: 1) a random force, $f(t)$ and 2) a means for dissipating the energy pumped into the system by $f(t)$—namely, frictional damping.

How does one *solve* a stochastic differential equation such as (2)? Or, perhaps more appropriately, what sort of useful information can we extract from a stochastic differential equation? The solution, $x(t)$, for one particular choice or *realization* of random functions is not very useful. We are interested in properties of $x(t)$ that are independent of a particular realization of $f(t)$ and we arrive at these properties by studying the behavior of $x(t)$ *averaged over all realizations* of $f(t)$. But before going further, let us make some reductions to equation (2) to make it more amenable to a computational treatment.

First, we are interested in how a small mass particle behaves in the solvent. Therefore, we will simplify (2) by letting $m \to 0$ and, therefore, the left hand side is zero. (The presence of the acceleration term does not qualitatively change the brownian motion.) Second, we will discretize the equation in time by making the familiar approximation for the time derivative:

$$x_{n+1} - x_n = \frac{\Delta t}{\gamma} f(t_n) \quad \text{or} \quad x_{n+1} = x_n + f_n \tag{3}$$

where the time step, Δt, and the frictional parameter, γ, have been absorbed into the definition of f_n. f_n is now a discrete random variable; we will look at the simplest case where f_n only takes on the values ± 1. A particular realization of f might be the sequence

$$\{f_j\} = \{\cdots +, +, +, -, +, +, -, +, -, -, +, -, -, +, -, +, -, -, -, -, +, \cdots\}$$

where $+$ and $-$ stand for $+1$ and -1. The random value f_n determines whether x_n is incremented or decremented by 1 to obtain x_{n+1}. The sequence of x values obtained for a particular sequence, $\{f_j\}$, are what we call a *random walk* on a one-dimensional lattice.

The strategy will be to solve equation (3) for an average of x^2 over all realizations of f, denoted by $\langle x^2 \rangle_f$; specifically, the angle brackets mean: "average the squared displacement from the origin, x^2, over the set of all possible sequences, $\{f\}$." For example, if the sequences were a finite length, N, the averaging operation would involve an average over the 2^N possible sequences. (Notice that the notation "$\{f\}$" means "the set of all possible sequences" as opposed to "$\{f_j\}$" which denotes a particular sequence like the one above.)

Consider the equation for x_{n+1} at the n^{th} step. There are two possibilities for the value of x_{n+1}:

$$x_{n+1} = x_n + 1 \quad \text{or} \quad x_{n+1} = x_n - 1$$

The (infinite) set of all possible sequences, $\{f\}$, may be separated into two infinite subsets based upon the value that appears in the n^{th} entry of each sequence. For instance, if the sequence below

$$\{\cdots +, +, +, -, +, +, -, +, -, -, \underbrace{+}_{n^{\text{th}}\,\text{entry}}, -, -, +, -, +, -, -, -, -, +, \cdots\}$$

has a $+$ for its n^{th} entry, it is placed in the subset $\{f_+\}$. Symbolically, the set of all sequences is the union of two disjoint sets (sets with no elements in common):

$$\{f\} = \{f_+\} \cup \{f_-\}$$

Now consider the equation for x_{n+1}^2 at the n^{th} step: $x_{n+1}^2 = x_n^2 + 2x_n f_n + 1$. The equation for the *average* value of x_{n+1}^2 is then:

$$\langle x_{n+1}^2 \rangle_f = \langle x_n^2 \rangle_f + \langle 2x_n f_n \rangle_f + 1$$

But the term involving f can be rewritten as the average over the two sets, $\{f_+\}$ and $\{f_-\}$,

$$\langle 2x_n f_n \rangle_f = \frac{1}{2}\left(\langle 2x_n f_n \rangle_{f_+} + \langle 2x_n f_n \rangle_{f_-}\right) = \langle x_n \rangle_{f_+} - \langle x_n \rangle_{f_-} = 0$$

The last two averages are equal and cancel out because up to the n^{th} entry, the two sets are identical.

i. In fact, the last two terms are independently zero. Show that this is true. That is, show that

$$\langle x_n \rangle_f = 0$$

ii. Find an equation similar to equation (4) directly below for $\langle x_{n+1}^4 \rangle_f$.

We are now left with the following equation for the average squared displacement of the particle after $n+1$ steps:

$$\langle x_{n+1}^2 \rangle_f = \langle x_n^2 \rangle_f + 1 \tag{4}$$

This equation is iterated to give the solution $\langle x_n^2 \rangle_f = n$. Since n is the discrete time variable, this result is simply the discrete version of the result (from sec. II. a. iii.) $\langle x^2 \rangle = 2Dt$ but obtained in a completely different way. It is significant that the diffusion equation (1), a parabolic PDE, has an equivalent description in terms of a Langevin equation for a *single particle*, whereas the wave equation, a hyperbolic equation, does not.

C. Computational Investigations of a Single Brownian Particle

The first step is to write a program that simulates the Langevin equation (3). A crucial part of the simulation of a stochastic equation is the generation of (pseudo) random numbers. For our purposes the native library random function for whatever language you are using will be sufficient. In the `gcc` version of the `C` language, the function `rand()` returns random values between `0` and `RAND_MAX`. (Function `rand()` and parameter `RAND_MAX` must be included with `#include<stdlib.h>`.) The function `ranpm()` in the code appearing in this manual returns a random `+1` or `-1`. Look at `ranpm()` and understand how it works.

Set up an integer array of dimension L (`int lattice[L]`). This will store the number of particles at each of the L sites of a one-dimensional lattice. Our initial studies will involve only one particle on the entire lattice, therefore, only one element of `lattice[]` will be nonzero. Choose an initial position for the particle—most conveniently, this is the site $L/2$. Your program should simulate the random propagation of the particle, in positive and negative directions, based on the outcome of the `ranpm()` function at each time step.

What happens when the particle hits the end of the lattice? There are two possible choices, corresponding to different physical properties of the boundaries: 1) The particle simply disappears and the simulation is over or 2) The particle reappears at the opposite end of the lattice. (These are the Langevin equation equivalents of *boundary condtitions* applied to the analytical solution of the diffusion PDE, equation (1).) Implement type (2), or *periodic*, boundary conditions, at first. To do this, make use of the `mad(x)` definition appearing in the preprocessor of example code:

```
#define mad(x) ((x+L)%L)
```

This statement defines periodic integers, e.g.,

$$-2 \sim L-2, \quad -1 \sim L-1, \quad 0 \sim 0 \quad \ldots \quad L-1 \sim L-1, \quad L \sim 0 \quad \ldots$$

(In **FORTRAN**, the modulo operation is an intrinsic function and `y=x%L` is replaced with `y=mod(x,L)`.) Over what range of `x` does this `mad` definition do what it is supposed to do?

The Langevin equation (3) is solved for the time dependence of various quantities averaged over *realizations* of the random function f. The utility of a computer simulation is that we can generate an approximate solution to the diffusion equation—a partial differential equation—by considering the repeated behavior of a brownian particle with a large (but not infinite) number of computer generated realizations of the random function f_n. Each one of these "repeats" will be called a *trial*; the particle will be placed at the same starting point and a set of T random hops (+ and -) will be generated. You will keep track of where the particle lands after each trial of T hops by incrementing the corresponding entry in an array of L counters. Call this array `probability[L]` as it will reflect the *probability* distribution of the particle and therefore the solution to the diffusion equation at time T.

i. After M trials, plot the array `probability[]`. Now normalize the probability distribution by dividing each element by M and plot the resulting function. (This should be a `float` divide.) Now compare `probability[l]/M` with the Gaussian solution to the diffusion equation

$$P(x,t) = (\frac{1}{4\pi Dt})^{1/2} e^{-x^2/4Dt}$$

where $x \leftrightarrow (\mathtt{l} - \mathtt{L}/2)$ and $t \leftrightarrow \mathtt{T}$. By comparison at several times `T`, determine the diffusion coefficient, D.

ii. Plot the average squared displacement $\langle(\mathtt{l} - \mathtt{L}/2)^2\rangle$ as a function of the number of hops, `T`. When does the linearity begin to fail? Compare this result to the analytical result $\langle x^2\rangle = \int_{-\infty}^{\infty} x^2 P(x,t)dx = 2Dt$ where $t \leftrightarrow \mathtt{T}$ for various times `T` and determine the diffusion coefficient D this way, as well.

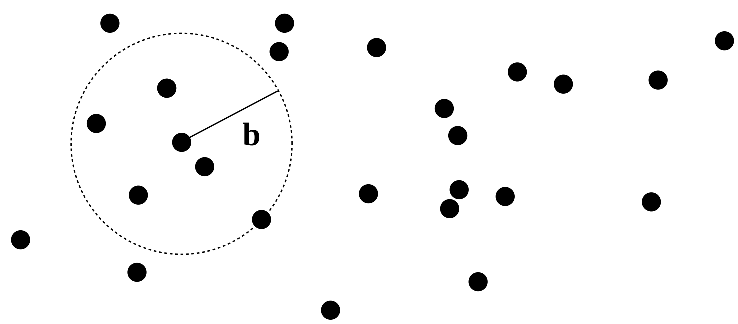
iii. Adapt your program for a single Brownian particle in two dimensions and three dimensions. Using the method in item (ii.), find the diffusion coefficients, $D_{2\mathrm{d}}$ and $D_{3\mathrm{d}}$.

III. Studies of Interacting Brownian Particles

A. Analytical Investigation of the Law of Mass Action (LMA).

Consider a bi-molecular chemical reaction between two identical species taking place in a solvent. If the solvent is not shaken or stirred, the reactant molecules move about exclusively through Brownian motion. Furthermore, we will consider this chemical reaction to be *irreversible*: once the reactants bond together, they will not unbond. Suppose there are intially N_0 reactant particles, how many particles are left after time t, $N(t)$? How does $N(t)$ depend upon the diffusion coefficient, D and the intrinsic reaction rate of the particles? These questions are probably familiar from an introductory chemistry course but they turn out to be enormously difficult to answer in a rigorous way.

Consider N particles randomly distributed throughout a volume V containing the solvent. The volume density of particles is then $n \equiv N/V$. Let's suppose that each particle is capable of reacting with other particles within a *reaction volume* of size b^d, where d is the spatial dimension.



Focusing on a single "test" particle, there are approximately $b^d n$ potential reactant particles within the reaction volume of the test particle. If the probability per unit time of a reaction between proximate particles is λ, then the probability that the test particle reacts and "vanishes" (remember the reaction is irreversible) in time dt is $\lambda b^d n dt$. Such reactions are taking place for all of the N reactant particles; therefore, the number of particles disappearing in time dt is $dN = -N\lambda b^d n dt$. We then arrive at the standard first order rate equation:

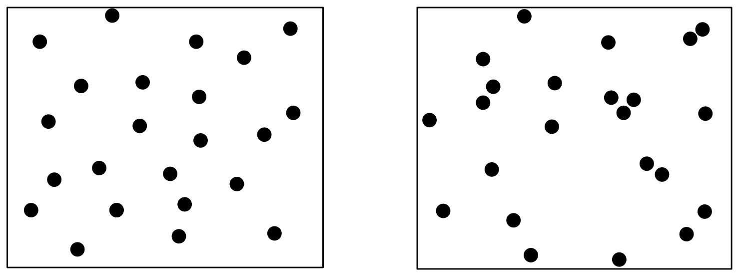
$$\frac{dn}{dt} = -\kappa n^2$$

where $\kappa \equiv \lambda b^d$. If the initial density of particles is n_0, the time dependence of n is given by

$$n(t) = \frac{n_0}{1 + n_0 \kappa t}$$

For long times, $n(t) \propto 1/\kappa t$. We will refer to the behavior described by the rate equation (5) as the Law of Mass Action (LMA). [note: LMA has a slightly different meaning here than in a chemistry text. However, the *argument* used above to derive equation (5) is the same argument used to derive the "chemistry" LMA and has the same flaws. We will now examine this argument more critically.]

The argument given above relies primarily upon one assumption: Each reactant particle sees, in its reaction volume b^d, a uniform distribution of other reactant particles. However, it is not obvious that this is true. If we consider the global distribution of reactants after the reaction has been allowed to progress for some time, we expect the distribution of particles to appear as if the particles avoid one another. It is relatively less likely to find two particles close to one another because "close" means there had been the potential for a reaction in the past which would have annihilated the particles. The two figures below illustrate a random distribution of particles (right) and a random distribution in which pairs of particles that are close have been removed (left). The two figures have been adjusted, though, to have the same overall density.



The derivation of the rate equation assumes, in some sense, that after reactions take place, the solvent is stirred to re-randomize it. In this way, *correlations* between particles resulting from their fortuitous avoidance of reactions in the past are never allowed to build up thereby reducing the number of available reactants within a distance b of the test particle. If you are having trouble following—or believing—this subtle argument, a computer simulation may clarify things a bit.

B. Computational Investigation of Reactions Between Brownian Particles

It is a simple matter to modify your one dimensional Brownian motion program to study Brownian particles that meet and annihilate. Now the array `probability[]` will have many nonzero entries correponding to the your chosen initial configuration of reacting particles. Each site will be visited and each particle moved according to the same random rules as before. However, when particles land on the same site, they are annihilated with some probability, κ. There are two easy choices for κ: $\kappa = 1$ (the particles always annihilate) or $\kappa = 1/2$ (easily implemented with the existing function `ranpm()`).

i. For a lattice of L sites, find $n(t)$ where $n \equiv N/L$ and N is the total number of surviving particles at time t. Choose ordered initial conditions at first (e.g. alternating sites occupied.) Again, you will have to make use of multiple trials—but some thought about the most efficient way to compute $n(t)$ is required here. The number of simulation time steps, t, should be chosen consistent with L.

ii. We expect $n(t) \propto \kappa t^{-\alpha}$ where $\alpha = 1$ for LMA behavior. Therefore,

$$\log n(t) \approx \log \kappa - \alpha \log t$$

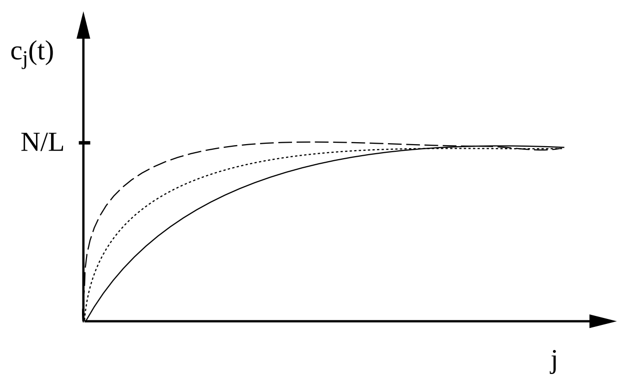
and a plot of $\log n(t)$ versus $\log t$ should give α as the slope and $\log \kappa$ as the intercept. Do your simulations support LMA behavior in one dimension?

It is useful to examine another quantity: the correlation function. The correlation function is another probability function like $P(x,t)$, however it is a *conditional* probability function.

Given that there is a particle on site i, what is the probability that there is a particle on a site j sites away? Let $n_i(t)$ be the number of particles at site i. (This is just `probability[i]` at a given time t in the simulation; after any reasonable t, $n_i(t)$ should be 0 or 1.) The correlation function $c_j(t)$ is then defined as:

$$c_j(t) \equiv \frac{1}{N} \sum_{i}^{L} n_i(t) n_{i+j}(t)$$

Qualitatively, we expect $c_j(t) \approx 0$ for small j because two particles close together are likely to have reacted and $c_j(t) \approx N/L$ as j grows large. For instance, if j is larger than average brownian displacement of a particle in time t, $d(t)$, (computed to be $d(t) \sim t^{1/2}$) then two particles a distance $j > d(t)$ apart have never *had* the opportunity to annihilate. Given that there is a particle at site i, the probability of a particle at $i + j$ is simply N/L. The three plots shown on the graph below are the correlation function at three times; the correlation function $c_j(t)$ for which t is largest has the *weakest* correlation at short distances (solid line). The weak correlations at short distances is referred to as the *correlation hole*.



To get a result for $c_j(t)$ resembling the graph above will invove averaging the correlation function over many trials (just as with $P(x,t)$). You will also have to pay attention to whether the diffusion length $d(t)$ is larger than L.

iii. Compute $c_j(t)$ for several simulation times t. Using a log-log plot, as described in (ii), find the correlation exponent, β, defined by

$$c_j(t) \sim j^{\beta}$$

Qualitatively describe the behavior of the correlation hole for increasing times. What are the implications for the LMA argument?

iv. Repeat this simulation for $d = 2$ and $d = 3$ (if possible). When $d \geq 2$, what is the behavior of the correlation hole in time?

The reason for the breakdown in LMA in one dimension may be understood as follows: In one dimension, a brownian particle visits, in simulation time t *all* of the sites in its diffusion length, $d(t) \sim t^{1/2}$. At large enough times, a given particle (even if only weakly reactive) will have reacted with any "target" in its exploration length $\sim t^{1/2}$. Thus, in a system with L sites, the number of particles varies at large t as $L/t^{1/2}$ (L divided by the empty volume between surviving particles.) Therefore $N \sim t^{-1/2}$.