

Introduction to Brownian Motion

L. Fillion

Introductory Remarks

This is first version of lecture notes and will be used in the academic year 2016 - 2017. While care has been taken to avoid mistakes, there are sure to be some mistakes/typos to be found. The author apologizes in advance for the inconvenience this may cause. All feedback, be it regarding mistakes, confusing text, typos, etc. will be sincerely appreciated and used in the future to improve this set of lecture notes.

The contents of these lecture notes have heavily drawn on statistical mechanics text books, and lecture notes.

Suggested extra reading material:

1. Lecture notes on Brownian Dynamics by Albert Phillipse (available on blackboard)
2. Colloidal Hydrodynamics, by Theo van de Ven
3. An Introduction to Dynamics of Colloids, by Jan Dhont

Chapter 1

Introduction to Brownian Motion

When we think of a liquid or gas (at finite temperature), the picture that comes to mind is a number of particles, i.e. atoms or molecules, zooming around in space, occasionally colliding with each other. Instinctively we know that if we colour a region of gas or liquid, the coloured region is slowly diluted and the entire liquid or gas is slowly colored (roughly homogeneously). This is due to the *diffusive* motion of the particles. Via their interaction with one another, they move around like a drunken man, continuously changing their velocity and direction at random due to the collisions. This motion is what we refer to as diffusion. See e.g. Figure 1.1.

If we place larger particles (lets say up to a few microns in size) in a liquid it is somewhat more difficult to predict what it would do. Do they stay put? Move inertially? On an experimental level, this problem was highlighted by Robert Brown in 1827, a Scottish botanist who was studying pollen grains in water. Some particles which “escaped” the pollen seemed to move around randomly in the water. The question arose: what “drives” these particles around? What causes this seemingly erratic motion? Were they somehow alive? The last of these questions was answered when similar behaviour was also observed in clearly non-living materials, for instance silica and clay. So, if not alive, what was the origin of this motion?

Although a number of authors contributed to this debate, our current understanding of this motion is usually attributed to Einstein. (For a more thorough historical account of the developments related to Brownian, please see the lecture notes of Albert Philipse available on blackboard.) In a publication in 1905, he described the relations governing the behaviour of these small particles in a liquid moving around erratically, a motion today frequently referred to as Brownian motion. Perhaps the most striking of his results is simply that the mean squared displacement of the particles is proportional to time. Specifically, $\langle r^2(t) \rangle = 2dDt$, where d is the dimension of the system and D is referred to as the “self-diffusion constant”. This can be directly compared to what happens to a particle when it moves inertially: in a system with zero acceleration the position is proportional to time, i.e. $r(t) = vt$ where v is the velocity. Hence, one can distinguish diffusive motion from inertial motion simply by looking at the behaviour of the mean squared displacement of a particle as a function of time.

Today we exploit this behaviour to great advantage. We can synthesize nano and micron-sized particles, which we call colloids, and since they move like atoms or molecules, they can self-assemble into a stunning variety of different materials. In addition to liquids and gases, they can be arranged into an enormous range of crystalline structures whose properties, i.e. electronic, photonic, etc, are exploited in

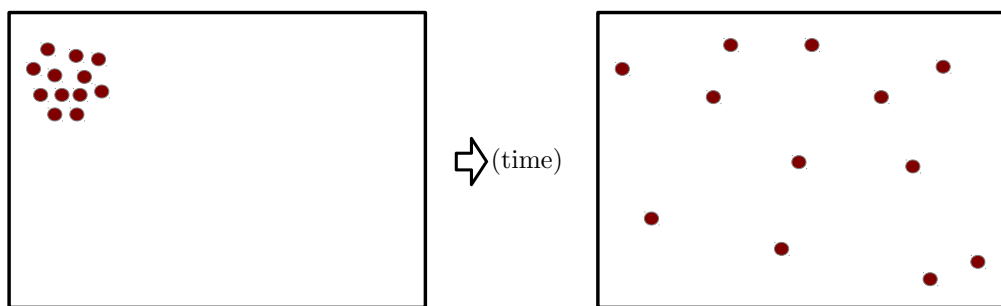


Figure 1.1: Example of diffusion; the random (diffusive) motion of the particles removes inhomogeneities hence the labeled particles grouped together on the left spread out such that eventually they are approximately evenly distributed throughout the available space. Note that there are a number of non-labeled particles in the background which are not depicted in this cartoon.

the design of “functional” new materials.

The goal of this set of lecture notes is to describe a number of different topics related to the diffusive motion of atoms, molecules, and colloids.

But first, let’s address the most simple question - what exactly *is* a colloid? Colloids are particles with at least one dimension somewhere between ~ 1 nm and ~ 1 μ m that are suspended in a solvent. Such particles are ubiquitous in everyday life. Many types of food are examples of colloidal systems, including e.g. milk, salad dressing, butter, and mayonnaise. Paints, toothpaste, and creams are other examples of colloidal systems. These systems can be composed of small solid-like particles suspended in a liquid or gas. For instance the fat droplets and protein clusters suspended in a water-like liquid which we call milk, or the solid particles suspended in air which we call smoke.

A colloidal system can also consist of liquid droplets suspended in another liquid, such as oil droplets suspended in water or foams composed of a gas phase suspended in a liquid or solid. In addition to many “natural” colloidal systems, material scientists are constantly designing and synthesizing new colloidal particles. See Figure 1.2 for examples of the types of colloidal particles chemists can synthesize today.

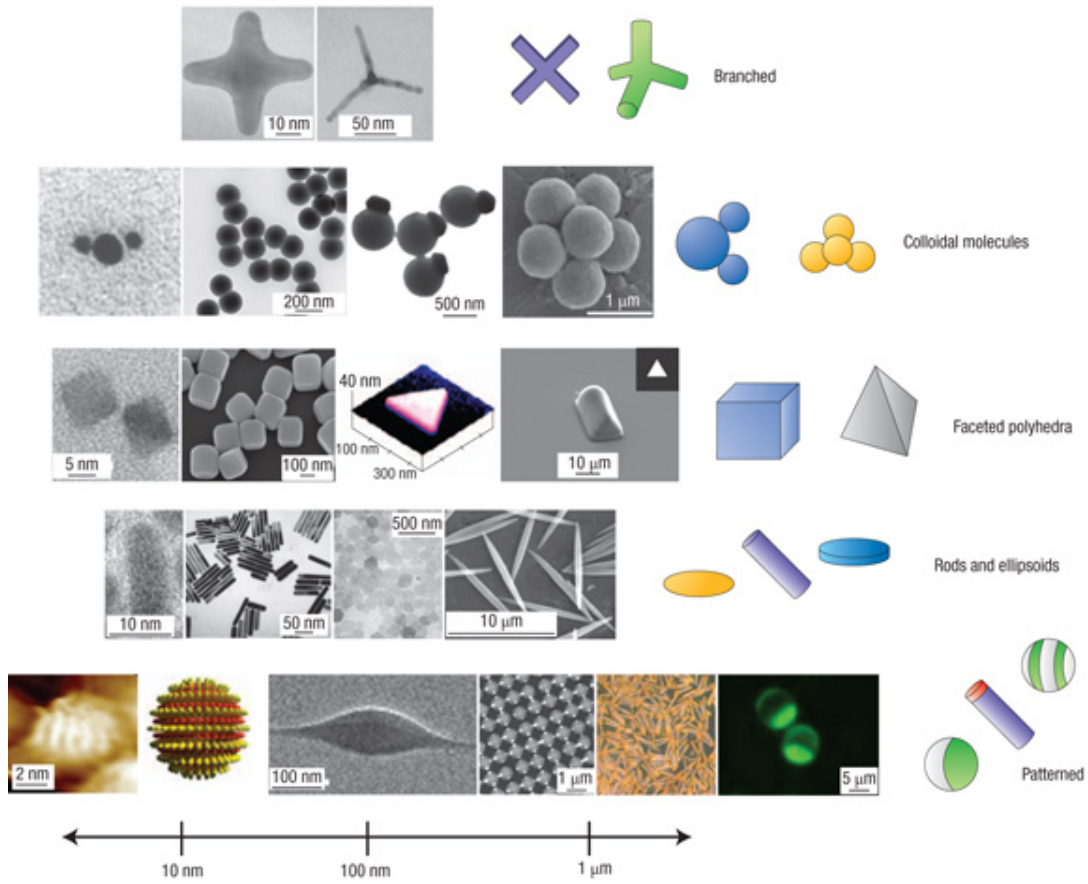


Figure 1.2: Overview of colloidal building blocks. Taken from Ref. [1].

Chapter 2

Brownian Motion of a Single Colloidal Particle

This section follows closely the discussion in “Colloidal Hydrodynamics” by Theo van de Ven.

2.1 Introduction

One way to examine Brownian motion is to revisit the way in which it was first discovered. Specifically, consider a single colloidal particle sitting in a solvent (a nice movie depicting this behaviour can be found on the wikipedia page https://en.wikipedia.org/wiki/Brownian_motion). If we imagine studying this system by taking pictures of the system using a camera, we will see the particle perform motion similar to that shown in Figure 2.1a). Assume that there are n snapshots per second: this means that the time interval Δt between snapshots is $1/n$.

We can then determine the “apparent” velocity exhibited by the particle. Specifically, if we look at Figure 2.1a), we would measure an apparent velocity

$$u_{\text{app}} = \frac{n}{3} (d_1 + d_2 + d_3). \quad (2.1)$$

Now, if we speed up the time between snapshots, namely if we take the time interval to be half as long ($2n$ snapshots per second), the motion of the particle would look somewhat different. A sketch of what might be seen is shown in Figure 2.1b). Again we can determine an “apparent” velocity from this sequence of particle positions. Specifically, we would obtain

$$u_{\text{app}} = \frac{2n}{6} (s_1 + s_2 + s_3 + s_4 + s_5 + s_6) \quad (2.2)$$

Clearly the apparent velocity associated with Figure 2.1b) is larger than the one from Figure 2.1a). This leads to the following question:

Question: A) Does the apparent velocity of a Brownian particle (as depicted in Figure 2.1) continue to

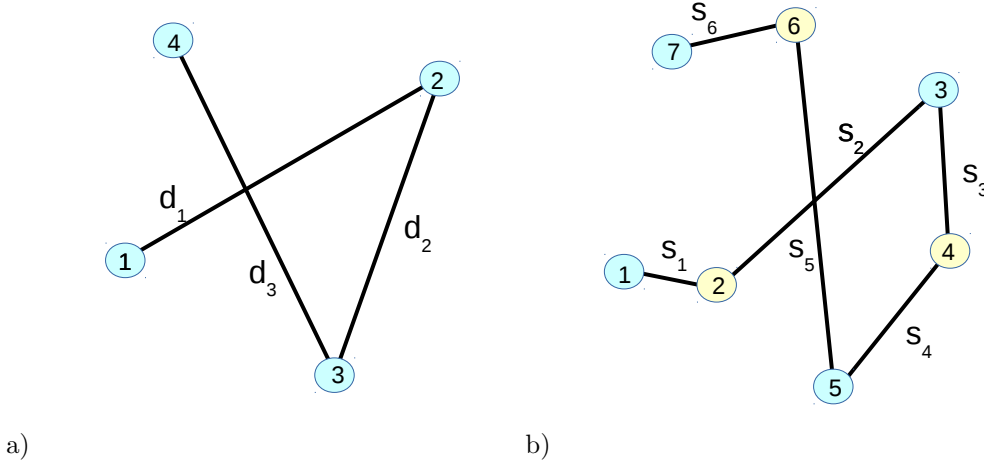


Figure 2.1: a) A trajectory of a Brownian particle where the time interval between snapshots is $1/n$. b) The same Brownian particle trajectory where the interval between snapshots is half as long: $1/2n$.

increase when we decrease the time between camera frames **OR** B) is there a time between snapshots beyond which the apparent velocity of the particles becomes well defined (i.e. stops changing)?

Our instinct should tell us that B) is more likely. If A) were true, that would mean that the apparent velocity would tend towards infinity as we decrease the time between snapshots - which seems very unlikely. Hence we are left with B). But if B) is true, a number of other questions arise: specifically, we can then ask “how fast should such time steps be?” and “how far does a particle travel during such a time step?”.

In the following we will try and address these questions as we examine the dynamics of the colloidal particle in more detail. Note that the following derivation is approximate, we will address this topic more accurately in Section 2.6.

2.2 Translational Brownian Motion

Let’s start by considering a colloidal particle, which due to collisions with fluid molecules in the solvent experiences a velocity \mathbf{u}_0 at time t_0 . As you learned earlier in this course, when such a particle moves through a liquid, it experiences a drag force that is given by Stoke’s law. Specifically,

$$\mathbf{F}_{drag} = -f_{tr}\mathbf{u} \quad (2.3)$$

where for a spherical particle $f_{tr} = 6\pi\mu a$ with μ the coefficient of viscosity, and a the radius of the sphere. (An exercise will be to show how this follows from Stoke’s law.) From Newton’s second law we have

$$\mathbf{F} = m\mathbf{a}, \quad (2.4)$$

where m is the mass of the particle and \mathbf{a} is the acceleration. Combining 2.3 with 2.4, we arrive at

$$m\mathbf{a} = -f_{tr}\mathbf{u}. \quad (2.5)$$

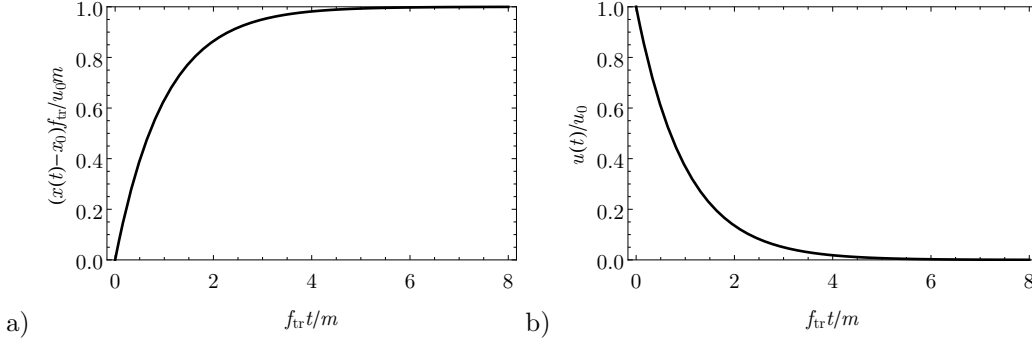


Figure 2.2: a) $x(t) - x_0$ and b) $u(t)$ for the simple random walk described in Section 2.2.

Without loss of generality we can assume that the particle moves purely in the x -direction. Then the equation of motion becomes:

$$\ddot{x} = -\frac{f_{\text{tr}}}{m} \dot{x}. \quad (2.6)$$

The solution for this differential equation is given by

$$x(t) = x_0 + \frac{u_0 m}{f_{\text{tr}}} \left(1 - e^{-\frac{f_{\text{tr}}}{m} t} \right), \quad (2.7)$$

where u_0 is a constant and corresponds to the initial velocity of the particle and x_0 is similarly the initial position of the particle. In Figure 2.2, the displacement $x(t) - x_0$ as a function of time is shown. Note that it quickly saturates. To determine the “saturation” value of $x(t) - x_0$, we can look in the long time limit, i.e.

$$l = x(t = \infty) - x_0 = \frac{u_0 m}{f_{\text{tr}}} \quad (2.8)$$

A plot of this expression is shown in Figure 2.2. From Eq. 2.8 we can obtain a characteristic relaxation time, namely $\beta_{\text{tr}} = \frac{1}{f_{\text{tr}}/m}$. Hence, we assume approximately β_{tr} jumps of length l per second. Note that as each of these jumps is caused by the random collisions of solvent molecules with the colloidal particle, the direction of each jump will be random. This type of motion is referred to as a **random walk**.

2.3 Random walks

An example random walk in 2d is shown in Figure 2.3. While we discuss random walks here in the context of Brownian motion, random walks are used frequently to model a wide variety of natural phenomena, in fields ranging from physics to biology, economics, chemistry, psychology, mathematics, etc.

2.3.1 Random Walk in $d = 1$

As a simple example, let's take a particle in one dimension which we assume can jump β times in a second. In each jump, the molecule either jumps to the right a distance (l) or left (a distance $-l$) with equal probability. The average distance the particle travels after a single jump is simply

$$\langle \Delta x \rangle_1 = \frac{1}{2}l + \frac{1}{2}(-l) = 0. \quad (2.9)$$

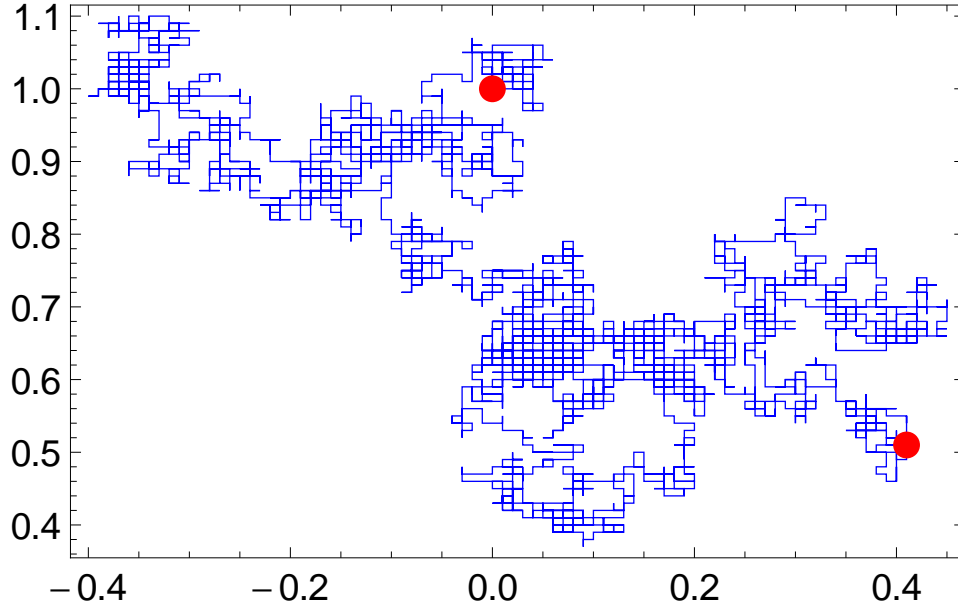


Figure 2.3: A 2d example of a random walk with 5000 steps. Each step is either $+l\hat{x}, -l\hat{x}, +l\hat{y}$ or $-l\hat{y}$, where $l = 0.01$ and \hat{x} is a unit vector in the x direction and \hat{y} is a unit vector in the y direction. The large dots indicate the beginning and the end of the random walk.

Similarly, at time $t = M/\beta$, where M is the total number of jumps in time t , the average distance is

$$\langle \Delta x \rangle_M = \left\langle \sum_{i=1}^M \Delta x_i \right\rangle = \sum_{i=1}^M \langle \Delta x_i \rangle = 0. \quad (2.10)$$

Hence, the average distance travelled by the particle is always zero.

However, the mean square displacement is non-zero. Specifically, after a single jump, the particle has travelled

$$\langle (\Delta x)^2 \rangle_1 = \frac{1}{2}l^2 + \frac{1}{2}(-l)^2 = l^2, \quad (2.11)$$

and similarly, after a time $t = M/\beta$, we have

$$\langle (\Delta x)^2 \rangle_M = \left\langle \left(\sum_{i=1}^M \Delta x_i \right)^2 \right\rangle = \left\langle \sum_{i=1}^M \sum_{j=1}^M \Delta x_i \Delta x_j \right\rangle = \sum_{i=1}^M \sum_{j=1}^M \langle \Delta x_i \Delta x_j \rangle. \quad (2.12)$$

Since jumps are completely uncorrelated we have that

$$\langle \Delta x_i \Delta x_j \rangle = \begin{cases} 0 & i \neq j \\ l^2 & i = j \end{cases} \quad (2.13)$$

which results in

$$\langle (\Delta x)^2 \rangle_M = \sum_{i=1}^M \langle (\Delta x_i)^2 \rangle = \sum_{i=1}^M l^2 = Ml^2. \quad (2.14)$$

thus using $M = \beta t$, we obtain

$$\langle (\Delta x(t))^2 \rangle = \beta l^2 t. \quad (2.15)$$

Hence, the mean square displacement is linear in t .

2.3.2 Random walk in 1d revisited

Here we follow a different approach to studying a random walk in 1d. Similar to the previous section, assume that the probability of going forward is exactly the same as going backwards (e.g. $1/2$). Clearly, the probability of any specific sequence of N jumps is given by

$$w(N) = \left(\frac{1}{2}\right)^N \quad (2.16)$$

Now let $n_s(m, N)$ be the number of such sequences that end at state m . The probability of a random walk ending up in state m after N jumps $W(m, N)$ can be written

$$W(m, N) = n_s(m, N)w(N). \quad (2.17)$$

Our goal is to determine $n_s(m, N)$. To start, consider the situation when $m > 0$. Clearly, to arrive at m , we must have made at least m forward steps. Moreover, the rest of the steps must average to zero - i.e. half must be forward and the other half must be backwards. We can summarize this as:

- Jumps in forward direction: $k^+(m, N) = m + \frac{1}{2}(N - m) = \frac{1}{2}(N + m)$
- Jumps in the backward direction $k^-(m, N) = \frac{1}{2}(N - m)$

The situation when $m < 0$ is identical.

Recall that $n_s(m, N)$ was the number of ways $k^+(m, N)$ steps can be **chosen** from N steps. Hence this is simply an example of the “choose” function. Thus

$$W(m, N) = n_s(m, N)w(N) = \frac{N!}{\left[\frac{1}{2}(N + m)\right]! \left[\frac{1}{2}(N - m)\right]!} \left(\frac{1}{2}\right)^N. \quad (2.18)$$

Note that for this expression to make sense, we have to assume that both m and N are either even or odd - this will be fine in the limit of large N and m . The distribution in Eq. 2.18 is an example of what is called a *Binomial distribution*. It will be left as an exercise to show that in the limit of large N , when m is much less than N , this reduces to a Gaussian distribution:

$$W(m, N) = \left(\frac{2}{\pi N}\right)^{1/2} e^{-m^2/2N} \quad (2.19)$$

Unfortunately, discrete variables such as N and m are not always very useful - for instance, we cannot integrate over them. Hence, it would be nice to convert this discrete distribution to a continuous one. The first thing we have to do to do this is determine what the length and time scales are for our continuous distribution. The natural “length” unit would seem to be $x = ml$. For a time scale we choose

$t = N/\beta$. Recall that for a continuous distribution we typically work in terms of the probabilities, in this case it will be the probability of finding a particle between x and $x + dx$ at time t , i.e. $W(x, t)dx$. Hence, we also need to determine the natural dx for our system. This turns out to be slightly less straightforward. As mentioned previously, we have implicitly assumed in this derivation that m and N are both either even or odd. Hence, the smallest “step” in our distribution is $2l$. Using this, we arrive at

$$W(x, t)dx = W(m, N)\frac{dx}{2l}. \quad (2.20)$$

Using these substitutions for N and m we finally obtain

$$W(x, t) = \frac{1}{(2\pi\beta l^2 t)^{1/2}} e^{(-x^2/2\beta l^2 t)} \quad (2.21)$$

which is normalized such that

$$\int_{-\infty}^{\infty} W(x, t)dx = 1 \quad (2.22)$$

Now that we have the distribution function we have all the information we require to calculate expectation values. (Recall from statistical physics that $\langle A \rangle = \int d\Gamma A(\Gamma)P(\Gamma)$ where $P(\Gamma)$ is the probability density function associated with A in state Γ and $A(\Gamma)$ is the value of A in state Γ .) Hence for the 1d random walk we have the following expectation values :

$$\langle x \rangle = \int_{-\infty}^{\infty} xW(x, t)dx = 0 \quad (2.23)$$

$$\langle |x| \rangle = 2 \int_0^{\infty} xW(x, t)dx = l\sqrt{\frac{2\beta t}{\pi}} \quad (2.24)$$

$$\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2W(x, t)dx = \beta l^2 t \quad (2.25)$$

It will be left as an exercise to work out the above relations.

2.4 Role of temperature

The equipartition theorem from statistical physics states that each quadratic degree of freedom contributes $\frac{1}{2}k_B T$ of energy (you will prove this in an exercise). Hence for our one dimensional system we can write

$$\frac{1}{2}m \langle u_0^2 \rangle = \frac{1}{2}k_B T. \quad (2.26)$$

Note that here m is the mass, unlike in the previous section. This gives us a way to relate l from our random walks to temperature. Specifically, $l = \frac{\sqrt{mk_B T}}{f_{tr}}$. Hence for our one dimensional system we obtain

$$\langle x^2 \rangle = \frac{k_B T}{f_{tr}^2} t. \quad (2.27)$$

2.5 Random walk in higher dimensions

Colloidal systems are rarely one dimensional. Hence if we want to be able to use random walks to describe Brownian motion, we need to be able to extend the previous section to 2 and 3 dimensions. It

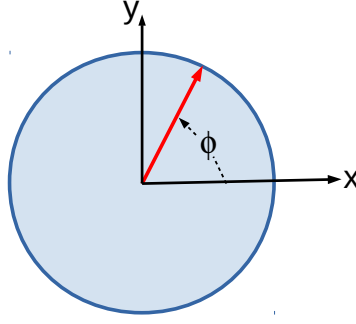


Figure 2.4: A Brownian disk with the polar coordinate (ϕ) indicated.

turns out that this can be done easily. Specifically, if the jumps associated with the random walk in the various directions are completely independent, then we can write

$$W(x, y, z, t) dx dy dz = W(x, t) W(y, t) W(z, t) dx dy dz. \quad (2.28)$$

It can then be shown that

$$\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \beta l^2 t \quad (2.29)$$

$$\langle xy \rangle = \langle xz \rangle = \langle yz \rangle = 0 \quad (2.30)$$

and hence

$$\langle r^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle = 3\beta l^2 t = 3 \frac{k_B T}{f_{\text{tr}}} t. \quad (2.31)$$

This is a very important result - we find that $\langle r^2(t) \rangle$ goes like t , independent of the dimension of the system. This should be considered one of the defining characteristics of Brownian motion.

2.5.1 Rotational Brownian Motion

So far we have considered only the translational motion of a colloidal particle. However, such a particle can both translate and rotate due to Brownian motion. In this section we will consider the rotational motion of a Brownian sphere. Later, we will examine both translational and rotational motion for an arbitrarily shaped particle.

A random walk approach to the rotational Brownian motion of a disk

For simplicity, we will begin our study of rotational Brownian motion by treating a simple 2d system, namely a disk. As we will see in the next session, our results for the 2d case can easily be transferred to a 3d system.

To begin, consider a colloidal disk with an initial orientation ϕ (as shown in Figure 2.4). Recall from classical mechanics that the rotational motion of such a particle is given by

$$\tau = I \ddot{\phi} \quad (2.32)$$

where I is the moment of inertia for the sphere, and τ is the torque exerted on the particle. $\ddot{\phi}$ is the angular acceleration. Similar to our treatment for translational motion, we can write a “torque” balance for this system. We obtain

$$I\ddot{\phi} = -f_{\text{rot}}\dot{\phi} \quad (2.33)$$

where f_{rot} is the rotary frictional force (analogous to f_{tr} for translation) and $\dot{\phi}$ is the angular velocity. This equation is essentially the same as the one we solved for translational motion. Following the same process we obtain the number of angular steps per second and the “size” of the steps. Specifically, we find that the angular “length” of a jump is given by

$$\epsilon = \omega_0 I / f_{\text{rot}} \quad (2.34)$$

and the number of such angular steps per second is $\beta_{\text{rot}} = f_{\text{rot}} / I$.

From the equipartition theory we obtain

$$\frac{1}{2} I \langle \omega_0^2 \rangle = \frac{1}{2} k_B T. \quad (2.35)$$

Again in analogy with the translation situation, we can determine a distribution function

$$W(\phi, t) = \frac{1}{(2\pi\beta_{\text{rot}}\epsilon^2 t)^{1/2}} e^{-\Delta\phi^2 / 2\pi\beta_{\text{rot}}\epsilon^2 t} \quad (2.36)$$

which gives the following expectation values

$$\langle \Delta\phi^2 \rangle = \beta_{\text{rot}} \epsilon^2 t = \frac{k_B T t}{f_{\text{rot}}} \quad (2.37)$$

A random walk approach to the rotational Brownian motion of a sphere

The situation for a sphere can be solved almost exactly the same way. The only important distinction is that the two relevant quantities become $\Delta\theta$ and $\sin\theta\Delta\phi$ (see Figure 2.5). Hence in 3d we obtain

$$\langle \Delta\theta^2 \rangle = \frac{k_B T t}{f_{\text{rot}}} \quad (2.38)$$

and

$$\langle (\sin\theta\Delta\phi)^2 \rangle = \frac{k_B T t}{f_{\text{rot}}} \quad (2.39)$$

Note that the rotational drag for a sphere is given by:

$$f_{\text{rot}} = 8\pi\mu a^3. \quad (2.40)$$

2.6 Langevin equation of motion

So far we have been treating Brownian motion as if it were a random walk with a fixed step size. As we shall see, this gets the qualitative behaviour correct but has an unfortunate error. In order to treat Brownian motion as a random walk, we had to determine approximate values for a stepsize l (or ϵ) and

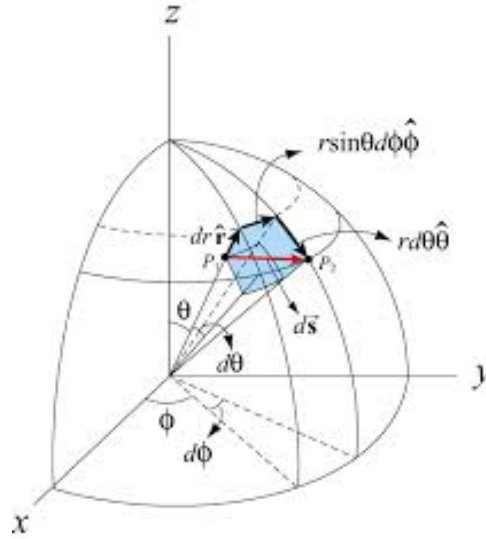


Figure 2.5: A Brownian sphere with spherical coordinates indicated taken from <http://web.mit.edu/8.01t/www/materials/modules/ReviewB.pdf>

the time between snapshots β_{tr} (β_{rot}). Our “best guess” was the relaxation time and length associated with a single “kick” from the solvent. However, in a real system, such kicks cannot be considered as isolated events, and more importantly, the particle does not come to rest between kicks. Hence, while the random walk picture describes perfectly the qualitative behaviour, we can expect that it is not fully exact. Here we will describe a more exact picture, namely the Langevin equation of motion.

In order to write down the Langevin equation of motion, we should start by returning to the question of what is exactly going on in a Brownian system. Specifically, we know that the trajectory of a Brownian particle is perpetually changing directions and magnitude due to random fluctuations in the net force of the solvent particle colliding with the colloidal particle. One way to picture this is that there is an additional random force $R(t)$ that acts on the colloid due to these fluctuations in the solvent. Since $R(t)$ is a random force - due to its random nature, the value of $R(t)$ is not known at any specific time t . However, its statistical average can be known. Specifically, we expect $\langle R(t) \rangle = 0$, and $\langle R(t_1)R(t_2) \rangle = K\delta(t_1 - t_2)$, with K a constant that depends on the system - we will see how it relates to other system parameters later. Another important point, $R(t)$ is clearly not a normal function, but is rather a so-called “stochastic function” and we will have to be careful with how we treat it. (We will not really delve into the concept of stochastic calculus in these notes, but be aware that the calculus for stochastic equations has been well studied and if you want to go on to working on these topics, you should dig into it).

Now, adding $R(t)$ to the total of forces acting on the particle, we obtain

$$\mathbf{F}_{tot} = -f_{tr}\mathbf{u} + R(t). \quad (2.41)$$

Combining this with Newton’s second law we obtain

$$m\ddot{x} = -f\dot{x} + R(t). \quad (2.42)$$

Rearranging slightly we get

$$\ddot{x} = -\alpha\dot{x} + A(t) \quad (2.43)$$

where $\alpha = f/m$ and $A(t) = R(t)/m$. The relevant statistical averages for $A(t)$ are $\langle A(t) \rangle = 0$, and $\langle A(t_1)A(t_2) \rangle = \tilde{K}\delta(t_1 - t_2)$, with $\tilde{K} = K/m^2$.

The equation for \dot{x} is an first-order differential equation with variable coefficients which has a solution (see Chapter 1) :

$$\dot{x} = u_0 e^{-\alpha t} + e^{-\alpha t} \int_0^t e^{\alpha t'} A(t') dt' \quad (2.44)$$

where u_0 is a constant and represents the velocity of the particle at $t = 0$. For notational simplicity, let $f(t) = \int_0^t e^{\alpha t'} A(t') dt'$. Then,

$$\dot{x} = u_0 e^{-\alpha t} + e^{-\alpha t} f(t) \quad (2.45)$$

Note that so far we have just assumed that $A(t)$ is a regular function. This is clearly not true, and the integrals involving $A(t)$ are stochastic functions as well. However, it will be useful to keep them around for a while, and later investigate how we can use them. To this end, we continue on and determine the position. Specifically, we just integrate the velocity \dot{x} . We obtain

$$x = x(0) + u_0 \int_0^t e^{-\alpha t'} dt' + \int_0^t e^{-\alpha t'} f(t') dt' \quad (2.46)$$

$$= x(0) + \frac{u_0}{\alpha} (1 - e^{-\alpha t}) - \frac{e^{-\alpha t}}{\alpha} \int_0^t e^{\alpha t'} A(t') dt' + \frac{1}{\alpha} \int_0^t A(t') dt' \quad (2.47)$$

where the second step was accomplished by integrating the term on the right using integration by parts. For simplicity let's assume that $x_0 = 0$. We can now start to investigate how to deal with the integrals over the stochastic function $A(t)$. We note that while the values of the integral are not well defined, **averages** of these integrals should be well defined. Hence, we can try and evaluate $\langle x \rangle$.

$$\langle x(t) \rangle = \left\langle \frac{u_0}{\alpha} (1 - e^{-\alpha t}) \right\rangle - \left\langle \frac{e^{-\alpha t}}{\alpha} \int_0^t e^{\alpha t'} A(t') dt' + \frac{1}{\alpha} \int_0^t A(t') dt' \right\rangle \quad (2.48)$$

$$= \frac{\langle u_0 \rangle}{\alpha} (1 - e^{-\alpha t}) - \frac{e^{-\alpha t}}{\alpha} \int_0^t e^{\alpha t'} \langle A(t') \rangle dt' + \frac{1}{\alpha} \int_0^t \langle A(t') \rangle dt' \quad (2.49)$$

$$= 0. \quad (2.50)$$

The last line comes from the fact that $\langle u_0 \rangle$ and $\langle A(t) \rangle$ are both zero.

A more interesting term to look at is $\langle x^2 \rangle$ (similar to what we saw for the random walk). Squaring Eq. 2.47, and then taking the average results in

$$\begin{aligned} \langle x^2(t) \rangle &= \frac{\langle u_0^2 \rangle}{\alpha^2} (1 - e^{-\alpha t})^2 + \frac{e^{-2\alpha t}}{\alpha^2} \int_0^t \int_0^t e^{\alpha(t_1+t_2)} \langle A(t_1)A(t_2) \rangle dt_1 dt_2 \\ &\quad + \frac{1}{\alpha^2} \int_0^t \int_0^t \langle A(t_1)A(t_2) \rangle dt_1 dt_2 - \frac{2e^{-\alpha t}}{\alpha^2} \int_0^t \int_0^t e^{\alpha t_1} \langle A(t_1)A(t_2) \rangle dt_1 dt_2 \end{aligned} \quad (2.51)$$

$$\begin{aligned} &= \frac{\langle u_0^2 \rangle}{\alpha^2} (1 - e^{-\alpha t})^2 + \frac{e^{-2\alpha t}}{\alpha^2} \int_0^t \int_0^t e^{\alpha(t_1+t_2)} \tilde{K} \delta(t_1 - t_2) dt_1 dt_2 \\ &\quad + \frac{1}{\alpha^2} \int_0^t \int_0^t \tilde{K} \delta(t_1 - t_2) dt_1 dt_2 - \frac{2e^{-\alpha t}}{\alpha^2} \int_0^t \int_0^t e^{\alpha t_1} \tilde{K} \delta(t_1 - t_2) dt_1 dt_2 \end{aligned} \quad (2.52)$$

$$= \frac{\langle u_0^2 \rangle}{\alpha^2} (1 - e^{-\alpha t})^2 + \frac{e^{-2\alpha t}}{\alpha^2} \int_0^t e^{\alpha(2t_1)} \tilde{K} dt_1$$

$$+ \frac{1}{\alpha^2} \int_0^t \tilde{K} dt_1 - \frac{2e^{-\alpha t}}{\alpha^2} \int_0^t e^{\alpha t_1} \tilde{K} dt_1 \quad (2.53)$$

$$= \frac{\langle u_0^2 \rangle}{\alpha^2} (1 - e^{-\alpha t})^2 + \frac{e^{-2\alpha t}}{\alpha^2} \frac{1}{2\alpha} (e^{\alpha(2t)} - 1) \tilde{K} \\ + \frac{1}{\alpha^2} \tilde{K} t - \frac{2e^{-\alpha t}}{\alpha^2} \frac{1}{\alpha} (e^{\alpha t} - 1) \tilde{K} \quad (2.54)$$

$$= \frac{\langle u_0^2 \rangle}{\alpha^2} (1 - e^{-\alpha t})^2 + \frac{\tilde{K} t}{\alpha^2} + \frac{\tilde{K}}{2\alpha^3} (-3 + 4e^{-\alpha t} - e^{-2\alpha t}) \quad (2.55)$$

Note that on the first line we have left out terms that contain $\langle A(t) \rangle$ as they are by definition zero.

As t goes to infinity, the dependence on t goes as

$$\frac{\tilde{K} t}{\alpha^2} \quad (2.56)$$

To determine K , we can now go back to the equipartition theorem. Specifically, we can determine the expectation value of u^2 (from Eq. 2.45) and relate it to the temperature via equipartition. From Eq. 2.45, the average value of u^2 is

$$\langle u^2 \rangle = \langle u_0^2 \rangle e^{-2\alpha t} + e^{-2\alpha t} \int_0^t \int_0^t e^{\alpha(t_1+t_2)} \langle A(t_1)A(t_2) \rangle dt_1 dt_2 \quad (2.57)$$

$$= \langle u_0^2 \rangle e^{-2\alpha t} + e^{-2\alpha t} \int_0^t \int_0^t e^{\alpha(t_1+t_2)} \tilde{K} \delta(t_1 - t_2) dt_1 dt_2 \quad (2.58)$$

$$= \langle u_0^2 \rangle e^{-2\alpha t} + e^{-2\alpha t} \int_0^t e^{\alpha(2t_1)} \tilde{K} dt_1 \quad (2.59)$$

$$= \langle u_0^2 \rangle e^{-2\alpha t} + \frac{\tilde{K} e^{-2\alpha t}}{2\alpha} (e^{2\alpha t} - 1) \quad (2.60)$$

$$= \langle u_0^2 \rangle e^{-2\alpha t} + \frac{\tilde{K}}{2\alpha} (1 - e^{-2\alpha t}) \quad (2.61)$$

As t goes to infinity we have

$$\langle u^2 \rangle \rightarrow \frac{\tilde{K}}{2\alpha}. \quad (2.62)$$

Finally, via equipartition we obtain

$$\tilde{K} = \frac{2f_{\text{tr}} k_B T}{m^2}. \quad (2.63)$$

Putting \tilde{K} into the long time behaviour of $\langle x^2 \rangle$ we obtain

$$\langle x^2 \rangle \rightarrow \frac{2k_B T t}{f_{\text{tr}}} \quad (2.64)$$

We should now compare this expression for the long term behaviour of $\langle x^2 \rangle$ with the simplified random walk picture we developed in Section 2.3. We note first that the qualitative behaviour is the same, namely we find that at long times $\langle x^2 \rangle$ goes with t . However, quantitatively, we find a factor of two difference between the two expressions. This arises due to our simplified approximation for the random walk stepsize l and time between steps β_{tr} .

A similar, Langevin treatment can be used to study the rotational motion. This will be left to an exercise.

2.7 The “Overdamped” Langevin equation

In colloidal systems the viscosity is generally high compared to so-called inertial forces. This is quantified by the “Reynolds” number. Recall that the Reynolds number is defined as

$$R = \frac{\rho U L}{\mu} \quad (2.65)$$

where U is the typical flow speed, and L the characteristic length scale of the flow.

Taking this into consideration, one can further approximate the Langevin equation by an “overdamped” version, specifically

$$m\ddot{x} = -f\dot{x} + R(t) \rightarrow 0 = -f\dot{x} + R(t). \quad (2.66)$$

Rearranging we obtain

$$\dot{x} = R(t)/f. \quad (2.67)$$

The dynamical behaviour associated with this equation of motion is generally called “Brownian dynamics”.

2.8 Numerical Integration

See slides for information on numerically integrating the Langevin equation.

Bibliography

- [1] S. C. Glotzer and M. J. Solomon, Nature materials **6**, 557 (2007).