SNAPSHOTS OF BROWNIAN MOTION: A PRIMER

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I. INTRODUCTION

Brownian motion is the incessant motion of small particles suspended in a fluid (liquid or gas). The phenomenon played an important role in the history of physics, because its explanation by Albert Einstein in 1905 settled the question if atoms were real or just a convenient way to keep track of and catalogue chemical reactions. The following discussion of Brownian motion is appropriate for students who have had algebra-based or calculus-based courses in physics. A few questions are interspersed in the discussion; the answers are given at the end.

Let's start off with a key result from thermal physics that will be used in what follows. We know from the kinetic theory of matter that all particles of matter are in motion, and that the average thermal kinetic energy of a particle of mass m at temperature T is $KE_{thermal} = mv_{thermal}^2 = 3k_BT/2$, where k_B is Boltzmann's constant, $1.38\text{x}10^{-23}$ J/K. Solving for $v_{thermal}$, we get:

$$v_{thermal} \equiv v_m = \sqrt{3k_BT/m}\,.$$

In this equation, m can be the mass of anything--a small particle suspended in a thermal bath (e.g., a liquid or gas) or even a parcel of liquid for as long as the parcel has integrity before mixing with surrounding liquid. As suggested by the equation, it will be convenient to designate $v_{thermal}$ for any particle of mass m, or M, or whatever other symbol might be used for mass, as simply v_m, v_M,…etc.

Section II will describe the parameters of a typical Brownian particle and give a conceptual explanation of the origin of the motion. Section III will discuss the experimental scenario involved in determining the mathematical properties of the motion. A graph of the particle's positions when snapshots are taken periodically suggests a jagged motion. The conceptual understanding of averages is also explained as the results of repeated experiments. Section IV introduces the all-important diffusion constant for the motion and warns against taking the jaggedness of the path too seriously. The particular snapshot time, which divides the jagged picture of Section III from the actual smooth motion of the particle, defines the "time scale" of the motion. Brownian motion is noted to be distinct from molecular diffusion where the motion of a molecule is for all practical purposes jagged. Section V goes on to discuss an important statistical property of the fluctuations which create the particle's motion and keep it going. This discussion shows the necessity to account for the frictional force between the moving particle and the fluid. Explicit expressions for the time and space scales characterizing the motion are given in Section VI, and values for a typical particle in water are given. In Section VII, the "Langevin equation" describing Brownian motion is used to derive the more conventional values of the time and space scales of the motion. Section VIII gives a very simple statement of the well-known "fluctuation-dissipation theorem" as it applies to Brownian motion. Section IX gives expressions for the diffusion constant in terms of the well-known fluid property of viscosity. The Einstein relation describing the drift speed of a particle when subject to a systematic force is also derived. Section X summarizes the paper.

II. GENESIS OF BROWNIAN MOTION FOR A TYPICAL BROWNIAN PARTICLE

It will be useful to have a particular particle in mind when discussing Brownian motion. Historically, Brownian motion was first observed for particles just visible in an ordinary microscope. We will therefore take our typical Brownian particle (BP for short) to have the following properties and to be suspended in water, as illustrated in Figure 1:

Particle density equal to water's = 1000 kg/m^3;
Particle radius $R = 0.5\text{x}10^{-6}$ m, which is large enough to be visible under a visible-light microscope;
Particle mass $M = 5.24\text{x}10^{-16}$ kg (that's almost 20 trillion atoms); and
Particle is suspended in water at 300 K.

Note that our typical BP is composed of many, many atoms and so is much heavier than a water molecule. This is one of the defining characteristics of a BP that often goes unmentioned in textbooks.

The motion of a Brownian particle suspended in a fluid (e.g., a typical particle like the one just described) is caused essentially by the fact that thermal motion of fluid molecules is random. In a low-density gas, the mechanism of Brownian motion is most simply understood: molecules collide with the Brownian particle randomly, and at any instant of time, there will be more collisions on one side than another. This fluctuation in impacts causes the particle's direction of motion to change *slightly* over short periods of time during which the BP nevertheless experiences many impacts from the much lighter fluid molecules. Over time, the accumulated fluctuations don't completely cancel (see Section V below), and their effect grows with the result that the particle's direction changes *gradually*, randomly, and constantly over time. A similar process occurs in a liquid too, though the more appropriate mechanism to describe the Brownian motion is fluctuation in liquid pressure.

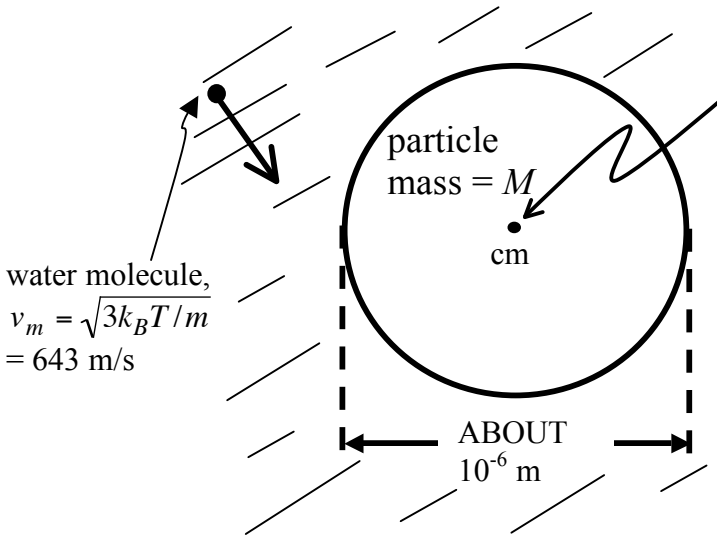


FIGURE 1:
Particle's center of mass (cm) obeys:

$$Mv_M^2/2 = 3k_BT/2,$$

$$v_M = \sqrt{\frac{3k_BT}{M}} = 0.00487 \text{ m/s}$$

For comparison: the thermal speed of a water molecule of mass $m = 3.01\text{x}10^{-26}$ kg is $v_m = 643$ m/s

The gradual change of a Brownian particle's motion is much unlike the motion of molecules colliding with each other, in which case the molecules suffer abrupt and random changes in direction of motion with every collision. This qualitative difference is why we require a BP to be much bigger than a fluid molecule. One purpose of this essay is to investigate the experimental division point between

smooth and random motion of a BP. We will see that the random BP motion is partly an artifact of the experimental "snapshot" method traditionally employed to observe Brownian motion. The snapshot picture gives rise to a jagged particle path.

III. EXPERIMENTAL SCENARIO

Take a snapshot of the Brownian particle's position every t_S seconds (i.e., "strobe" the particle), the first snapshot being at $t = 0$. Do it for a total of $t = Nt_S$ seconds so we observe the particle $N + 1$ times in time t, as shown in Figure 2. The first step, $\boldsymbol{r}_1$, is constructed from snapshots at $t_0 = 0$ and $t_1 = t_S$, and in general, step $\boldsymbol{r}_i$ is between snapshot positions taken at times $t_{i-1} = (i-1)t_S$ and $t_i = it_S$. The total displacement after N steps is:

$$\boldsymbol{r} = \sum_{i=1}^{N} \boldsymbol{r}_i \,. \tag{A}$$

Squaring both sides, we get:

$$r^2 = \sum_{i=1}^{N} r_i^2 + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \boldsymbol{r}_i \cdot \boldsymbol{r}_j \quad . \tag{B}$$

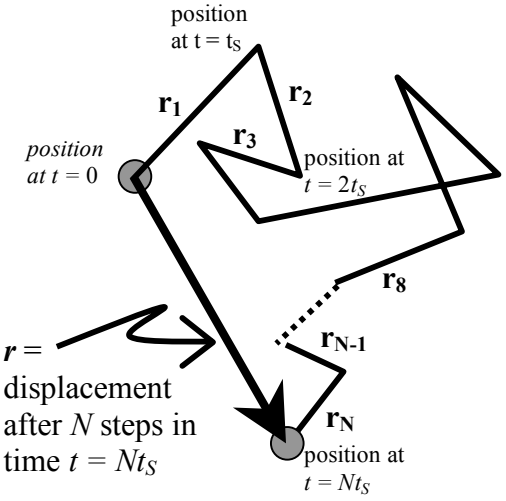


FIGURE 2: Brownian steps in a 2-dimensional walk.

Now repeat the identical experiment (same *snapshot time* t_S, N snapshots, total time $t = Nt_S$) many times and take averages of Eq. (B) across experiments for each step:

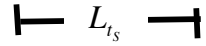
$$\left\langle r^2(t) \right\rangle = \sum_{i=1}^{N} \left\langle r_i^2 \right\rangle = NL_{t_s}^2 = (t/t_s)L_{t_s}^2 = (L_{t_s}^2/t_s)t \,. \tag{C}$$

(For details of the averaging process, see below for answers to questions.) Note that there is nothing special about step i, and the average value for all steps in the experiment is the same: $\left\langle \boldsymbol{r}_i^2 \right\rangle = L_{t_S}^2$ for all i.

QUESTION 1: What happened to $\sum_{i=1}^{N}\sum_{j\neq i}^{N}\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \rangle$ in going from (B) to (C)?

QUESTION 2: Explain why $\langle \boldsymbol{r}_i^2 \rangle = L_{t_S}^2$ for all steps if in any one experiment different steps have different lengths.

L_{t_S}, the *snapshot distance*, is a measure of how far the particle travels on average in time t_S. L_{t_S} is about this big for the above diagram:



And here's a real example: for a typical Brownian particle in water, and an observation or strobe time of t_S = 60 s,

$$L_{t_s=60} = 1.26\text{x}10^{-5} \text{ m},$$

about 10 times the diameter of the Brownian particle and easy to observe with a microscope, as was done laboriously by Jean Perrin in 1911 in his Nobel Prize-winning experiments.

IV. A KEY EXPERIMENTAL RESULT; SELF-SIMILARITY AT SMALLER SCALES

Our result for $L_{t_s=60}$ raises an immediate concern: the apparent speed of the BP along the line joining its two positions 60 seconds apart, i.e., the "snapshot" speed of the particle, v_S, is $v_S = 1.26\text{x}10^{-5}/60$ m/s = $2.10\text{x}10^{-7}$ m/s, *much* smaller than its thermal speed of 0.00487 m/s. But the BP is not immune from the laws of thermal physics: it must really be traveling much faster, at 0.00487 m/s (on average), so we can only conclude that it must have traveled over a longer round-about distance in 60 s between the observed start and end points, and not just along the straight line joining the two observed points. This suspicion is of course true: if we observed more frequently, say every 15 seconds, we would again observe a jagged path *between* the end points originally observed to be 60 seconds apart. Consider, then, the average snapshot distance $L_{t_S 0}$ associated with an initial snapshot time t_{S0}. The quantitative dependence of snapshot distance L_{t_S} traveled between these same two points as a function of snapshot time $t_S < t_{S0}$ can be derived from the following most important experimental fact.

For given liquid, particle size and temperature, $L_{t_s}^2/t_s$ in Eq. (C) is observed experimentally to be constant (unless t_S is very small, as will be shown shortly): so if, e.g., t_S is reduced by a factor of a quarter, L_{t_s} is reduced by a factor of 1/2 (as suggested by Figure 3). This constant ratio defines the diffusion constant *D*, "diffusion" referring to the process of a particle or group of particles spreading out from an initial region. For one component, e.g., the *x*-component of the displacement *x*(*t*) in time *t* after a number of snapshots, $\langle x^2(t) \rangle = (L_{xt_s}^2/t_s)t = 2Dt$, so:

$$D \equiv \frac{L_{xt_s}^2}{2t_s}. \qquad \text{(D)}$$

(The factor of 2 is a pure convention.) To turn this relation around: the displacement from the $t = 0$ position after time t is proportional to $\sqrt{t}$, reflecting the fact that the path is not really in a straight line but wanders randomly in the time t.

The diffusion constant D is defined to work for two or three dimensions also, but the constant factor of 1/2 changes. Thus, for three dimensions: $\left\langle r^2(t) \right\rangle = (L_{t_s}^2 / t_s)t = 6Dt$, so:

$$D \equiv \frac{L_{t_s}^2}{6t_s}. \qquad \text{(E)}$$

Question 3: Show that for three dimensions, the factor 1/2 in Eq. (D) becomes 1/6 in (E).

But also, $D \equiv \frac{L_{t_s 0}^2}{6t_{s0}}$. Equating the two expressions for D, we see that:

$$L_{t_s} = L_{t_s 0}\sqrt{\frac{t_S}{t_{S0}}}. \qquad \text{(F)}$$

So as expected, making t_S 1/4 of t_{S0} cuts the snapshot length in half, as illustrated in Figure 3. Furthermore, if t_S is again reduced, each of the smaller steps shown on the right side of Figure 3 will again be seen to consist of a jagged path between the endpoints. This reproduction of jaggedness with shorter and shorter time scales is known as "self-similarity": the jaggedness is reproduced but on a smaller scale when t_S is reduced.

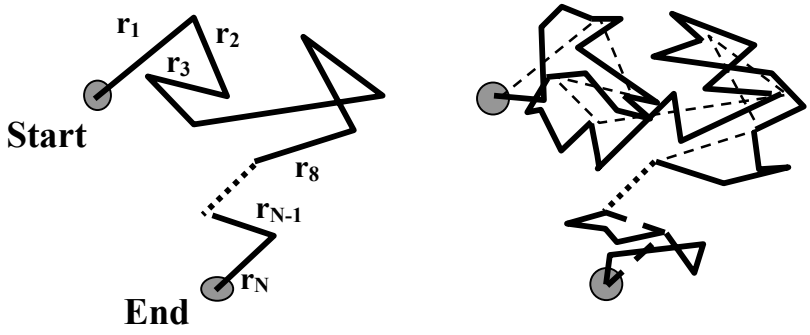


FIGURE 3: the effect of shortening the snapshot time by 1/4. On the left: snapshot time t_S; on the right: snapshot time $t_S/4$, showing smaller random steps and the greater distance the particle actually traveled.

Mathematically: for a given t_S, the average speed over a step length is $v_s = \sqrt{6D}/\sqrt{t_s}$. But since D is constant, this raises a new concern: if t_S is made smaller and smaller, v_S gets bigger and bigger and will eventually be greater than the speed of light, because the path length between two points grows bigger and bigger without limit as t_S approaches zero. (Technically, the jagged Brownian path is a *fractal* of dimension 2: it would cover the plane if the jaggedness persisted down to vanishingly small snapshot times!) Clearly this is impossible, and we are led to the following conclusion:

The jaggedness must give way to a nice, smooth path when the snapshot time reaches small enough a value. The particle must therefore move with its thermal speed v_M when the snapshot time is very small.

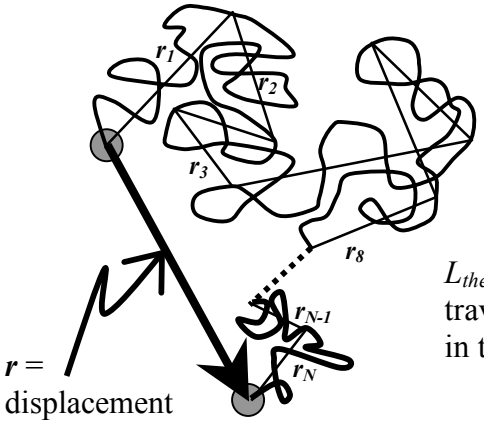
Our next task is to discover the "natural" snapshot times, i.e., the natural time and space scales of Brownian motion, call them $t_{thermal}$ and $L_{thermal}$, that mark the transition between jagged motion and smooth thermal motion. For convenience, abbreviate the scales to t_{th} and L_{th}.

QUESTION 4: Show that $v_s = \sqrt{6D}/\sqrt{t_s}$.

In most circumstances, the change in direction of the particle occurs very gradually compared to the rate of molecular impacts. In the words of Edward Nelson in his essential book *Dynamical Theories of Brownian Motion*,[1]

> It is not correct to think simply that the jiggles in a Brownian trajectory are due to kicks from molecules. Brownian motion is unbelievably gentle. Each collision has an entirely negligible effect on the position of the Brownian particle, and it is only fluctuations in the accumulation of an enormous number of very slight changes in the particle's velocity that give the trajectory its irregular appearance.

So a realistic picture emerges if "snapshots" are taken very fast. A more accurate picture of the underlying smooth motion underlying Figure 2's jagged appearance is shown in Figure 4.



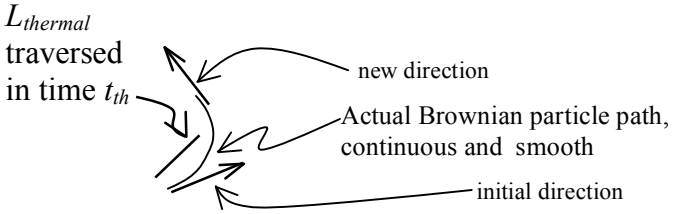


FIGURE 4: The particle's motion is smooth if observed with an extremely short shapshot time, and on average, it travels with its thermal speed along its continuous path: $v_M = \sqrt{3k_BT/M}$ (=0.00487 m/s for our typical BP). It takes about a distance L_{th} for the path direction to change significantly.

As the figure suggests, on average, the particle drifts a distance $L_{thermal}$ in an *almost* straight, just gradually curving, path (gradually because fluctuations are weak but constantly operate) before its direction is substantially changed from what it started with.

[1] A copy of Nelson's book can be obtained on line at by pasting the following into your browser address window: http://www.math.princeton.edu/~nelson/books/b**motion**.pdf

CAUTION

Molecular diffusion differs in an important way from the diffusion of Brownian particles. In gaseous molecular diffusion, a molecule flies freely in a straight line between collisions, and its direction of motion is changed abruptly with each collision. So the jagged picture shown in Figure 1 is accurate for molecules on any time scales bigger than the collision time (which is usually very small). Some textbooks tend to confuse the two cases.[2]

V. BEFORE CONTINUING, AN IMPORTANT STATISTICAL PROPERTY

Consider the simple case of flipping a coin. If you flip it N times., do you get exactly $N/2$ heads (H) and $N/2$ tails (T)? Of course not. But very likely (with about a 95% probability) you'll get something in this range:

$$N \pm 2\sqrt{N}\ \text{H},\ \text{N} \mp 2\sqrt{\text{N}}\ \text{T}.$$

These equations show that the deviation (or in our context, the "fluctuation") from equal H and T GROWS as N increases, even though the fractional deviation or *precision*, $\pm 2\sqrt{N}/N = \pm 2/\sqrt{N}$, decreases. People usually focus on how small $\sqrt{N}$ is compared to N when N gets very large, forgetting that $\sqrt{N}$ is getting larger too!

For Brownian motion, the key thing is the growth in the *fluctuation* in the impact of molecules on the particle. Most of the molecular impacts cancel out—for every impact driving the particle in one direction, there is very likely another driving it equally in the opposite direction. But the balance is not perfect—"most" is not "all," and the resulting imbalance grows over time as impacts accumulate on the particle. Put another way: *as time increases, fluctuation effects grow*, until after a time, fluctuations cause a particle's initial direction of motion to change.

One loose thread remains from our discussion of fluctuations. As noted, fluctuation effects grow with time, and by themselves would cause the BP to go faster and faster! That doesn't happen because there is a frictional force as the BP moves through the fluid. *The frictional force increases as the particle's speed increases, and tends to slow the particle down*. So while fluctuations are causing the particle to go faster, the frictional force is causing it to go slower. On average, these two influences cancel each other so the particle moves through the fluid (on average) with its thermal speed v_M.

CONCLUSION: When observed frequently enough, the motion of the Brownian particle no longer appears jagged. We instead observe smooth motion, *also called "ballistic Brownian motion,"* known to exist since 1905 but not observed experimentally in an indirect way until 1989,[3] and not directly until 1995![4] Finally, only in 2010[5] was ballistic motion observed in such detail, i.e., with such rapid snapshots, that the particle's actual ballistic path could be observed and the speed distribution

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[2] For example, Philip Nelson, in his otherwise excellent text *Biological Physics: Energy, information, life*, (p. 118, Eq. (4.11) starts off talking about Brownian motion but then develops a diffusion equation appropriate of molecular diffusion.

[3] D.A. Weitz, *et al.*, "Nondiffusive Brownian Motion Studied by Diffusing-Wave Spectroscopy," *Phys. Rev. Lett.*, **63** (16), 1747-1750 (1989).

[4] B. Lukic *et al*, "Direct Observation of Nondiffusive Motion of a Brownian Particle," *Phys. Rev. Lett.* **95**, 160601 (2005).

[5] T. Li *et al.*, "Measurement of the Instantaneous Velocity of a Brownian Particle," *Science* **328**, 1673-1675 (2010).

determined. But what timescale for snapshots is "sufficiently rapid"? That question introduces the important concepts of the natural time and space scales for Brownian motion.

VI. TIME AND SPACE SCALES

As we saw above, when the snapshot period is large, we have the impression that the BP's speed is smaller than the thermal speed it really moves at. On the other hand, when the snapshot period is sufficiently small, the particle is seen to travel (on average, of course) with its average thermal speed. So when does the snapshot period make the transition from too long to "just right"? This transition snapshot period defines what we call the "time scale" of the motion.

A simple way to estimate the time scale for Brownian motion is to determine the snapshot period for which v_S ($= \sqrt{\frac{6D}{t_s}}$) is just equal to the thermal speed v_M ($=\sqrt{\frac{3k_BT}{M}}$) : $\sqrt{\frac{6D}{t_s}} = \sqrt{\frac{3k_BT}{M}}$. Letting t_{th} be this special "thermal motion" value of t_s, we get:

$$t_{th} = \frac{6D}{v_M^2} = \frac{6DM}{3k_BT}. \qquad \text{(G)}$$

It is important to recognize that the time scale t_{th} represents a transition from a jagged snapshot path (where the particle appears to move slower than v_M) to a smooth one where the particle moves with v_M. Experimentally, for our typical BP in water, $D = 4.39\text{x}10^{-13}$ m^2/s, so for $M = 5.24\text{x}10^{-16}$ kg and $T = 300$ K:

$$t_{th} = 1.11\text{x}10^{-7}\ \text{s}.$$

Note that t_{th} is very small, and to observe ballistic Brownian motion an even shorter time scale is necessary. So it is no wonder that this motion wasn't directly observed until 1995!

IMPORTANT NOTE: t_{th} is bigger (10^{14} times bigger!) than the time between collisions of water molecules with the BP, which is about 10^{-21} s![6] The fluctuation effects of individual collisions must accumulate over many collisions to have an effect on the BP.

The space scale associated with t_{th} is:

$$L_{th} = v_M t_{th},$$

which for our example ($v_M = 0.0048$ m/s, $t_{th} = 1.11\text{x}10^{-7}$ s) is:

$$L_{th} = \text{transition snapshot step size} = 5.41\text{x}10^{-10}\ \text{m}.$$

So L_{th} is only about 50 H-atom radii, much smaller than the radius of the BP. So the particle travels approximately this very small distance before its direction of travel changes substantially, which shows why it is easy to think the particle motion is always jagged.

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[6] S. Chandrasekhar, "Stochastic Problems in Physics and Astronomy," *Rev. Mod. Phys.*, **15** (1), January 1943 (p. 23)

VII. CONVENTIONAL VALUES FOR TIME AND SPACE SCALES

From the discussion of the preceding section, an alternative way of determining the time scale is to determine how long it takes a particle moving with its thermal speed in a particular direction to lose that speed. Towards this end, suppose a BP is traveling with its thermal speed to the right:

$$v_M = \sqrt{\frac{3k_BT}{M}}$$ 

With no fluctuations, how long does it take for friction to bring it to a stop, or more precisely, to bring its speed down significantly? This time can be found by using the fact that the friction between a fluid and a slowly-moving particle is proportional to the particle's velocity, the proportionality or friction constant being ζ. In many ordinary fluids, like water and air at standard temperature and pressure (but not low-density gases), the friction constant is the well-known one given by Stokes: $\zeta \equiv -6\pi\eta R$. The the motion of the BP can be described (again, neglecting fluctuations) by Newton's 2nd Law:

$$M\frac{dv}{dt} = -\zeta v = -6\pi\eta R v.$$

Solve for v:

$$v = v_M e^{-t/\tau},$$

where the "relaxation time" is:

$$\tau = \frac{M}{6\pi\eta R} = \frac{M}{\zeta}.$$

The relaxation time is a measure of the time scale for Brownian motion and should be comparable to the time t_{th} found in Eq. (G). For our "typical Brownian particle" (density equal to water's, $R = 0.5\text{x}10^{-6}$ m, $M = 5.24\text{x}10^{-16}$ kg, in water at 300K):

$$\tau = 5.60\text{x}10^{-8} \text{ s}.$$

We see that τ is half the value of our original t_S calculated above to be $1.11\text{x}10^{-7}$ s.

Note that the velocity decreases exponentially, which implies an infinite time for the velocity to go to zero. But exponential decay is very fast: for $t = \tau$, v is only 37% of v_M, and for $t = 2\tau$, v is only 13% of v_M.

The space scale associated with τ can be taken as how far it would travel with thermal speed v_M in time τ:

$$\Delta = v_M\tau,$$

and for our typical Brownian particle,

$$\Delta = 2.73\text{x}10^{-10} \text{ m},$$

about half of what we got for L_{th}.

CAUTION: A "time scale" marks the division between two types of behavior, in our case between smooth Brownian particle paths for $t_S << \tau$ and jagged, randomly-directed paths observed for $t_S >> \tau$. From this perspective, it matters not a great deal if we use τ or t_{th} as the " time scale" for Brownian motion, and likewise for using Δ or L_{th} for the "space scale." In other words, the time scale is not valuable for its exactness, but for telling us the approximate conditions under which a transition between jagged and smooth motion is observed to occur. In what follows, we will take τ as the time scale for the BP's motion since it is most commonly used.

VIII. THE FLUCTUATION-DISSIPATION THEOREM

The distinct geometric properties of a BP's path associated with snapshot times below and above t_{th} show the important relationship between the frictional and fluctuation effects of the fluid on the BP. For $t < \tau$, a BP with an initial average speed of v_M in a particular direction travels in a path that is almost straight. Fluctuations gradually change the direction, but it will significantly change only over a time $t > \tau$. In other words, it takes approximately the time τ for friction to wipe out the initial speed and for the effects of fluctuations to accumulate to the point where there is a significant change in direction. In short, the time needed for the fluid to dissipate an initial thermal speed is the same as the time for fluctuations to replenish that speed but in a new (random) direction. This tight connection between fluctuation and friction effects is known as the *fluctuation-dissipation or F-D theorem*.

The technical statement of the F-D theorem relates the friction constant ζ to the time correlation of the fluid's fluctuating force on the particle, $F(t)$:[7]

$$\xi = \frac{1}{2k_B T}\int_{-\infty}^{\infty}\langle F(0)F(t)\rangle dt\,. \qquad \text{(H)}$$

This abstract recipe should give us the result $\zeta \equiv -6\pi\eta R$ for a liquid like water or a gas like air at STP. But left unsaid is exactly what the random agitating force $F(t)$ is. For a low-density gas, $F(t)$ is the force of a collision of a molecule with the BP, which is very difficult to specify precisely except to say that it lasts for only a very short time . For a liquid like water, $F(t)$ is the force from a pressure fluctuation, whose time dependence can be specified. In any case, the recipe leaves a lot to be desired, given its abstractness. A more direct way to determine ζ for a low-density gas is to impose the condition that the time needed for a change in direction from fluctuations is just τ, i.e., M/ζ. For an approximate derivation of ζ using this approach, go here. An exact treatment can be obtained from the author.

Another version of the F-D theorem has to do with the response of a system to an outside influence. Consider, for example, a paramagnetic substance, which for our purposes is a system that can be magnetized only if an external magnetic field is placed on it. How magnetized does it get? The answer is that it depends on how much the magentization in a small volume of the paramagnet, ideally a single molecule or atom, fluctuates with time. If it fluctuates a lot, we can say it is "loose" and "susceptible" to being influenced by an external magnetic field. If it fluctuates very little, it is pretty much locked in place and won't respond much at all to an external magnetic field. So in this version of the F-D theorem, we say that "response is proportional to fluctuation." This is an extremely useful form of the theorem.

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[7] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), p. p 572, Eq. (15.8.8).

IX. THE DIFFUSION CONSTANT AND THE EINSTEIN RELATION

From Eq. (E) above, $D = L_{t_s}^2/(6t_s)$, we should be able to substitute in our alternative time and space scales τ and Δ to obtain *D*. Since $\Delta = v_M\tau$,

$$D = v_M^2\tau = \frac{k_BT}{4\pi\eta R}. \quad \text{(INCORRECT!)}$$

QUESTION 5: Show that $D = v_M^2\tau$.

The functional form of *D* is correct: it is directly proportional to k_BT and inversely proportional to $\pi\eta R$. But the factor of 1/4 is incorrect—it should be 1/6:

$$D = \frac{k_BT}{6\pi\eta R}. \qquad \text{(CORRECT!)} \qquad \text{(G)}$$

This equation for *D* expresses the *Einstein relation* relating the friction coefficient and diffusion constant to the temperature, since the Stokes friction coefficient is $\zeta = 6\pi\eta R$, and $D\zeta = k_BT$, QED.

QUESTION 6: What condition is required to get the correct result, Eq. (G), for *D*? And how does violation of that condition arise in our calculation of the "Incorrect" version of *D*? (Hint: look at the transition from Eq. (B) to Eq. (C), as explained in the answer to Question 1.)

A more general form of Einstein's relation can be obtained that applies to molecules as well as to Brownian particles. A Brownian particle dragged through a viscous medium due to an externally imposed force *f* reaches a terminal or drift speed of $v_{drift} = f/(6\pi\eta R)$, i.e., $6\pi\eta R = f/v_{drift}$, so:

$$Df = k_BTv_{drift}.$$

This more general form of Einstein's relation applies to molecular diffusion, because even though the concept of viscosity does not directly apply to such motion, terminal or drift speed under an externally applied force does.

Another common way of showing the Einstein relation is for an electric field *E* putting a force $f = qE$ on charged particles immersed in a fluid and pulling them through the fluid. In terms of the "mobility" $\mu = v_{drift}/E$, Einstein's relation reads

$$D/\mu = k_BT/q.$$

Answers to Questions

QUESTION 1: What happened to $\left\langle \sum_{i=1}^{N} \sum_{j\neq i}^{N} \boldsymbol{r}_i \cdot \boldsymbol{r}_j \right\rangle$ in going from (B) to (C)?

ANSWER: First, note that $\left\langle \sum_{i=1}^{N} \sum_{j\neq i}^{N} \boldsymbol{r}_i \cdot \boldsymbol{r}_j \right\rangle = \sum_{i=1}^{N} \sum_{j\neq i}^{N} \left\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \right\rangle$, which you should be able to prove easily remembering that the average is obtained by doing the experiment a large number of times and summing the results of all experiments for each step. If you still feel uneasy about this point, read on.

In concise terms, for t_S sufficiently large, the fluid exerts many random forces on the particle between consecutive snapshots. The effects of these forces in each time interval t_S accumulate to make the consecutive steps relatively random. Consequently, the dot product between any two consecutive steps in an N-step experiment is sure to be the negative of that dot product in some other run of the experiment, so the dot product between any two consecutive steps will be zero when summed over many experimental runs. What is true for two consecutive steps is all the more true for snapshots separated by a larger time. So $\left\langle \sum_{i=1}^{N} \sum_{j\neq i}^{N} \boldsymbol{r}_i \cdot \boldsymbol{r}_j \right\rangle$ is zero.

Here's a long-winded expansion of the concise answer, showing precisely what an average, represented by the angular brackets $\langle ... \rangle$, is. Consider a single run of, say, $N = 1000$ steps, and consider two consecutive steps $\boldsymbol{r}_i$ and $\boldsymbol{r}_{i+1}$, formed by connecting the positions recorded by three snapshots at $t_{i-1} = (i-1)t_S$, $t_i = it_S$, and $t_{i+1} = (i+1)t_S$ For concreteness, imagine that $i = 123$, so we're looking at the 123rd and 124th steps of the experiment, i.e., the straight lines connecting positions observed at times $122t_S$, $123t_S$, and $124t_S$ (the first position being at $t = 0$). These two steps, one occurring right after the other, have the best chance of having a dot product that is non-zero (in which case we say they are correlated), because occurring consecutively, there might not be much change between them. But if the snapshot time is large enough, there will be enough random pushes from the fluid between snapshots to substantially change the motion of the particle.

We are most interested in the average for the 123rd and 124th steps, or more generally, we have to determine the average of the i^{th} and i+1st steps, i.e., $\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_{i+1} \rangle$. This average is constructed by repeating the experiment of $N = 1000$ steps many, many times, say a billion (10^9) times. A large t_S means that in each run of the experiment there are many "mini-steps" (observable only with a smaller t_S) along bigger step as suggested above in Figure 3 of Section IV (which shows only 4 mini-steps for each big step but there could be many more). These mini-steps, as shown in that figure, are in random directions, and so the same is true of the i^{th} and $i+1^{st}$ steps. Because of this randomness from step to step, then for every experiment where there is some angle, say θ, between these two steps, there will be an experiment where the angle will be $\pi \pm \theta$, and the dot product for $\pi \pm \theta$ is the negative of the dot product for θ. For example, the angle might be $\theta = 89.4$ deg for the 123rd and 124th steps in the 1,563,255th run of the experiment and $\pi + 89.4$ deg for these same steps in the 92,569,759th run of the experiment. The average for the i^{th} and $i+1^{st}$ steps (e.g., the 123rd and 124th steps) is formed by summing over these particular steps for all billion experimental runs, and cancellation is sure to occur pair by pair. Since this occurs for any of the 1000 steps we are getting an average of, it follows in general that $\sum_{i=1}^{N} \sum_{j\neq i}^{N} \left\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \right\rangle = 0$.

One final point. Although the conceptual idea described above is very useful to understand what we really mean by an average, it is not necessary to actually carry out a billion experiments! Normally, a collection of many, many particles are observed to diffuse in one or several experiments, and all the averages associated with observing a single particle many times turn out to be the same when the average behavior of a large number of particles is observed for a single experiment. This equivalence is

an example of a general idea: observing one particle over many experiments gives the same result as observing a collection of many particles in a single experiment. (Note: The only complication that can result from the single-experiment result is that the particles are so densely packed that they affect each other's motion, a situation which is beyond the scope of this discussion and which, in any case, can be avoided by not having the particles initially densely packed.)

QUESTION 2: Explain why $\langle \boldsymbol{r}_i^2 \rangle = L_{t_S}^2$ for all steps if in any one experiment different steps have different lengths.

ANSWER: The following table of step lengths (just lengths, not directions!) shows what might occur for, say, three consecutive steps, (the *1st,* 2nd and 3rd), the *i*th and the last (*N*th one in each of a billion repetitive experiments (each experiment starting, e.g., with each particle moving with its thermal speed), and each experiment consisting of *N* steps, where *N* can be anything.

Experiment #	*1st step*	*2nd*	*3rd*	. . .	*i*th	. . .	*N*th step
1	→	→	→	. . .	→	. . .	→
2	→	→	→	. . .	→	. . .	→
3	→	→	→	. . .	→	. . .	→
.	.	.	.	. . .	. . .	. . .	
.	.	.	.	. . .	. . .	. . .	
.	.	.	.	. . .	. . .	. . .	
10^9	→	→	→	. . .	→	. . .	→
Average length	→	→	→	. . .	→	. . .	→

Do enough experiments (a billion is quite sufficient), and randomness from experiment to experiment insures that each step will go through the same range of lengths and frequencies of occurrence of lengths, as every other step. Therefore, the average after 10^9 experiments will be the same for each step, as shown in the bottom row. Please note: for simplicity, only five steps (1st, 2nd, 3rd, *i*th, and *N*th) are shown for only four experiments (#1,2,3, and 10^9). The step sizes shown certainly don't average to the same thing. One has to average over a large number of experiments to get the same result for each one. Also note: it would be strange if we didn't get the same result by averaging across experiment #1, so if another column were provided for an average across steps for each experiment, the same result would be obtained as shown for the arrow lengths in the bottom row.

QUESTION 3: Show that for three dimensions, the factor 1/2 in Eq. (D) becomes 1/6 in (E).

ANSWER: Starting with, note that the Brownian motion we are considering in this paper is free from any systematic force, so the diffusion occurs equally along *x*, *y*, and *z*. Therefore, the 3-dimensional step distance is on average $L_{t_S}^2 = L_{xt_S}^2 + L_{yt_S}^2 + L_{zt_S}^2 = 3L_{xt_S}^2$. Therefore, from $\langle x^2(t) \rangle = (L_{xt_s}^2 / t_s)t = 2Dt$, we have $L_{xtS}^2 = L_{t_S}^2 / 3$, so $\langle x^2(t) \rangle = (L_{t_s}^2 / 3t_s)t = 2Dt$, so $D = L_{t_s}^2 / 6t_s$, QED.

QUESTION 4: Show that $v_s = \sqrt{6D} / \sqrt{t_s}$.

ANSWER: The average step speed is $v_S = L_S / t_S$. But $D = 6L_S^2 / t_S$, so eliminating L_S immediately leads to the result.

QUESTION 5: Show that $D = v_M^2 \tau$.

ANSWER: This is shown simply by using $D = 6L_S^2 / t_S$, or its close equivalent $D = 6\Delta^2 / \tau$. Since $\Delta = v_M \tau$, we can substitute for Δ and the desired result is immediately obtained.

QUESTION 6: Under what condition is Eq. (E) precise, giving the correct expression for *D*? And how does violation of that condition arise in our calculation of the "Incorrect" version of *D*? (Hint: look at the transition from Eq. (B) to Eq. (C).)

ANSWER: As suggested at several points in the discussion and in the answer to Question 1, successive steps are random so long as t_S is sufficiently large. This condition that t_S be large ($>>\tau$) is necessary, because if t_S is too small, the snapshot path is smooth—rapid successive snapshots trace out a slowly-varying path. This means that there is not enough time from snapshot to snapshot for consecutive steps to be random. In other words, if the particle is traveling along the *x* axis, two successive snapshots will show a step, call it step *i*, along that axis. Then step *i+1*, which is the straight line between the second and a third snapshot, will show the particle still traveling very close to the *x* axis, because not enough time has passed for fluctuations to accumulate and change the particle's direction of motion significantly. (This is essentially ballistic Brownian motion.) Therefore, $\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_{i+1} \rangle$ will not be zero. In fact, this average will start going to zero only as t_S increases significantly beyond t_{th} or τ. The "Incorrect" version is obtained by using the time scale τ, which is not large enough, despite its usefulness as a measure below which the motion smooths out and above which the motion starts to become jagged.