FLUCTUATION AND RELAXATION TIME IN BROWNIAN MOTION

Frank Munley[(a)]
Department of Physics
Roanoke College
Salem, VA 24153

Abstract

Brownian motion of a particle is characterized by the fluid producing simultaneous effects of drag tending to bring the particle to rest and a fluctuating force that keeps it in motion. Einstein's diffusion equation for Brownian motion holds only for times larger than a minimum time τ which is a measure of the time it takes for drag to dissipate a particle's initial speed. This implies that the fluctuating force re-directs the motion of the particle for times approximately equal to τ. This fact is used to derive an approximation for the dissipation time in a rare gas where individual molecular collisions are responsible for both drag and fluctuation, and leads to a transparent interpretation of the fluctuation-dissipation theorem.

I. INTRODUCTION

Brownian motion, the incessant motion of small particles suspended in a fluid, is readily observable for particles sufficiently small—most conveniently about a micron or so in diameter and invisible to the naked eye, but big enough to be seen in a microscope.

The discovery of Brownian motion is usually credited to botanist Robert Brown in 1828.[1] But as Edward Nelson pointed out,[2] Brown himself credited others with observing it, the first recorded instance being by Leeuwenhoek over a hundred years earlier. Nelson recognizes Brown's historical primacy on the subject because his contribution was "… to establish Brownian motion as an important phenomenon, to demonstrate clearly its presence in inorganic as well as organic matter, and to refute by experiment facile mechanical explanations of the phenomenon."[3]

In 1905, Albert Einstein provided the first accurate explanation of Brownian motion[4] by treating Brownian particles as large molecules executing thermal motions. Einstein predicted that $\langle \mathbf{R}^2 \rangle$, the average squared distance a particle diffuses from its starting point in three dimensions, is proportional to the time:

$$\langle \mathbf{R}^2 \rangle = 6Dt, \tag{1}$$

where D is the diffusion constant. He also showed that the diffusion constant of a Brownian particle (BP for short) of radius a in a fluid such as air or water of viscosity η at temperature T is:

$$D = \frac{k_B T}{\beta} = \frac{k_B T}{6\pi\eta a}, \tag{2}$$

where k_B = Boltzmann's constant and β, in the well-known Langevin model (developed three years after Einstein's initial results), is the drag coefficient such that $\beta \mathbf{v}$ is the drag force on a particle moving with velocity **v** through the fluid. Einstein's assumption for the viscous drag coefficient, $6\pi\eta a$, was derived by Stokes more than fifty years earlier.[5]

One purpose of this paper is to review the reason why Eq. (1) must fail when the time between observations falls below a minimum value. Einstein's derivation of the minimum time and its value for situations where Stokes friction applies will then be given. The results of the review will then be used to derive the time scale in a low-density gas for which the drag coefficient has a different form. The derivation will suggest a transparent re-phrasing of the fluctuation-dissipation theorem relating β to the fluctuating force that keeps the particle in motion.

II. MINIMUM TIME AND SPACE SCALES

Eq. (1) shows that the average squared displacement is proportional to *t* rather than t^2. This is because the path followed by a particle is assumed to be highly irregular, with the velocity changing rapidly and randomly. But this assumption cannot hold without limit, as can be seen by considering the time and space scales over which the motion is observed, i.e., the time between repeated observations and the displacements of the particle between those times. If the irregular nature extended down to arbitrarily small time and space scales, the particle would have to travel at an infinite speed to get anywhere, as discussed recently by J. Bernstein.[6] Expanding a bit on Bernstein's argument, let $\sqrt{\langle \mathbf{R^2} \rangle}$ be a measure of the average displacement in the time between consecutive observations, t_{ob}. Then the speed the particle must travel if it went along the straight-line segment connecting the points of observation is $v = \sqrt{\langle \mathbf{R^2} \rangle}/t_{ob} = \sqrt{2D/t_{ob}}$. Taking *D* as a *finite* observed quantity, the expression for *v* shows that the straight-line speed must increase without limit as the time between observations decreases without limit. Put differently, if the path were jagged down to arbitrarily small space scales, then the actual distance the BP must travel between finitely-spaced endpoints would be infinite, which requires an infinite speed if the path is to be traversed in a finite time.[7]

The pathological "infinite speed" property of Eq. (1) was recognized by Einstein,[8] by Jean Perrin[9] in his Nobel Prize-winning work that verified Einstein's work, and by many others. As Einstein recognized early on, the particle must really travel with a speed determined by the well-known equipartition rule, which says that the total kinetic energy (in three dimensions) is $3k_BT/2$. For a particle of mass *M,* this yields the root-mean-square thermal speed of:

$$v_M = \sqrt{3k_BT/M}. \qquad (3)$$

The finite particle speed implies that there exist minimum time and space scales below which the particle motions loses its jagged character and Eq. (1) ceases to hold. This is

shown in Figure 1(a), which is a conceptual illustration of the continuous smooth path that would be observed if the particle could be tracked at a very small time scale. The solid line Figure 1(b) is typical of the type of path observed by Perrin,[10] who made observations at very large time scales of the order of 30 seconds. The smooth, almost straight-line motion at very small scales is known as "ballistic" Brownian motion,[11] and illustrates Nelson's statement that Brownian motion is "unbelievably gentle."[12] This is a useful antidote to the idea that individual molecular impacts determine the roughness of a Brownian trajectory,[13] because typically, a huge number of molecular collisions must occur during the time it takes for the direction of travel of the BP to substantially change.[14]

Einstein[15] estimated the minimum time scale for a particle of mass M by considering the time dependence of the velocity of a particle coasting under the influence of a Stokes drag force but in the absence of thermal agitation. The simple differential equation describing the motion, $M d\mathbf{v}/dt = -\beta \mathbf{v}$, yields $\mathbf{v} = \mathbf{v}_o e^{-t/\tau}$, where the minimum time scale is:

$$\tau = \frac{M}{\beta}. \qquad (4)$$

The minimum time scale τ is also referred to as the relaxation or dissipation time, because it is the time needed for an initial velocity to be dissipated by friction. In what follows, it will be referred to as the dissipation time.

The space scale associated with τ is easily obtained by integrating the equation for velocity and setting the time to τ, which yields:

$$\Delta = v_o \tau (1 - 1/e) \approx v_o \tau. \qquad (5)$$

Since irregularity in the particle's path appears for times greater than τ, τ is a lower limit on the time needed for the random fluctuating force that keeps the particle in motion to have a significant effect on the direction of motion, because it is this random force that gives rise to the jaggedness of the path. This interpretation of the meaning of τ will be used explicitly in Section III.

It is instructive to determine the magnitudes of τ and Δ for air and water, using Eqs. (4) and (5). In thermal equilibrium, we can take v_o in Eq. (5) to be the root-mean-square average speed v_M given in Eq. (3). For a typical Brownian particle which has a radius of 10^{-6} m and a density approximately equal to that of water, its mass is M = $4.2\text{x}10^{-15}$ kg and its thermal speed for T = 300 K is v_M = 0.00172 m/s. Therefore, in water with viscosity 0.001 kg/ms, Stokes drag is appropriate so $\beta = 6\pi\eta a = 1.885\text{x}10^{-8}$ kg/s, which gives τ =$2.23\text{x}10^{-7}$ s and Δ = $3.84\text{x}10^{-10}$ m. The lower limit for Δ is only about seven times the radius of a hydrogen atom! For air (η = $1.81\text{x}10^{-5}$ kg/ms) at standard temperature and pressure, Stokes friction is also appropriate,[16] and we get τ = $1.23\text{x}10^{-5}$ s and Δ = $2.12\text{x}10^{-8}$ m. Clearly, there was no way Perrin could have observed

smooth Brownian paths on a scale below Δ and τ, since he was tracking them visually.

The tiny value of Δ for water deserves comment. The usual form of Stokes drag assumes that the particle does not undergo rapid oscillatory-type accelerations,[17] but with such small values of Δ and τ, this is a questionable assumption. Stokes also presented a lesser-known form appropriate for oscillatory motion,[18] and the implications have been investigated by D. Selmeczia, *et al*. for application to microparticles subject to optical tweezers.[19] The correction for acceleration in most cases is small and can be ignored. Other recent research involves the inertial effects of the liquid around the particle.[20] So although many consider Brownian motion is to be a settled subject, it is still an active field of investigation.

III. DERIVATION OF THE DISSIPATION TIME FROM FLUCTUATIONS

The Stokes drag coefficient in Eq. (1) is appropriate when the molecular mean free path, λ, is much smaller than a in which case the laws of continuous fluid mechanics apply.[21] For a micron-size BP, Stokes friction holds very well in water. It holds adequately in air, but for precise work, corrections are necessary.[22] In the opposite case where $\lambda >> a$, β can be described in terms of individual collisions of molecules with the particle.[23]

The vast majority of papers on Brownian motion refer to molecular collisions as the essential causative agent, but strictly speaking, this is correct only for rare gases. In denser fluids, where Stokes friction holds, collisions are not strictly local, because collision of a molecule with the BP surface exerts an effect that depends on what other molecules are doing. For example, a molecule about to impinge on the BP might be subject to the pressure distributed throughout a fluid element of which it is a part. Also, viscosity, which describes the drag on a BP in the most common media of air and water, is not local because it involves the velocity correlation between molecules in fluid elements adjacent to and at rest on the BP surface (in the commonly used "no slip" condition) and molecules in fluid elements farther away from the surface. In liquids and sufficiently dense gases, this correlation is described not just by boundary conditions, but also by intermolecular forces.[24] Of course, rare gases have viscosity too, but the drag effect is described by individual collisions, not the Stokes law. As we shall see, the collision drag force depends on a^2, unlike the Stokes drag's linear dependence on a.

To simplify the following discussion, consider a BP in a gas sufficiently rarified that $\lambda >> a$, so its behavior is determined through the mechanism of molecular collisions. (Denser fluids like water or air at standard temperature and pressure are more difficult to deal with.) We will now determine the correct functional form of the dissipation time by first determining the fluctuation in the number of collisions of molecules with the BP in an arbitrary time interval t, and then finding the value of t that produces a momentum change in the BP equal to its equilibrium momentum. This will lead to an interpretation of the fluctuation-dissipation relating the drag coefficient β to the random fluctuating force responsible for Brownian motion.

Simple kinetic theory tells us that the number of collisions per unit area per unit time is $f_{coll,1} = n\bar{v}_m/4$, where $\bar{v}_m = \sqrt{\frac{8k_BT}{\pi m}}$ is the average molecular speed. Therefore, in time *t*, the average number of collisions on each side of the Brownian particle is approximately:

$$n_{coll,t} \approx f_{coll,1}\pi a^2 t, \tag{9}$$

where the effective collision area of the particle is approximated as πa^2. The average fluctuation in the imbalance in the number of collisions is $\delta n_{coll,t} = \sqrt{n_{coll,t}}$, and each unbalanced collision (for simplicity, assumed elastic) produces a momentum change $\Delta p_1 \approx 2m\bar{v}_m$. Substituting for $n_{coll,\tau}$ and $f_{coll,1}$, we get for the total change in particle momentum in time *t*:

$$\Delta p_t = \Delta p_1 \delta n_{coll,t} = 2m\bar{v}_m (f_{coll,1}\pi a^2 t)^{1/2}. \tag{10}$$

From what was said following Eq. (5), the accumulated imbalance in a time equal to the dissipation time τ should lead to a significant change in direction of motion of the particle, i.e., the momentum change should be $\Delta p \approx Mv_M = \sqrt{3Mk_BT}$. Substituting for $\bar{v}_m$ and $f_{coll,1}$ in Eq. (10), setting the result equal to $\sqrt{3Mk_BT}$ and solving for $t \equiv \tau$, we obtain:

$$\tau = \frac{M}{\beta} \approx \frac{M}{a^2 n\sqrt{8\pi m k_B T}}. \tag{11}$$

As promised, the implied value of β in Eq. (11) is proportional to a^2, unlike the Stokes β which is proportional to *a*. This is a reflection of the physical difference between the two types of drag, one being entirely local in nature and the other being non-local.

Epstein[25] gives the precise value $\beta = [4a^2 n\sqrt{8\pi m k_B T}]/3$, i.e., $\tau = 0.750M/\left[a^2 n\sqrt{8\pi m k_B T}\right]$. So the value in Eq. (11) is only about 33% above the correct value.

The conventional way of stating the fluctuation-dissipation theorem is to relate the friction constant β to the expectation value of the time correlation function of the fluctuating force.[26] Eq. (11) is based on the relationship between fluctuations and drag, and offers a more transparent interpretation of the fluctuation-dissipation theorem for Brownian motion:

> *The time it takes for friction to dissipate the particle's original thermal speed is equivalent to the time it takes for the fluctuating force to re-establish the thermal speed in a different random direction.*

It is interesting to imagine what would happen if this theorem were not true. Consider an ensemble of BPs each with mass *M*, in a fluid at temperature *T*. Assume that each particle in the ensemble is initially traveling with exactly the thermal speed, but particle velocities are in random directions. If the time to dissipate a particle's original thermal velocity were on average greater than the time needed for the fluctuating impulses to change a particle's velocity by an amount equal to the thermal speed but in a random direction, then a particle on average would still have what's left of its original velocity and so the average speed would increase without bound. If the dissipation time were less than the time it takes fluctuating impulses to change a particle's velocity by an amount equal to its thermal speed, then the particle would spend too much time with a speed below the thermal average before impulses could boost it back to the thermal speed, and the average speed would fall below the level of the thermal average. So the fluctuation-dissipation theorem is required so that the average particle speed stays at the thermal average at constant temperature.

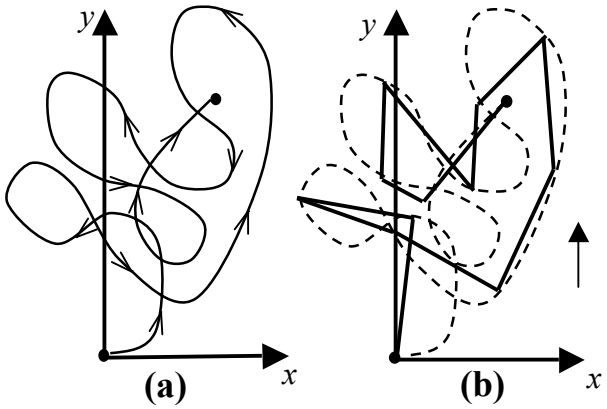

Fig. 1: A conceptual diagram of the continuous nature of a Brownian trajectory and how it appears as a random walk when sampled at a sufficiently large time interval. (a) The continuous path of a Brownian particle. (b) The random walk of the same particle, with straight lines drawn between positions of the particles at equal intervals of time. The vertical arrow on the right is a "guesstimate" of the minimum space scale. On average, a displacement greater than this results in a significant change in direction.

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[6] J. Bernstein, "Einstein and the existence of atoms," *Am. J. Phys.,* **74** (10), 863-872 (2006).

[7] In modern parlance, the path implied by Eq. (1) is a fractal of Hausdorff dimension 2. See, e.g., M. Schroeder, *Fractals, Chaos, Power Laws* (W.H. Freeman & Co., New York), 1991), pp. 140-141. An extensive discussion of the Hausdorff dimension and its relevance to Brownian motion can be found in B. Mandelbrot, *Fractals: Form, chance, and dimension* (W.H. Freeman & Co., San Francisco, 1977), Ch. 3.

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[9] J. Perrin, *Atoms* (Oxbow Press, Woodbridge, CT, 1990), p. 111.

[10] J. Perrin, *Atoms*, pp. 115-116.

[11] This is a well-known result from the Langevin approach to Brownian motion. See, e.g., the short-time approximation in F. Reif, *Fundamentals of statistical and thermal physics* (McGraw-Hill, New York, 1965), pp. 565-556.

[12] E. Nelson, *op.cit.*, p. 58.

[13] See, e.g., F. J. Belinfante, "On the mechanism of Brownian motion in liquids," *Am. J. Phys.*, **17**, 468-476 (1949).

[14] *Ibid.*, p. 57.

[15] A. Einstein, "On the theory of the Brownian movement," *op. cit.*

[16] Millikan's use of Stokes is described in Perrin *op.cit.*, pp. 97-99 and 185.

[17] Brownian motion is a "white noise" or Wiener process, so that all frequencies in the Fourier decomposition of the motion are present. See Daniel T. Gillespie, "The mathematics of Brownian motion and Johnson noise," *Am. J. Phys.*, **64** (3), 225-240 (1996), and "Fluctuation and dissipation in Brownian motion," *Am. J. Phys.,* **61** (12), 1077-1083 (1993).

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[23] Many articles treat Brownian motion from the collision perspective. See, e.g., R.S. Modak, *op.cit.*, P. Grassia, "Dissipation, fluctuations, and conservation laws, *Am. J. Phys.,* **69** (2), 2001, and B.G. de Grooth, "A simple model for Brownian motion leading to the Langevin equation," *Am. J. Phys.*, **67** (12), 1999, and references therein.

[24] Ultimately, forces exerted on the particle come from molecules that are more or less adjacent to the particle. But in a liquid or dense gas, drag arises because slower molecules farther away, *via*

intermolecular forces, drag molecules situated closer to the particle, and ultimately the drag is transmitted to the particle. Collisions *per se* have little or nothing to do with the drag force.

[25] P.S. Epstein, Ref. **Error! Bookmark not defined.**.

[26] F. Reif, *Fundamentals of statistical and thermal physics* (McGraw-Hill, New York, 1965), p. 572.