PRESSURE FLUCTUATIONS, VISCOSITY, AND BROWNIAN MOTION

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ABSTRACT

Brownian motion occurs in a variety of fluids, from rare gases to liquids. The Langevin equation, describing friction and agitation forces in statistical balance, is one of the most successful ways to treat the phenomenon.

In relatively dense fluids, such as water and air at standard temperature and pressure, friction is normally treated as a mesoscopic effect arising from the coordinated viscous action of fluid surrounding the particle. It is often assumed that the friction in denser fluids obeys Stokes' law. The appropriateness of this assumption involves a discussion of recent experimental research in the ballistic or "coasting" phase of motion occurring at a very short time scale.

Given the mesoscopic nature of the friction force for relatively dense fluids, we should expect the agitation force to also be mesoscopic. It has been suggested occasionally that pressure fluctuations with a well-defined minimum time scale are an appropriate mesoscopic agitation force for denser fluids. The purpose of this paper is to do that in the simplest possible way. To accomplish the goal, the simple random walk will be used to approximate the time and space scales below which ballistic motion begins and diffusive motion ends. Following that, pressure fluctuations and the associated time scale will be introduced and shown to be consistent with the fluctuation-dissipation theorem describing the statistical balance between agitation and friction.

As successful as the pressure fluctuation model is, it fails for fluids like glycerin that have viscosities a thousand times and more that of water. A simple phenomenological model of collective fluid motion will be presented to explain Brownian motion in such fluids.

I. INTRODUCTION

Brownian motion is the incessant irregular motion of small particles suspended in a fluid. Robert Brown considered the phenomenon in depth in 1827, following earlier observations by several other investigators. Brownian motion is observed with pollen grains as in Brown's original experiments, or with milk fat cells, smoke particles, or other micron-size particles. The modern choice is engineered polystyrene beads of uniform size. For convenience, the particles must be small enough for motion to be easily observed in an optical microscope, typically 10^{-6} m or smaller. More advanced techniques are able to observe even smaller particles.

Albert Einstein provided a firm theoretical basis for the phenomenon in 1905. Einstein described the phenomenon in terms of well-known partial differential equations describing diffusion of chemical species in solution. His approach exploited an analogy between diffusion of solute molecules in a fluid solvent and the diffusion of the much larger Brownian particles (BP for short) in a fluid. The analogy today seems compelling and even obvious, but in Einstein's day it was a bold one for two reasons. First, diffusion was seen only as a phenomenon in which molecules of more or less equal size and mass interact, so each collision between two molecules has a large effect on both. How could a series of single impacts of very tiny molecules cause a much larger BP to move significant distances? Wouldn't the small impacts occurring in random directions cancel out? And second, some eminent chemists and physicists at the time, such as Ostwald and Mach, still doubted to various degrees the existence of atoms and molecules, considering them to be just a convenient construction to help explain chemical reactions and physical properties of materials and therefore not a real explanation of Brownian motion.

Einstein also provided an alternative "random walk" model which assumes the particle takes steps of finite length in random directions, the changes in direction resulting from a random agitation force acting on the BP. The diffusion equation then results in the limit of rapid, very short steps. The random jaggedness of the particle path, though only an artifact from connecting successive plot points of periodic observations of a Brownian particle, correctly leads to the conclusion that the average squared displacement of a Brownian particle is
proportional to time. This dependence, plus other characteristics of the motion based on the atomic theory of matter and statistical methods Einstein himself devised, provided the basis for the experimental verification of his theory by Jean Perrin in a number of experimental investigations published in 1908-1909. Perrin's work convinced most if not all skeptics that the atomic composition of matter was indeed the reality and not just a contrivance to understand chemical reactions.

In 1908, Paul Langevin proposed a theory of Brownian motion based on Newton's second law of motion in which two fluid forces guide the particle's motion. First, as the BP drifts through the fluid, it is subject to a frictional or drag force on it that alone would bring it to a stop and erase any memory of its original motion. And second, there is fluctuating thermal agitation from the fluid that sustains the motion by providing impulses in random directions to the BP. The two processes together—the random impulses keeping the particle in motion and the systematic friction erasing the motion—tend to balance each other so the speed of the BP is, on average, the thermal speed one would expect from the equipartition theorem of statistical mechanics for a very heavy molecule with a mass equal to the BP's. In this way, thermal equilibrium is maintained. Investigations of Brownian motion did not stop with Langevin and common liquids like air and water. Research continues today, with important work being done on novel materials consisting of traps that temporarily trap Brownian particles, soft materials, and hydrodynamic subtleties affecting motion, which lead to anomalous Brownian motion that exhibit non-Gaussian time distribution, contrary to Brownian motion in a homogeneous fluid.

This paper will discuss differences and similarities between various fluids in their friction and agitation mechanisms in the context of the Langevin equation. For example, the friction force on a BP in either a very low-density (rarified) gases or denser fluids (like air and water) is proportional to particle speed, but these forces differ in their dependence on BP size. Particular attention will be paid to time and space scales for friction and agitation processes. These considerations lead to the main purpose of the paper: to propose pressure fluctuations as the proper mesoscopic counterpart to viscous effects used for friction in denser fluids. Pressure fluctuations are characterized by a well-defined time scale, thus allowing an alternative to the physically unrealistic Wiener process, which has an infinitesimal time scale and is often used incorrectly for motion in denser fluids.

In Section II, the random walk model will be used to illustrate the relationship between the experimentally measurable diffusion constant and the step size and time between steps of the random walk process. This will lead to estimates of the minimal step and time possible for a random walk model, shorter times leading to smooth ballistic motion. In Section III, the Langevin equation will be introduced and the conditions needed for the oft-used Stokes (or Stokes-Einstein) friction to be used. Several recent developments involving novel conditions for Brownian motion will be mentioned. Pressure fluctuations will be introduced in Section IV and a simple intuitive derivation of the fluctuation-dissipation theorem given. The theorem will be used to verify the proper time scale and magnitude for pressure fluctuations. Section V shows why the pressure fluctuation mechanism fails for extremely viscous substances such as glycerin, where somewhat paradoxically it takes a shorter time for a particle at rest to be boosted to its thermal speed. A modification of the Langevin equation will be proposed to deal with high-viscosity liquids like glycerin. Section VI will summarize the results.

II. RANDOM WALK, MINIMUM TIME AND SPACE SCALES, BALLISTIC MOTION

A random walk picture of Brownian motion can be constructed when a BP is observed under a microscope to diffuse from its initial position. The particle is observed to undergo a tiny jiggling motion so rapid it is impossible to follow with the eye in detail. But single-particle positions can be observed and recorded periodically at equal intervals of time, during which the particle noticeably changes position. When successive positions are plotted and connected by points, a jagged "random walk" is contrived as a visualization of the underlying physical process. For example, some of the famous experiments of Jean Perrin in 1908-1909 recorded a single particle's position in water every 30 seconds. Perrin's particles were about 10^-6 m in diameter, and on average a particle moved a few particle diameters between observations. During the time between observations, random agitation from the fluid results in the direction gradually
changing. An idealized example of such a picture in Figure 1 shows the contrived jagged path of the particle. One of the steps is magnified to show what happens if another observer were to track the same particle at the same time, but recorded the particle's positions more frequently, say every few seconds. As shown, the jaggedness, but now with shorter steps, persists even over the shorter times.

![Image of a random walk](image)

**Figure 1**: A random walk where the particle position is periodically observed, say every minute or so. The circle magnifies one step showing the extra detail if the particle is observed on a shorter time scale, say every 30 seconds or so.

Knowing the time between observations, say 30 s as in Figure 1, the particle's average speed on segments between consecutively observed positions can be calculated. But as the magnified step in Figure 1 shows, if a smaller period between observations shows the jaggedness to persist along the smaller steps, the distance moved between two end points 30 s apart in time is really greater than would be calculated just using the straight-line distance between those two end points. Consequently, the particle's speed in traveling between two points is really greater than that calculated with a 30 s between observations. Suppose now a third observer had recorded positions with an even shorter period, say a few tenths of a second. Then if the jaggedness persists, but now on an even smaller scale, the distance the particle moved in 30 s is again bigger than originally thought, and its speed is again greater than thought. Clearly, since a particle can't move faster than the speed of light (in fact, it moves much slower than that), the jaggedness must stop at some minimum observation time, typically about a microsecond or smaller, the motion smoothing out to "ballistic motion" for shorter observation times.\(^7\) This is shown in Figure 2.

Despite the necessity of jaggedness giving way to smoothness, careless statements are sometimes made implying that the jaggedness continues to arbitrarily small time and space scales, which as mentioned would require an infinite particle speed. The reason for the misleading claim is that the well-known Wiener process assumes a minimum time scale of zero. This technique can be useful for applications where precise values of minimum time and space scales are not of interest, or are not easily modeled,\(^8\) but the importance of the minimums where jaggedness gives way to a smooth ballistic motion cannot be ignored.

Ballistic motion was first observed in 2005.\(^9\) Since then, a number of excellent experiments have been done for gases and liquids, the simplest result for the latter being in acetone which has a very low viscosity compared to water and many other liquids.\(^10\) The true ballistic path is not absolutely smooth because of the quasi-continuous randomly acting agitation force, as suggested in the magnified portion of Figure 2(a). Individual distortions are fantastically small, but like a typical random walk process, agitation impulses combine to produce larger changes in direction over longer times. The agitation forces for fluids such as air and water will be looked at more closely in the next section.

We will now see that good approximations to the minimum scales are derivable from a simple random walk model. The results follow from the very important property of a random walk, that the average *squared* distance a particle wanders from its starting point is proportional to the number of steps taken. This property is easily proved as follows.
Imagine a BP's position in three dimensions to be observed and recorded every $t_0$ seconds for a total time $t_n = nt_0$, with $t_0$ of the order of seconds so the number of steps is $n >> 1$. The net vector displacement is:

$$r(t_n) = \sum_{i=1}^{n} r_i.$$  \hspace{1cm} (1)

The square of the displacement from the starting point after these $n$ steps taken in time $nt_0$ is:

$$r^2(t_n) = \sum_{i=1}^{n} r_i^2 + \sum_{i\neq k}^{n} r_i \cdot r_k.$$  \hspace{1cm} (2)

But because the steps are random in direction, the sum of the cross-products for the $i \neq k$ sum is negligible compared to the first term, which means the dot products are as likely to be positive as negative for $n >> 1$. Now let the same procedure be carried out for a large number of particles so a good average value of the first sum can be obtained, giving $\langle r^2(t_n) \rangle = \left( \sum_{i=1}^{n} r_i^2 \right)$. Then the

Figure 2: (a) The solid line shows the random walk of a BP in a rare gas or denser fluids (like water or air at standard temperature and pressure (STP)), the straight lines being drawn between positions of the particles "strobed" at equal intervals of time. (b) The true continuous path of the same BP is almost perfectly smooth on a very small, essentially continuous, time scale. The magnified portion of a very tiny part of the curve shows over very short distances the slight, random drifts around the average direction of motion due to thermal impulses from the fluid that barely change the particle's direction of travel but combine over time and larger distances to gradually change the direction of motion. The smooth "ballistic" almost-straight-line drift motion indicated in (b) is observable only with a very short period between observations.
average squared single-step size, $\Delta_{t_0}^2$, is:  
$$\Delta_{t_0}^2 = \frac{1}{n} \left( \sum_{i=1}^{n} r_i^2 \right) = \frac{\langle r^2(t_n) \rangle}{n},$$
so $\langle r^2(t_n) \rangle = n\Delta_{t_0}^2$.
QED.

Assuming spatial isotropy, the average squared displacement projections along $x$, $y$, and $z$ are equal:  
$$\Delta_{t_0}^2 = \Delta_{t_0}^2_{x} = \Delta_{t_0}^2_{y} = \Delta_{t_0}^2_{z},$$
and so if the data is recorded in $d$ dimensions ($d = 1, 2, 3$), then  
$$\Delta_{t_0}^2 = d\Delta_{t_0}^2_{x},$$
which leads to:
$$\langle r^2(t_n) \rangle = nd\Delta_{t_{1x}}^2. \quad (3)$$

For example, it is common to observe Brownian particles through a microscope, with positions recorded on a $d=2$ grid system. Perrin published pictures of such two-dimensional trajectories, observations being made every 30 s as mentioned above. But his numerical analysis was based only on projections of the path segments on the $x$-axis, so $d = 1$.

In Eq. (3), replace $n$ by $t_n / t_0$. Then the diffusion parameter $D$ in the random walk context is defined from the following equation:
$$\langle r^2(t) \rangle = n\Delta_{t_0}^2 = nd\Delta_{t_{0x}}^2 = \langle t / t_0 \rangle d\Delta_{t_{0x}}^2 = 2dDt_0, \quad (4)$$
the factor of 2 being an oft-used convention. Eq. (4) shows that the root mean square displacement $\langle r^2 \rangle$ goes as $t$, as we expect from random steps reflected in data obtained by observing every $t_0$ seconds. Solving for $D$, we get:
$$D = \frac{\Delta_{t_{0x}}^2}{2t_0} = \frac{\Delta_{t_{0}}^2}{2dt_0}. \quad (5)$$

Note that Eqs. (4) and (5) are robust results as long as the value of $t_0$ is not so small that ballistic motion is involved.

It might appear from Eq. (5) that $D$ depends on $t_0$ and $\Delta_{t_0}$ (or $\Delta_{t_{0x}}$), but in fact $D$ is a constant because $\Delta_{t_0}^2$ is proportional to $t_0$. Another way to see the constancy is to note that the same particle can be simultaneously tracked by two observers with two different values of $t_0$ for the same total time $t$, and they agree on the total diffused distance $\langle r^2 \rangle$. The constancy of $D$ will appear again in the next section, Eq. (17), where $D$ is calculated in terms of parameters which are physical constants or constants of the experimental procedure such as particle mass and temperature.

Eq. (5) implies the speed problem mentioned above and suggested in Figure 1’s depiction of jaggedness. To see this explicitly, note that the apparent average squared speed between two position observations along a straight-line segment of average squared length $\Delta_{t_0}^2$ is:
$$\langle \bar{v}_{t_0}^2 \rangle = \left( \Delta_{t_0} / t_0 \right)^2 = d\Delta_{t_{0x}}^2 / t_0^2 = 2Dd / t_0, \quad (6)$$
where the final member of the equation substitutes for $\Delta_{t_0}^2$ from Eq. (5). Therefore, since $D$ and $d$ are constants, $\langle v^2_{t_0} \rangle \to \infty$ as $t_0 \to 0$, which is impossible. So there must exist a minimum time $t_{rw}$, below which the increasing jaggedness smooths out to the "ballistic motion" phase. And associated with $t_{rw}$ in the ballistic phase, there is an average three-dimensional distance $\Delta_{rw}$ over which the particle travels with a more-or-less constant velocity which changes only gradually as tiny random impulses affect its motion.

The random walk parameters $t_{rw}$ and $\Delta_{rw}$ below which the ballistic phase appears can be determined by imposing two conditions: (1) the speed of the particle over the ballistic path should on average be the thermal equilibrium speed required by the equipartition theorem:

$$\frac{\Delta_{rw}}{t_{rw}} = \sqrt{\frac{d k_B T}{M}} = v_{th}; \quad (7)$$

and: (2) the expression for the diffusion constant in Eq. (5) must be obeyed for these values:

$$D = \frac{\Delta_{rw}^2}{2d t_{rw}}. \quad (8)$$

Solving Eqs. (7) and (8) for $t_{rw}$ and $\Delta_{rw}$, we get:

$$t_{rw} = \frac{2DM}{k_BT} \quad (9)$$

$$\Delta_{rw} = 2D \sqrt{\frac{dM}{k_BT}}. \quad (10)$$

To illustrate for water and $d = 3$, consider a BP with a radius of $a = 10^{-6}$ m and a density of twice that of water, so its mass is $M = 8.34 \times 10^{-15}$ kg. Then at room temperature (300 K), using the experimentally measured value $D = 2.2 \times 10^{-13}$ m$^2$/s, we find $t_{rw} = 10^{-6}$ s and $\Delta_{rw} = 10^{-9}$ m. So to observe ballistic motion, a stroboscopic time $<< 10^{-6}$ s is needed. For air, $D = 1.3 \times 10^{-11}$ m$^2$/s, so a strobe time $<< 10^{-5}$ s is needed.

### III. THE LANGEVIN EQUATION: GENERAL CONSIDERATIONS AND FRICTION FORCE

The random walk is a useful model to understand some of the basic parameters of Brownian motion, but the more precise, well-worn, and fruitful approach was proposed by Paul Langevin in 1908. Langevin's equation, which provides deeper insight into the phenomenon, is a variant of Newton's second law $F = ma$ with two independent force terms, both arising from the action of the fluid: (1) the viscous friction force slowing the particle as it moves through the fluid, and (2) a random agitation force that keeps the particle moving.

The independence of friction and agitation forces is suggested by the fact that a BP initially not moving and so with zero friction force, will not stay that way but will start moving because of random thermal agitation forces from the fluid. The independence also turns on the assumption that the basic events causing the agitation occur on a much shorter time scale than the relaxation time, i.e., the time it takes friction to dissipate an initial motion. To put it another way, it takes many impulses from agitation to significantly change the velocity. This is
manifestly true for a rarified gas, where a random series of individual molecular impacts agitate the particle, a single impact having a very small effect on the particle whose mass is $10^{12}$ times that of a molecular mass. Friction in this case also relies on individual molecular impacts, but it depends on the "raindrop effect" whereby impacts are greater on the front side of a moving particle. Given the much slower thermal speed of the particle compared to the molecular speed, the asymmetry of impacts is small, making the relaxation time much larger than the time needed for a single impact to occur. Since the BP mass is so much smaller than the molecular mass, the frictional force is proportional to $\nu$ for a rarified gas.\(^{12}\)

The molecular impact model for low-density gases fits nicely with the tendency of modern physics to reduce phenomena to the most elementary level, and this model is often presented as a general mechanism for friction and agitation. But for air, water, and similar fluids, it is not individual molecular impacts in random directions that cause the agitation, but a collective action of many molecules on a space scale roughly the dimensions of the BP.\(^{14}\) This random collective action will be modeled below as pressure fluctuations in random directions, and again the time for a single agitation event will be much smaller than the relaxation time. In terms of the number of fluctuation events needed to substantially change the velocity, a single pressure fluctuation event in air causes a velocity change of only about $10^{-5}$ of the particle's thermal speed, and the change is even less for water. For fluids similar to air and water, and for low-density gases too, it is these tiny changes that lead to the "unbelievably gentle" (ballistic) motion emphasized by Edward Nelson\(^ {15} \) and depicted in Figure 2. These time scale conveniences do not hold for an extremely viscous liquid like glycerin, where the relaxation time is no larger than the agitation time. In this case, the agitation and friction forces no longer add independently, and Langevin equation must be significantly modified to work.

For denser fluids like air and water, as for low-density gases, the friction term under conditions to be discussed is again proportional to the BP's thermal speed (unlike for a baseball pitched in air, where it is proportional to the square of the speed). Then the general form of the Langevin's version of Newton's second law is:

$$ M \frac{dv}{dt} = -f v + \delta F_a(t), \quad (11) $$

where $f$ is the friction constant, $v$ is the BP velocity measured in the lab frame, and $\delta F_a(t)$ is the agitation force rapidly changing in direction and magnitude. The friction constant reveals another reason why a collective model is more appropriate for denser fluids and why a molecular impact model is deficient. Molecular impacts for a spherical particle of radius $a$ lead to a friction constant proportional to the cross-sectional area $\pi a^2$ of the particle. But for a spherical BP of radius $a$, it is often most appropriate for many fluids to use the well-known Stokes friction constant, $f_{\text{Stokes}}$, which is proportional to $a$ rather than $\pi a^2$:

$$ f_{\text{Stokes}} \equiv f_{\text{St}} = 6\pi \eta a, \quad (12) $$

where $\eta$ is the shear viscosity of the fluid.

Stokes friction is an excellent representation of the frictional force under the following assumptions: (1) the mean free path of the fluid molecules is much smaller than the size of the particle; (2) the speed of the particle through the fluid is not too great; (3) the particle is not significantly accelerated, so the velocity of the particle through the fluid is approximately constant;\(^ {16} \) and (4) the "no stick" condition holds, i.e., the fluid molecules do not slide over the particle surface but move along with the particle surface.

The mean free path is about $6\times10^{-8}$ m for air at STP and much shorter for water, so condition (1) is satisfied for particles about a micrometer in radius. In condition (2), "not too great" in the case of speed means that the Reynolds number is small. This dimensionless
number, a ratio of inertial to viscous forces on a particle of linear dimension \( a \) moving with speed \( v \) through the fluid of density \( \rho \), is:

\[
Re = \frac{av\rho}{\eta}.
\]

(13)

When \( Re \) is \( \ll 1 \), the fluid undergoes laminar flow around a particle moving at constant velocity. Since the average \( v \) in Brownian motion is the thermal speed of the particle, it is a simple matter to show that \( Re \ll 1 \) for any conceivable combination of the parameters in Eq. (13) consistent with the mean free path of the molecules being much less than the particle size. Therefore, condition (2) is satisfied. Condition (3), well satisfied in air where accelerations are small, is problematic for any liquid, including water. But the requirement can be met to a good degree of approximation by using particles of high density (e.g., barium titanate) and a liquid of low viscosity (e.g., acetone). Condition (4) is generally satisfied, and leads to excellent agreement with a variety of experiments with liquids. (The no-stick condition does entrain fluid with the particle, giving the complex a mass greater than the particle mass, a fact accounted for in Eq. (12) when Condition (3) is satisfied.)\(^{17} \) So \( f_s \) in Eq. (12) an excellent approximation for a particle moving with negligible acceleration, particularly for a fluid with as low a viscosity as air at STP.\(^{18} \)

For water, although the conditions (1)—(4) are sufficiently satisfied for the diffusion (long-time) phase of motion, it turns out that Stokes friction is not precisely valid in the ballistic motion phase. In that phase, the particle is affected by a vortical type of motion set up in the fluid by the particle's motion through it. These vortices swirl around and then interact with the particle at a slightly later time, causing a memory effect in the motion and an increase in the particle's effective mass beyond that accompanying Stokes friction. This complex hydrodynamic action, first recognized and explained in the 1880s,\(^{19} \) causes the ballistic motion to differ a bit from what it would be with an ideal Stokes friction. But for longer times, the simpler Stokes friction leads to the correct mean-square displacement and hence the correct diffusion constant, as shown in Eq. (4). This immunity of diffusion to the hydrodynamic effect's increase of the particle's effective mass is a consequence of \( D \) being independent of the mass of the particle, which is shown in the discussion following Eq. (17) below. As mentioned above, for fluids with low viscosity, such as acetone, and for particles several microns in radius and several times more dense than water, the particle motion in the ballistic phase is close to the speed expected thermally in Eq. (7).\(^{20} \) Since the ballistic phase is not the focus of this paper, the simpler Stokes friction will be used in what follows.

Because the friction and agitation terms in the Langevin equation add linearly and therefore are assumed to act independently, the characteristic relaxation time for the friction term can be calculated by looking at the action of friction alone. Assume a BP has the velocity \( v_0 \) at time \( t = 0 \). (For smooth motion as in Figure 1, the magnitude, \( v_0 \), of \( v_0 \) will be on average equal to the thermal speed \( v_{th} \) in Eq. (7).) If we re-write Eq. (11) and neglect the agitation term, we obtain upon solving for \( v(t) \):

\[
v(t) = v_0 e^{-t/\tau},
\]

(14)

where the relaxation time \( \tau \) due to friction is \( \tau = M / f \), or for Stokes friction,

\[
\tau = \frac{M}{6\pi \eta a}.
\]

(15)

This is the time it takes friction to bring \( v(t) \) to \( 1/e = 0.37 \) of its initial velocity, and twice \( \tau \) brings it down to \( 1/e^2 = 0.13 \). This process of "erasing" an original velocity occurs continuously as a BP undergoes its motion.
The erasure time \( \tau \) in Eq. (15) should be comparable to the random walk characteristic time in Eq. (9). Substituting \( \tau \) for \( t_{rw} \) in Eq. (9) and solving for \( D \), we get \( D = \frac{k_B T}{12\pi \eta a} \). But as will now be shown, this is half the true value, showing the limitations of the simple random walk model when used for times approaching \( t_{rw} \) or smaller where ballistic motion, not diffusion, is the primary process.

For a rigorous derivation of \( D \), dot both sides of Eq. (11) with \( r \), use the identities \( r \cdot \dot{r} = d^2 r^2 / 2 dt^2 - v^2 \) and \( d(v^2) / dt = 2r \cdot (dr / dt) = 2r \cdot \dot{v} \). Taking averages and substituting into Eq. (11), we get:

\[
\frac{M}{2} \frac{d^2 \langle r^2 \rangle}{dt^2} - M \langle v^2 \rangle = - \frac{f}{2} \frac{d\langle r^2 \rangle}{dt} + \langle r \cdot \delta F_a \rangle.
\]

But \( \langle r \cdot \delta F_a \rangle = 0 \), leading to the solution: \( \langle r^2 \rangle = C_1 e^{-t/\tau} + C_2 + C_3 t \). Assuming the particle starts at \( r = 0 \), then \( C_2 = 0 \). And in the diffusion realm where \( t >> \tau \), the first term, \( C_1 e^{-t/\tau} \), can be neglected. Then \( \langle r^2 \rangle = C_3 t \). Substituting this into Eq. (16), we get \( \langle f / 2 \rangle C_3 = M \langle v^2 \rangle \), which gives \( \langle r^2 \rangle = 2M \langle \sigma^2 \rangle / f t \). Substituting \( dk_B T / M \) for \( \langle \sigma^2 \rangle \), we get the diffusion equation: \( \langle r^2 \rangle = 2dk_B T t / f \equiv 2D t \), showing that:

\[
D = \frac{k_B T}{f}.
\]

For Stokes friction, \( f_s = 6\pi \eta a \), so \( D \) depends on fluid viscosity, particle radius, but not on particle mass. This is true in general for \( f \), and hence for \( D \). This independence of \( D \) on particle mass occurs because a bigger particle mass causes the relaxation time in Eq. (15) to increase, but a larger mass also has a smaller thermal speed as shown in Eq. (7), tending to decrease \( D \), and the two tendencies cancel each other. This independence is shown clearly in the random walk model: when Eqs. (9) and (10) are substituted into Eq. (8), the mass cancels.

**IV. THE LANGEVIN EQUATION: PRESSURE FLUCTUATION AS AGITATION MECHANISM**

The viscous Stokes drag force appropriate for dense fluids like air and water, arises from collective effects between many molecules, only a small proportion of which, over any short period of time, actually touch the particle. In light of the collective nature of the Stokes friction, it is only natural to expect the agitation term to also be of a collective nature, i.e., arising from mesoscopic processes on the spatial scale of the Brownian particle. In other words, for Stokes friction, molecular impacts are the cause of the agitation force only in the trivial sense that they convey to the particle physical occurrences on a wider scale. F.L. Markley and D. Park made that point in 1972 and provided the motivation for the present work. After pointing out that Brownian motion results from a large number of collisions, Markley and Park say:

“[I]t must be considered to be a macroscopic rather than a microscopic phenomenon. We can think of it as caused by pressure fluctuations due to statistical fluctuations in the number of molecules in a volume of order of magnitude of the volume of the Brownian particle.”

A month later, Kivelson *et al* presented a theory of the role of pressure fluctuations in Brownian motion. Kivelson *et al*’s treatment relied on derivations of fluid properties using complex
statistical mechanics involving microscopic analysis of molecular interactions. Here, we will present a much more accessible treatment of pressure fluctuations as the agitation force.

Before looking at details of the pressure fluctuation mechanism, the fluctuation-dissipation (F-D) theorem governing the motion will be derived. This is an important relationship that any fluctuation mechanism must obey. We assume that the agitation force varies in magnitude and direction, but that on average it persists for a correlation time \( t_1 \) before changing significantly. The correlation time is associated with the force correlation function, \( \left\langle \delta F_a(t) \cdot \delta F_a(t + t') \right\rangle \). When \( t' = t \), the correlation function is at its maximum value of \( \left\langle \delta F_a^2 \right\rangle \).

As \( t' \) increases, it becomes increasingly likely that the agitation force changes its value at time \( t \). Since the change is random, the dot product \( \delta F_a(t) \cdot \delta F_a(t + t') \) tends on average to decrease from its maximum, going to zero for large \( t' \). In terms of the force correlation function, \( t_1 \) and is given by:

\[
t_1 = \frac{1}{\left\langle \delta F_a^2 \right\rangle} \int_0^\infty \left\langle \delta F_a(t) \cdot \delta F_a(t + t') \right\rangle dt',
\]

where:

\[
\left\langle \delta F_a^2 \right\rangle = \lim_{t \to \infty} \frac{1}{t} \int_0^t \delta F_a(t') \cdot \delta F_a(t') dt'.
\]

When applied to Brownian motion, the F-D theorem states that the friction constant \( f \) is directly related to the force correlation shown in Eq. (18). The simplest and most intuitive approach to the theorem focuses on an equivalence between the fluctuation and dissipation processes: during the time \( \tau \) it takes for an initial thermal equilibrium speed to be exponentially reduced by dissipation, the agitation force \( \delta F_a \) must replenish the thermal speed. This temporal equivalence between dissipation and fluctuation will now be used to provide a relatively simple derivation of the F-D theorem.

Let \( \delta v \) be the random change in velocity from a single random agitation event of duration \( t_1 \). In velocity space, the random velocity impulses add together in a random walk. And like any random walk, the net velocity change in time \( t \) is proportional to the square root of the number of impulses received in that time. This is illustrated in Figure 3. In time \( \tau \), the number of agitation impulses received is then \( N_\tau = \tau / t_1 \). To obtain a good result from this random walk, we must assume that the number of events is large, so we must assume that \( t_1 << \tau \). This condition will be seen to hold very well for a particle of radius \( 10^{-6} \text{m} \) in air or water. Equating the speed obtained from the \( N_\tau \) impulses to the thermal speed, and using the equipartition result \( v_{th}^2 = \frac{dk_B T}{M} \), we get:

\[
\left\langle \delta v^2 \right\rangle (\tau / t_1) = \left\langle \delta v^2 \right\rangle N_\tau = v_{th}^2 = \frac{dk_B T}{M}.
\]

By the impulse-momentum theorem in average expected value form, \( \left\langle \delta v^2 \right\rangle = \left\langle \delta F_a^2 \right\rangle t_1^2 / M^2 \), so substituting into Eq. (20), we get a version of the F-D theorem that shows clearly the relationship that must hold between agitation and dissipation:

\[
\left\langle \delta v^2 \right\rangle (\tau / t_1) = \left\langle \delta F_a^2 \right\rangle \tau t_1 / M^2 = \frac{dk_B T}{M}.
\]
To get the more formal version of the theorem, use Eq. (18) for $\delta F_a^2$ in the middle member of Eq. (21) and substitute for $\tau$ from Eq. (15). This leads to the oft-cited result:

$$\int_0^\infty \langle \delta F_a(t) \cdot \delta F_a(t + t') \rangle dt' = Mdk_BT / \tau = 6\pi \eta a d_kBT. \tag{22}$$

Eqs. (18) and (22) yield an alternative form that will serve useful in the following:

$$\langle \delta F_a^2 \rangle t_1 = 6\pi \eta a d_kBT. \tag{23}$$

Note that the simple derivation presented here uses the thermal equilibrium speed required by the equipartition theorem of statistical physics. In general, if a process obeys the F-D theorem, then we can be assured that the thermal equilibrium speed is implied. Note also that we had to assume that $t_1 << \tau$. More rigorous derivations of the F-D theorem must assume the same thing.

We are now prepared to determine if pressure fluctuation as the agitating mechanism is consistent with Eq. (23). Since we are focusing on pressure fluctuations for the agitation force, we change the subscript on $\delta F_a(t)$ so it is now $\delta F_p(t)$.

A pressure fluctuation in a parcel of liquid surrounding a Brownian particle can result in a number of ways: a fluctuation in the density at constant temperature, which would result from a temporary influx or efflux of particles from a given volume; a thermal fluctuation at constant density, or an adiabatic volume change in which density and temperature change. The simplest case is an adiabatic volume change. In fact, if the number of molecules in the parcel is constant, a rigorous application of statistical mechanics shows that an adiabatic volume change is equivalent to a combination of the other two mechanisms.

Consider a parcel of fluid of volume $V$. For an adiabatic process,

$$\langle \delta P \rangle = -k_B T \left( \frac{\partial P}{\partial V} \right) = \sqrt{\frac{B_s k_BT}{V}}, \tag{24}$$

where $B_s = -\left( \frac{\partial P}{\partial V} \right)$. is the adiabatic bulk modulus. The simplest guess for the net pressure fluctuation force on the Brownian particle would be $\langle \delta P \rangle$ times the cross-sectional area of the particle, $\pi a^2$, where $\delta P$ is calculated from Eq. (24) for a fluid element of volume equal to the particle's volume. Multiplying $\delta P$ by $\pi a^2$ and substituting $4\pi a^3 / 3$ for $V$, we get...
\( \langle \delta F_p^2 \rangle = 3\pi a B k_B T \), which we take as an approximation for \( \langle \delta F_a^2 \rangle \) in Eq. (23). This is roughly correct, but it is easy to imagine an increase in pressure on one side of a particle and a decrease on the other side, with parcels in other directions balancing, in which case the total force on the particle would be twice \( \langle \delta P \rangle \pi a^2 \). In addition, pressure fluctuations occur at all scales, bigger and smaller than the volume of the particle. Like Kivelson et al., a correction constant \( \kappa \) will be used to account for the fact that the estimate is not rigorous. \(^{31}\)

\[
\langle \delta F_p^2 \rangle = \kappa^2 (3\pi a B k_B T). \quad (25)
\]

The next step is to determine the value of \( t_1 \), which we write as the relaxation time \( t_p \) for a pressure fluctuation. This relaxation time is essentially the time constant for an exponential decay of excess stress inside a material. Kivelson et al were focused on the Stokes drag term and didn't use the relaxation time explicitly, \(^{32}\) but it is given by a number of authors to be approximately \( \eta / B_1 \). \(^{33}\) So we take \( t_p \) to be:

\[
t_p = \frac{\eta}{B_1}. \quad (26)
\]

Now when this value of \( t_p \) is multiplied by \( \langle \delta F_p^2 \rangle \) in Eq. (25), we find exact equivalence with Eq. (23) subject to the condition:

\[
\kappa^2 = 3. \quad (27)
\]

The occurrence of \( \eta \) in Eqs. (23) and (26) requires some discussion. A shear distortion of a fluid parcel occurs when the parcel changes shape without changing its volume. \(^{34}\) An adiabatic pressure fluctuation, on the other hand, arises from a change in volume of a fluid parcel without changing its shape, involving what is called the "bulk viscosity" \( \zeta \). But there is a close relationship between \( \eta \) and \( \zeta \). \(^{35}\) Just as \( \eta \) is the proportionality constant between shear viscous force and velocity gradient, so \( \zeta \) is the proportionality constant between a normal force on a fluid parcel and the velocity gradient. In either case, a rearrangement of average molecular positions relative to each other is involved, and this requires a velocity gradient which rearranges the positions. Since \( \eta \) and \( \zeta \) are not exactly the same, a correction constant could be used in Eq. (26). But it would occur in a product with \( \kappa \) in Eq. (23), so for simplicity we just use the single factor \( \kappa \).

A reasonable approximation to \( t_p \) is the time between collisions of neighboring molecules, since it is collisions that adjust molecular positions and velocities to a sudden increase in pressure. For example, the distance between water molecules is \( d = 3.2 \times 10^{-10} \) m. Since the molecules are close-packed, this may be taken as the mean free path \( \lambda \). The thermal speed is 642 m/s, which gives the time between collisions of water molecules under STP to be \( t_{coll} = \lambda / v_{th} = 4.8 \times 10^{-13} \) s. This is very close to the value for \( t_p \) in Table 1 obtained from Eq. (26) and taking \( \mu = 1 \). For air at STP, approximating it as nitrogen, the mean free path is \( \lambda = 6.28 \times 10^{-8} \) m, and the average molecular speed is 515 m/s, giving \( t_{coll} = \lambda / v_{th} = 1.2 \times 10^{-10} \) s. Again, this is very close to \( t_p \) in Table 1.

Table 1 give values of \( \eta \), \( B_1 \), \( t_p \), and the self-diffusion constant, \( D_{mol} \), for molecules of water and air at STP. The \( D_{mol} \) values are used to calculate the root-mean-square displacement \( r_{rms}^{mol} \) of a molecule over the time \( t_p \) in three dimensions using Eq. (6) to test if the assumption of a fixed fluid parcel is valid. For water, \( r_{rms}^{mol} = \sqrt{6D_{mol}t_p} \) is much smaller than the
diameter of a BP of radius of $10^{-6}$ m. This validates the assumption implied in Eq. (23) (24) that the number of molecules in a fluid parcel of BP size doesn't change significantly over the time $t_p$, i.e., that we are dealing with a fixed parcel of fluid. For air, $v_{rms}$ is about 5% of the diameter of a particle of radius $10^{-6}$ m, so the assumption of a stable parcel is acceptable.

### V. FAILURE OF PRESSURE FLUCTUATIONS FOR LARGE VISCOSITY

From Table 1, $t_p << \tau$, so the time-scales for agitation and dissipation are clearly well-separated. Let $\delta v_p$ be the random change in particle velocity from a single pressure-fluctuation event. From the impulse-momentum relationship $\delta F_p \delta t_p = M \delta v_p$ (and neglecting the values of the correction constants $\mu$ and $\kappa$), we get an approximate value of $\delta v_p$ for water of $5 \times 10^{-7}$ m/s, and for air about $10^{-5}$ m/s. After the time $2 \tau$ an initial equilibrium thermal velocity $v_{th}$ has greatly dissipated. In this time, the random impulses restore the thermal speed, so for water it takes about $2 \tau / t_p = 450,000$ impulses, and for air about 100,000 impulses.

### TABLE 1: Physical Characteristics of Water and Air ($a = 10^{-6}$ m, $M = 8.34 \times 10^{-15}$ kg)

|        | $\eta$, kg/sm | $B_s$, Pa* | $t_p / \mu$, s | $\tau$, s | $D_{vis}$, m$^2$/s | $D_{mol}$, m$^2$/s | $v_{rms}(t_p)$, m |
|--------|----------------|------------|-----------------|-----------|-------------------|-------------------|------------------|
| Water  | 0.001          | 2.1x10$^9$ | 4.76x10$^{13}$  | 2.12x10$^{13}$ | 2.20x10$^{13}$    | 2.02x10$^9$      | 5.34x10$^{13}$   |
| Air    | 1.73x10$^5$   | 1.41x10$^7$| 1.24x10$^{10}$  | 1.23x10$^{10}$| 1.27x10$^{11}$    | 1.85x10$^5$      | 1.17x10$^7$      |

* $B_s$ for water taken from A. Hudson & R. Nelson, *University Physics* (2nd ed., Saunders College Publishing, Philadelphia, 1990), p. 360; $B_s$ for air calculated from ideal gas law as $\gamma P$, with $\gamma = 1.4$.

**Value for water taken from online article: "https://dtx.de/od/diff/index.html". Value for air taken as the experimental value for nitrogen from F. Reif, *Fundamentals of statistical and thermal physics* (McGraw-Hill, New York, 1965), p. 485.

From Table 1, $t_p << \tau$, so the time-scales for agitation and dissipation are clearly well-separated. Let $\delta v_p$ be the random change in particle velocity from a single pressure-fluctuation event. From the impulse-momentum relationship $\delta F_p \delta t_p = M \delta v_p$ (and neglecting the values of the correction constants $\mu$ and $\kappa$), we get an approximate value of $\delta v_p$ for water of $5 \times 10^{-7}$ m/s, and for air about $10^{-5}$ m/s. After the time $2 \tau$ an initial equilibrium thermal velocity $v_{th}$ has greatly dissipated. In this time, the random impulses restore the thermal speed, so for water it takes about $2 \tau / t_p = 450,000$ impulses, and for air about 100,000 impulses.

### V. FAILURE OF PRESSURE FLUCTUATIONS FOR LARGE VISCOSITY

The derivation of Eq. (23) depends on the assumption that $t_p << \tau$. But as Table 2 shows, the assumption fails for glycerin for which $\eta$ is 1500 times water's, $t_p$ is about 700 times water's, while $\tau = 1.48 \times 10^{-10}$ s is much smaller than water's. The seriousness of the violation of the condition $t_p << \tau$ follows when we consider a BP that starts with zero velocity. Then pressure fluctuations cannot bring it to its thermal speed of 0.00122 m/s, because even if a pressure fluctuation $\delta F_p$ acts for an infinite time, in contrast to a series of random fluctuations, the particle achieves a terminal speed $v_{term}$ (when $\delta F_p = 6 \pi \eta a v_{term}$) of only $v_{term} = 9.48 \times 10^{-4}$ m/s, about half its thermal speed. This same exercise shows that, for water, a constant pressure fluctuation would accelerate the particle to a terminal speed of 0.48 m/s, far above its expected thermal speed. (Of course, a fluctuating random pressure gives it precisely its thermal speed.) We must conclude that pressure fluctuations are insufficient to overcome the drag effect of glycerin's very large viscosity.

### TABLE 2: Some Physical Characteristics of Glycerin

| $\eta$, kg/sm* | $B_s$, Pa* | $t_p$, s | $\tau$, s |
|----------------|------------|---------|---------|
| 1.5            | 4.5x10$^7$ | 3.33x10$^{10}$ | 1.48x10$^{10}$ |

* $\eta$ taken from https://www.ecourses.ou.edu/cgi-bin/ebook.cgi?topic=fl&chap_sec=01.3&page=theory. $B_s$ taken as reciprocal of compressibility from http://hyperphysics.phy-astr.gsu.edu/hbase/Tables/compress.html.
A consistent treatment of the large-viscosity case requires the motion of the center of mass of a fluid parcel adjacent to the Brownian particle to be taken into account. Such a parcel has its own thermal velocity given by $v_{\text{ parcel}} = \sqrt{\frac{3k_B T}{M_{\text{ parcel}}}}$. Therefore, for a parcel of the same mass as the BP, adjacent to and moving towards it, this coherent motion of molecules in the parcel exerts a large viscous force on the BP, thus forcing it to move in approximately the same direction as the parcel. In other words, there is an inelastic "collision" between the moving parcel and particle, which results in both having the same velocity after the interaction is complete. In the reference frame of the parcel, the particle plows into it and by Eq. (14), the particle is brought to rest relative to the parcel in a very short time $\tau$. This is also the effective lifetime of a parcel's impact on the BP. So for very large viscosity, when pressure fluctuations are largely irrelevant, Brownian motion is completely characterized by the single time scale $\tau$ for both drag and agitation force. Consequently, the motion is more like a random walk as in Figure 1(b) even at very small observation intervals.

It is interesting to look at how far into a parcel of glycerin the particle plows in a collision between the two. The coasting distance from Eq. (14) is:

$$\Delta_{\text{coast}} = \int_0^\infty v_o e^{-t/\tau} dt = \int_0^\infty v_{\text{ therm}} e^{-t/\tau} dt = \tau v_{\text{ therm}} = \frac{\sqrt{3Mk_BT}}{6\pi a}.$$  \hspace{1cm} (28)

For a BP in glycerin, this is only $3.60 \times 10^{-13}$ m, about the size of an atomic nucleus—much smaller than the BP. So the interaction between parcels and between parcels and BP is similar to a bunch of very rigid balls colliding with each other and with the BP; the fluid nature of the parcels is not so obvious.

A detailed treatment of an agitation force based directly on viscosity is beyond the scope of this paper, but the following reformulation of the Langevin equation presents a simple phenomenological model shedding insight into this aspect of Brownian motion.

Let the macroscopic motion of fluid enveloping the particle be described by an effective velocity $v_{\text{ parcel}}$, measured relative to the lab frame as is $v$. Since the viscous force depends on the relative motion $v_{\text{ parcel}} - v$ between the BP and the surrounding liquid, Newton's second law is:

$$M \frac{dv}{dt} = \delta F_p + 6\pi a (v_{\text{ parcel}} - v) = \left( \delta F_p + 6\pi a v_{\text{ parcel}} \right) - 6\pi a v = \delta F_{\text{ total}} - 6\pi a v.$$  \hspace{1cm} (29)

This is just the Langevin equation, showing the agitation force consisting of pressure fluctuations and fluid parcel motion. Since $v_{\text{ parcel}} = v_{\text{ therm}} = \sqrt{3k_BT/M}$, the criterion for pressure fluctuations to dominate is:

$$\frac{6\pi a v_{\text{ parcel}}}{\delta F_p} = \frac{6\pi a v_{\text{ therm}}}{2\kappa\sqrt{3\pi ak_BTb_S}} = \frac{\eta a}{\sqrt{aB_S M}} \ll 1,$$  \hspace{1cm} (30)
where factors of order unity have been ignored. Substituting for $M$ in terms of the fluid's mass density $\rho$, $M = 4\pi a^3 \rho / 3$, and using the fact that the speed of sound in a fluid is $v_s = \sqrt{B_s / \rho}$, we obtain the condition:

$$\eta \ll \rho a v_s .$$

(31)

Applying this condition to a BP ($a = 10^{-6}$ m), the reader may easily verify that it holds well for water ($\rho = 1000$ kg/m$^3$, $v_s = 1400$ m/s, $\eta = 0.001$ kg/sm) but fails for glycerin ($\rho = 1261$ kg/m$^3$, $v_s = 1900$ m/s, $\eta = 1.5$ kg/sm).

VI. SUMMARY

The diffusion rate of Brownian particles in relatively dense fluids like air at STP and water can be described by the Langevin equation with a Stokes form of friction involving collective viscous effects of the surrounding fluid. We have shown that the agitation term can be described by pressure fluctuations which also involve collective action of fluid surrounding the particle. The combination of Stokes friction and agitation from pressure fluctuations obeys the fluctuation-dissipation relationship. But the agitation model was shown to fail for very viscous fluids, taking glycerin as an example. In this case, the agitation results from both pressure fluctuations and from thermal motion of parcels of fluid surrounding the Brownian particle.

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\[ \Delta P \approx \frac{1}{2} \left( \frac{\partial P}{\partial V} \right)_S \Delta V \]

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\[ \Delta W = \int_0^{\Delta V_f} \Delta P d(\Delta V) = \int_{\Delta P_0}^{\Delta P_f} \left( \frac{\partial P}{\partial V} \right)_S \Delta V = \left( \frac{\partial P}{\partial V} \right)_S \frac{\Delta V_f^2}{2}. \]  

(A)

From \( \Delta P_f = -\left( \frac{\partial P}{\partial V} \right)_S \Delta V_f \), \( \Delta V_f^2 = \Delta P_f^2 / \left( \frac{\partial P}{\partial V} \right)_S^2 \), so Eq. (A) is:

\[ \Delta W = -\frac{1}{2} \left( \frac{\partial P}{\partial V} \right)_S \Delta P_f^2, \]

(B)

so:

\[ \Delta P_f^2 = -2 \left( \frac{\partial P}{\partial V} \right)_S \Delta W. \]  

(C)

Then taking expectation values, we get

\[ \delta P_f = \sqrt{\left\langle \Delta P_f^2 \right\rangle} = \sqrt{-2 \left( \frac{\partial P}{\partial V} \right)_S \left\langle \Delta W \right\rangle}. \]  

(D)

Since \( \Delta W \) in Eq. (A) is quadratic in the volume change, the equipartition theorem applies, so \( \left\langle \Delta W \right\rangle = k_B T / 2 \). Therefore, substituting for \( \left\langle \Delta W \right\rangle \) in Eq. (D), we get:

\[ \delta P_f = \sqrt{-k_B T \left( \frac{\partial P}{\partial V} \right)_S}. \]  

(E)
18

31 See Kivelson et al. (Ref. 24, Eq. (12)) They do not use the modulus $B_s$, but use their own modulus $K$ which corresponds to fluctuations at constant density (see last sentence of their Appendix B).

32 Kivelson et al. (Ref. 24) say that the force correlation time can be associated with the time $4\eta/(3\rho c^2)$ where $c =$ speed of sound $= \sqrt{K_0/\rho}$, and $K_0 \equiv B_s$ is the "zero frequency bulk modulus." So their value is, apart from a small numerical factor, equal to $\eta/B_s$.

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34 P.A. Egelstaff, *An Introduction to the Liquid State* (Clarendon Press, Oxford, 1994), Appendix 5.

35 A.B. Bhatia, *Ultrasonic Absorption* (Dover Publications, New York, 1967), pp. 50, ff; P.A. Egelstaff, *An Introduction to the Liquid State* (Clarendon Press, Oxford, 1994), Appendix 5; L. Hall, "The Origin of Ultrasonic Absorption in Water, Physical Review, 75, No. 7, 775-781. It is well known that $\zeta$ is a small multiple of $\eta$ for low-viscosity fluids like water and air. See A.B. Bhatia, pp. 63-64 etc., … L. Hall, "The Origin of Ultrasonic Absorption in Water, Physical Review, 75, No. 7, pp. 775-781, p. 780; L.E. Kinsler and A.R. Frey, *Fundamentals of Acoustics* (2nd ed., John Wiley & Sons, New York, 1962), p. 224, Eq. (9.15a), and p. 235; R.W.B. Stephens and A.E. Bates, *Acoustics and Vibrational Physics* (Edward Arnold Ltd., London, 2nd ed., 1966), p. 763.

36 E.M. Lifshitz and L.P. Pitaevskii, *Statistical Physics*, Part 2 (Pergamon Press, New York, 1980), p. 371 (Eq. 88.5); F. Munley, "Answer to Question #1 ["How does a Brownian particle at rest get kicked up to kT?", Frank Munley, *Am. J. Phys.* 62(10), 871 (1994)], *Am. J. Phys.* 64(3), 1996, p. 203.