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Relaxation of Brownian particles in a gravitational field

Halil Saka, Roger D. Bengtson, and Linda E. Reichl
Department of Physics, University of Texas, Austin, Texas 78712

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We describe an upper level undergraduate experiment on the time-dependent behavior of a suspension of Brownian particles under gravitational attraction. We employed the Fokker-Planck equation in the strong friction limit and measured the time-evolution of the probability distribution for 1.0 μm diameter latex Brownian particles in water at room temperature and pressure. The experiment provides evidence of the atomic nature of water.

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I. INTRODUCTION

Brownian motion is the manifestation of the atomic nature of matter at the macroscopic scale. Because matter is made of atoms and molecules in a state of constant motion, the mass density continually fluctuates in space and time. When macroscopically observable particles are embedded in such a medium, they undergo continuous random motion due to the forces induced by density fluctuations in the medium.

The first published observation of Brownian motion is credited to Brown,[1] who observed the agitated motion of grains of pollen in water. The first person to relate Brownian motion to the atomic nature of matter was Einstein[2] (although he did not know of Brown's published work), who derived an expression for the diffusion coefficient for Brownian particles. In 1913 Perrin pointed out that emulsions of macroscopic particles behave the same way as ideal gases. Thus we can consider equilibrium states in which the suspended particles form a stable distribution within a liquid medium, similar to the atmospheric distribution of air molecules. Perrin described this stable distribution as the state in which an equilibrium is established between "the opposing effects of gravity, which pulls the particles downwards, and of the Brownian movement, which tends to scatter them."[3] (Perrin received the 1926 Nobel prize in physics for this work.) It is this process of "pulling" and "scattering" that will be central to our discussion of suspended Brownian particles.

It can easily be shown using purely equilibrium requirements that a suspension of particles in a liquid will eventually acquire a steady state exponential probability density function as a function of height. More detailed discussion of this phenomenon can be found in many introductory texts.[4] The Fokker-Planck equation, which governs the time-dependence of such systems, can be used to describe the transition from a uniform distribution to an exponential distribution.

Brownian motion on the horizontal plane (a random walk) and the long-time equilibrium state along the vertical axis have been discussed at the undergraduate level in Refs. 5–8, but the random walk problem under gravitational attraction has been largely neglected. Our experimental setup is similar to that of Ref. 3, with the major difference being the time dependent nature of the question we have asked. We employ similar data capture and analysis techniques as Nakroshis *et al.*[5] In the following sections we give the theoretical model, experimental procedure, and observations of the relaxation of Brownian particles in the presence of a gravitational field.

II. THEORY

We consider the relaxation of spherical latex particles (B-particles) of mass m and radius r in water in a vertical container of height H in the presence of a gravitational field. At the initial time the B-particles are thoroughly mixed with the water and are uniformly distributed throughout the container. In the horizontal direction, the uniform distribution will not change with time because a uniform distribution in this direction is the stationary (equilibrium) state of the system after long times. In the vertical direction the B-particles will relax to a non-uniform stationary state due to the presence of the gravitational field.

The net force on a single B-particle in the vertical direction is given by the gravitational force minus the buoyant force and can be written as $m^*g=(\rho_w-\rho_b)V_b g$, where g is the acceleration of gravity, ρ_w is the density of water, ρ_b is the density of the B-particle, V_b is the volume of a B-particle, and m^* is the effective mass of a B-particle. As the B-particles move through water they also experience a frictional force characterized by the Stokes friction parameter $\gamma=6\pi\eta r$, where η is the shear viscosity of water. The equation of motion for the vertical position z of a B-particle is given by the Langevin equation

$$m\frac{d^2z}{dt^2}=\gamma\frac{dz}{dt}-m^*g+\xi(t), \tag{1}$$

where $\xi(t)$ is a white noise force on the B-particle due to density fluctuations of the water.

Each B-particle will experience a different realization of the random force $\xi(t)$. Therefore, it is useful to describe the vertical relaxation of the B-particles in terms of the probability density $P(z,t)$ of finding a given B-particle in the interval z to $z+dz$. The evolution of this probability density is given by the Fokker-Planck equation. In the limit of strong friction γ the Fokker-Planck equation that governs the relaxation of the probability density $P(z,t)$ is given by

$$\frac{\partial P(z,t)}{\partial t}=\frac{\partial}{\partial z}\left(\frac{m^*g}{\gamma}P(z,t)+\frac{D}{2\gamma^2}\frac{\partial P(z,t)}{\partial z}\right)=-\frac{\partial J(z,t)}{\partial z}, \tag{2}$$

where $D=2\gamma k_B T$ is the diffusion coefficient and $J(z,t)$ is the probability current. The derivation of Eq. (2) from Eq. (1) can be found in Refs. 9–11.

To solve Eq. (2) we assume that it has a solution of the form $P_\lambda(z,t)=e^{-\lambda t}F_\lambda(z)$, where $\lambda\geq 0$. Then $F_\lambda(z)$ satisfies the following equation:

$$-\lambda F_\lambda(z) = \frac{m^* g}{\gamma}\frac{dF_\lambda(z)}{dz} + \frac{D}{2\gamma^2}\frac{d^2F_\lambda(z)}{dz^2}. \quad (3)$$

The solution to Eq. (3) can be written in the form

$$F_\lambda(z) = e^{-\alpha z}[A_\lambda \cos(\alpha R_\lambda z) + B_\lambda \sin(\alpha R_\lambda z)], \quad (4)$$

where $\alpha = m^* g\gamma/D$ and $R_\lambda = \pm\sqrt{2D\lambda/m^{*2}g^2 - 1}$. The B-particle current, $J = -(mgP/\gamma + (D/2\gamma^2)\partial P/\partial z)$, can be written as

$$J_\lambda(z,t) = -\frac{D}{\gamma^2}e^{-\lambda t}e^{-\alpha z}\frac{\alpha}{2}[(A_\lambda + R_\lambda B_\lambda)\cos(\alpha R_\lambda z) + (B_\lambda - R_\lambda A_\lambda)\sin(\alpha R_\lambda z)]. \quad (5)$$

In the experiment the vertical column of B-particles is closed by hard walls at $z=0$ and $z=H$. Therefore, no current can flow through these end walls, and we require that $J(0,t)=0$ and $J(H,t)=0$.

At the boundary $z=0$ the condition $J_\lambda(0,t)=0$ yields the relation $A_\lambda = -R_\lambda B_\lambda$ and eliminates the cosine dependence from the current. Thus,

$$J_\lambda(z,t) = -\frac{D}{\gamma^2}e^{-\lambda t}e^{-\alpha z}\frac{\alpha}{2}B_\lambda(1 + R_\lambda^2)\sin(\alpha R_\lambda z). \quad (6)$$

At the boundary $z=H$ the condition $J_\lambda(H,t)=0$ is satisfied differently for $\lambda=0$ and for $\lambda \neq 0$. The case $\lambda=0$ corresponds to the long time stationary state because $P_0(z) \equiv P_0(z,t)$ is independent of time. For $\lambda=0$, $R_0=-i$ and $J_0(H,t)=0$ due to the coefficient $(1+R_0^2)$ in Eq. (6). Then $F_0(z) = iB_0 \exp[-m^* gz/k_BT]$. The long-time stationary state carries all the probability. If we normalize the solution to unity over the interval $0 \leq z \leq H$, we obtain

$$P_0(z) = \frac{m^* g}{k_BT}\frac{e^{-m^* gz/k_BT}}{1 - e^{-m^* gz/k_BT}}. \quad (7)$$

For $\lambda \neq 0$ the condition $J_\lambda(H,t)=0$ yields the requirement that $\alpha R_{\lambda_n} H = n\pi$, where $n=1,2,\ldots,\infty$. Thus,

$$\lambda_n = \frac{m^{*2}g^2}{2D} + \frac{n^2\pi^2 D}{2\gamma^2 H^2}, \quad (8)$$

so there are a countable but infinite number of decay rates governing the evolution of the B-particles. The solution to the Fokker-Planck equation can then be written

$$P(x,t) = P_0(x) + \sum_{n=1}^{\infty} \mathrm{e}^{-\lambda_n t}F_{\lambda_n}(z), \quad (9)$$

or, using Eqs. (4) and (8), we obtain

$$P(z,t) = P_0(z) + \sum_{n=1}^{\infty} A_n e^{-(m^{*2}g^2/4\gamma k_BT + k_BTn^2\pi^2/\gamma H^2)t}e^{-m^* gz/2k_BT} \times \left[\cos\left(\frac{n\pi z}{H}\right) - \frac{m^* gH}{2k_BTn\pi}\sin\left(\frac{n\pi z}{H}\right)\right], \quad (10)$$

where the constants A_n are determined from the initial conditions.

Because the B-particles are thoroughly mixed with the water at the beginning of the experiment, the initial probability distribution in the vertical direction is well approximated as $P(z,0)=1/H$. We use this initial condition to determine the coefficients A_n in Eq. (10), and we finally obtain (see the Appendix)

$$P(z,t) = \frac{2\alpha}{1 - e^{-2\alpha H}}e^{-2\alpha z} + \sum_{n=1}^{\infty}\frac{(e^{\alpha H}\cos(n\pi) - 1)\alpha n^2\pi^2}{(\alpha^2H^2 + n^2\pi^2)^2} \times \left[\cos\left(\frac{n\pi z}{H}\right) - \frac{\alpha H}{Tn\pi}\sin\left(\frac{n\pi z}{H}\right)\right]e^{-(\lambda_n t + \alpha z)}. \quad (11)$$

[The solution for the initial condition $P(z,0)=\delta(z-z_0)$ can be found in Ref. 9, p. 58.]

The B-particles used in the experiment were 1 μm diameter latex spheres suspended in water at room temperature, although in our theoretical analysis it proved useful to consider both 1.0 and 0.5 μm diameter particles. The viscosity of water at 293 K is $\eta=0.001$ Pa s and its density is $\rho_w = 1000\ \mathrm{kg/m^3}$. The density of the B-particles is $\rho_b = 1050\ \mathrm{kg/m^3}$. The height of the sample was $H = 0.000\,58$ m. For 1.0 μm diameter B-particles $\alpha H = 18.4$ and the longest relaxation time was $\tau_1 = 1/\lambda_1 = 37.5$ min. For 0.5 μm diameter B-particles, $\alpha H = 2.30$, and the longest relaxation time was $\tau_1 = 1/\lambda_1 = 7.2$ h.

To compare the theory with our experimental results we use $P(z,t)$ from Eq. (11) and plot the probability density function at times that correspond to our measured times. The expression for $P(z,t)$ in Eq. (11) contains an infinite number of terms. We can truncate it according to how well it approximates the initial condition $P(z,0)=1/H$. We find that for 0.5 μm diameter B-particles that we need to keep only 15 terms in the expansion. For 1.0 μm diameter B-particles, at $t=0$ min, more than 5000 terms are required to obtain a reasonable approximation to $P(z,0)$. However, at $t=5$ min, we only need to keep 150 terms to obtain a good approximation for $P(z,t)$ at $t=5$ min. Because we cannot start acquiring data for times less then 5 min due to experimental reasons 150 terms are adequate for 1.0 μm diameter B-particles.

Figure 1 shows $P(z,t)$ for the 1.0 μm B-particles at times $t=5$ min, $t=1$ h, $t=3$ h, $t=7$ h, and the steady state solution. Because the $t=7$ h distribution is almost indistinguishable

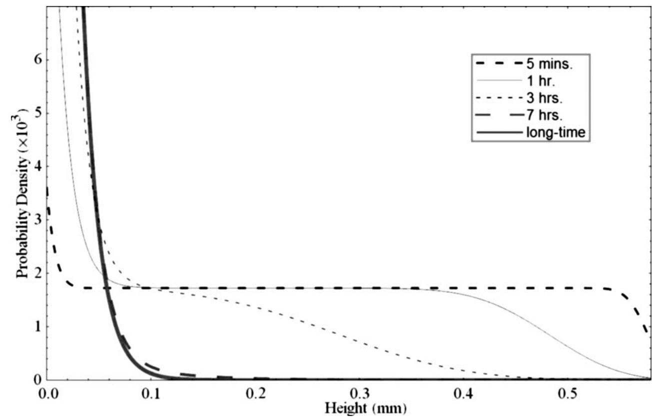

Fig. 1. Plot of the probability density function $P(z,t)$ versus the height z for 1.0 μm diameter B-particles in water at $t=5$ min, $t=1$ h, $t=3$ h, $t=7$ h, and the long-time stationary state.

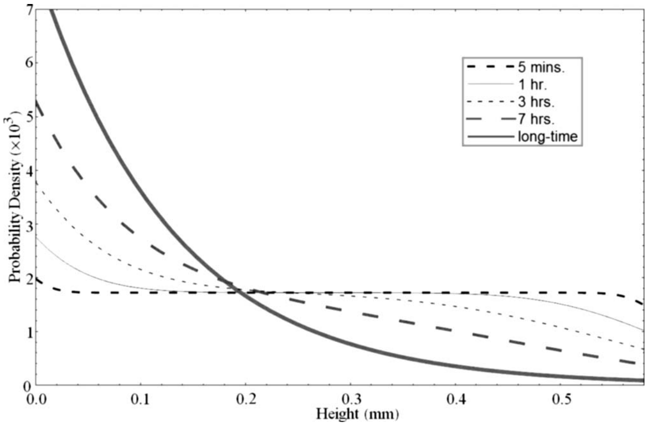

Fig. 2. Plot of $P(z,t)$ versus z for 0.5 μm diameter B-particles in water at $t=5$ min, $t=1$ h, $t=3$ h, $t=7$ h, and the long-time stationary state.

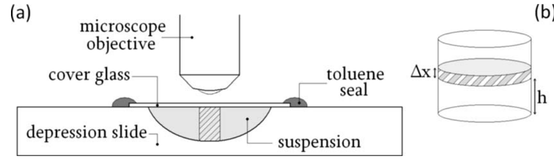

Fig. 3. (a) Experimental setup and the slice of the suspension which we analyzed at varying heights. (b) Note that Δx is the focal depth of the microscope, which was 3.04 μm, and h is the height at which the measurement was taken.

from the steady state distribution, we conclude that the time to reach equilibrium for 1.0 μm B-particles suspended in water of height 0.58 mm is $\approx$7 h.

Figure 2 shows $P(z,t)$ for the 0.5 μm B-particles at $t=5$ min, $t=1$ h, $t=3$ h, $t=7$ h, and a the steady state solution. We see that the smaller B-particles have a much broader dispersion in the vertical direction because of their smaller mass. Note that at $t=7$ h $P(z,t)$ has not yet reached the steady state. It takes the smaller B-particles $\approx$23 h to reach equilibrium in contrast to the 7 h required for 1 μm particles.

III. EXPERIMENTAL PROCEDURE AND DATA ANALYSIS

The experimental procedure is based on the direct observation of Brownian particles suspended in solution at varying heights and at different time intervals. The experiment was done as a part of the junior laboratory course at the University of Texas at Austin, and the results reported here are part of the undergraduate thesis.[12] The principal goal was to construct a time-dependent histogram of particle counts at varying heights, and then compare the experimental data with the probability distribution function in Eq. (11).

We prepared our suspension samples using Duke Scientific latex spheres with 1 μm diameter and density of 1.05 g/cm^3 The height H of the suspension (depression depth) was measured to be 0.58 ± 0.01 mm, and we did 48 measurements along the height of the suspension. We prepared the suspension of particles in solution by cleaning the slides with ethanol and de-ionized water. The latex spheres were diluted in de-ionized water to a sphere density low enough that sphere-sphere collisions were infrequent during the time of the observation. The diluted particle solution was put in the slide depression and a coverglass slide was placed over the depression and sealed with Permount (a toluene solution). As soon as the sample was sealed, we began taking pictures of the suspended B-particles. We used the Olympus CX41 System Microscope at 40$\times$ magnification, Olympus C-7070 wide zoom digital camera,[13] and a personal computer with ImageJ software[14] to collect and analyze data. (It is important that the magnification and pixel size be such that the image of the particle covers several pixels.) The total cost of the equipment was less than \$2500. The experimental setup is shown in Fig. 3.

Pictures of the B-particles were taken at a range of heights and analyzed in ImageJ software to count the number of particles present in the particular in-focus slice (the focal depth is 3.04 μm). In Fig. 4 we show a picture of a typical dataset of B-particles. The well defined black spots are the desired in-focus B-particles (within the focal depth of the microscope), whereas the blurry gray and white spots were eliminated during the counting process. We set a threshold gray value of 0–120 in the ImageJ software for our 8 bit pictures. We also corrected the "zero" height measurements in each run because only approximately half of the expected number of particles were observed within the focal depth near the bottom due to the fact that half of the focal depth coincides with the lower wall of the specimen slide where no particles can exist.

Figure 5 shows the experimental results for 1 μm particles superimposed on the theoretical prediction at $t=5$ min, $t=1$ h, $t=7$ h, and the steady state (approximated as $t=16$ h). We estimated the total number of particles within the column of water under observation using the uniform distribution measurements at time $t=0$. The theoretical and experimental data points were binned. The bins for the theoretical points were obtained by integrating the corresponding probability distribution functions, multiplied by the total particle number, over the focal depth at each level. The "particle overshoots" observed in long time measurements at zero height are most likely due to the Brownian particles that adhered to the lower-wall of our slide and were unable to exhibit Brownian motion but nevertheless contributed to the measurements. This explanation of the "overshoots" is supported by the fact that the higher measured values are consistently in good agreement with theory, where the measurements are not affected by the walls.

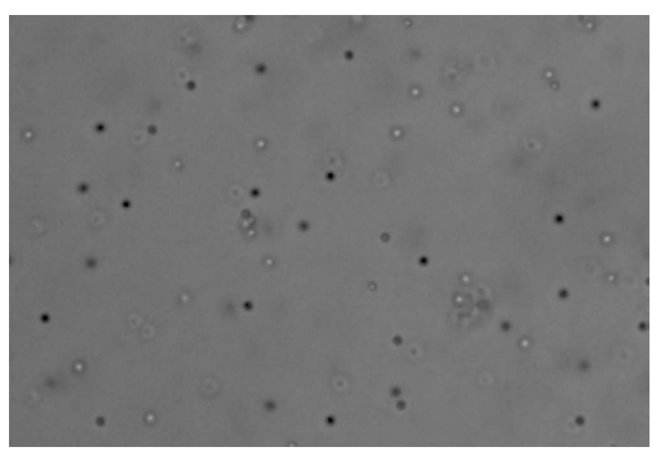

Fig. 4. A picture of 1.0 μm B-particles taken at time $t=24$ h.

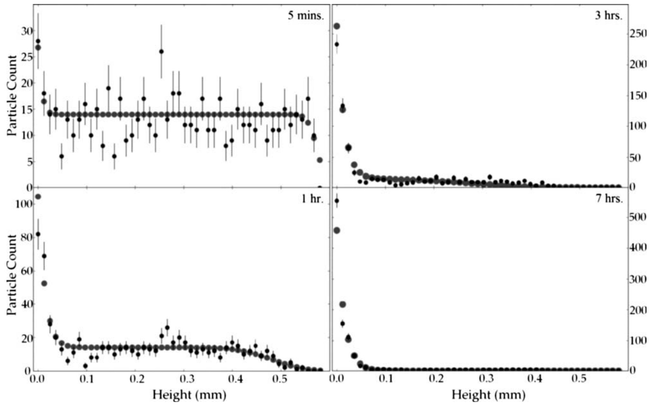

Fig. 5. Experimental data points (black circles with error bars) and predictions of theory (plain black circles) at $t=5$ min, $t=1$ h, $t=3$ h, and $t=7$ h.

Our data at $t=16$ h and $t=22$ h yielded almost identical plots as the $t=7$ h case, further suggesting that the evolution of the probability density function stops after about 7 h. Note that $(\lambda_1)^{-1} \sim 37.5$ min [see Eq. (8)], which gives the time for the longest lived mode to reach e^{-1} of its amplitude, but the time to actually reach the long-time stationary state is considerably longer.

Data collection for a suspension of 0.5 μm diameter B-particles requires 100× magnification, rather than the 40× magnification needed for 1.0 μm diameter B-particles to be able to count the particles with sufficient accuracy. We were unable to obtain experimental data points for 0.5 μm B-particles with the equipment available to us. However, we show the theoretical results for the 0.5 μm B-particles because it illustrates the unexpectedly large effect of B-particle size on the time to reach equilibrium.

IV. CONCLUSIONS

We investigated the time-dependence of the probability density function for a suspension of latex Brownian particles in water and showed that it is governed by the effect of a random Brownian walk and the gravitational potential. The experimental apparatus and computing power needed are within the reach of most undergraduate labs and if the half micron particles are used (with sufficient magnification), data acquisition may be spread over two lab sessions, enabling the students to observe different phases of the probability density evolution. Different decay times may be achieved if suspension liquids of different densities are used.

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APPENDIX A: DERIVATION OF COEFFICIENT

The derivation of the coefficients A_n in Eq. (10) is greatly simplified if we note that the Fokker-Planck equation (for strong friction) can be written in terms of a Hermitian operator.[11] Let $P(z,t)=e^{-\gamma m^* gz/D}\Phi(z,t)$. Then $\partial\Phi/\partial t=\mathcal{H}\Phi$, where $\mathcal{H}$ is a Hermitian operator with eigenvalues λ_n and a complete set of eigenfunctions $\Phi_n(z,t)$. The probability density $P(z,t)$ can be expanded in terms of these eigenstates,

$$P(z,t) = \Phi_0^2(z) + \sum_{n=1}^{\infty} C_n e^{-\lambda_n t}\Phi_0(z)\Phi_n(z), \tag{A1}$$

where $\Phi_0(z)=\sqrt{2\alpha/1-e^{-2\alpha H}}e^{-\alpha z}$ (the stationary state distribution) and $\Phi_n(z)$ is given by

$$\Phi_n(z) = \sqrt{\frac{2}{H}}\frac{n\pi}{\sqrt{\alpha^2H^2+n^2\pi^2}}\left[\cos\left(\frac{n\pi z}{H}\right) - \frac{\alpha H}{n\pi}\sin\left(\frac{n\pi z}{H}\right)\right], \tag{A2}$$

with $\alpha=m^*g/2k_BT$. Because the eigenfunctions $\Phi_n(z)$ form a complete orthonormal basis, that is, $\int_0^H\Phi_n(z)\Phi_{n'}(z)=\delta_{n,n'}$, and $P(z,t=0)=1/H$, we can solve for the coefficients as follows:

$$C_n = \int_0^H \frac{\Phi_n(z)}{\Phi_0(z)}\frac{1}{H}dz = \sqrt{\frac{1-e^{-2\alpha H}}{\alpha H}}\frac{(2\alpha H n\pi)(e^{\alpha H}\cos(n\pi)-1)}{(\alpha^2H^2+n^2\pi^2)^{3/2}}. \tag{A3}$$

If we substitute the coefficients C_n into Eq. (A1), we obtain the probability density for the suspended Brownian particles, given that the system starts as a uniform distribution.

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