

The time, size, viscosity, and temperature dependence of the Brownian motion of polystyrene microspheres

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An upper division undergraduate laboratory module to study Brownian motion was developed using polystyrene microspheres suspended in a sample liquid cell that was isolated from its surroundings. The dependence of the Brownian motion of the microspheres on their radius, the time, the viscosity of the suspension liquid, and the temperature were measured using a CCD camera interfaced with a frame grabber and a computer. The motion of each particle was monitored for 5 minutes and was found to be consistent with the Langevin formula for Brownian motion. © 2007 American Association of Physics Teachers.

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I. INTRODUCTION

Brownian motion can be used to introduce the atomic nature of matter to students. Many demonstrations involving Brownian particles suspended in fluid have been developed for the undergraduate curriculum.^{1,2} For example, trapped smoke in a cell was used to demonstrate Brownian motion using a video camera attached to a low powered microscope eye piece.¹ In this demonstration a laser pointer was used as a light source to observe and trace the path of individual smoke particles for up to half a minute, but no quantitative measurements were attempted. Another example is the video recording of the Brownian motion of 1 μm latex spheres for a class demonstration, with suggested student experiments to measure the distance a particle travels as a function of time.² The authors recommended tracing the path that a particle travels by stopping the video tape recordings of the motion at 10 s intervals. The maximum observation time of a single particle was 2 min.

More recently an upper level undergraduate laboratory experiment used automated computer based video microscopy of polystyrene spheres to obtain an estimate of Boltzmann's constant k .³ The results were based on simultaneously tracking 107 spheres at 5 Hz for a total of 12.8 s.

In this paper we describe an experimental arrangement that can track a single microsphere for up to 5 min, providing a large amount of data. Our method allows the study of Brownian motion as a function of time, various sized microspheres, different viscous liquid suspensions, and the temperature to determine quantitatively the dependence of the motion on these parameters. The experiment has been successfully tested and implemented in upper division undergraduate physics and chemistry courses at seven universities in the Pennsylvania State System of Higher Education.

II. THEORETICAL BACKGROUND

The velocities of the small particles suspended in a fluid due to collisions with molecules obey a Maxwellian velocity distribution. This random motion was first observed by Ingenhousz in 1785⁴ and was subsequently rediscovered by Brown in 1828.⁵ Einstein used kinetic theory⁶ to derive the diffusion constant in terms of the fundamental parameters of the particles and liquid; this relation was subsequently used by Perrin to determine Avogadro's number.^{7,8}

Brownian trajectories are continuous, random, and irregular. Following Refs. 7 and 8 we derive a physically measurable quantity, the mean squared displacement, beginning with the Langevin formula and Stokes flow for a sphere given by Eqs. (1) and (2), respectively,

$$m \frac{dv}{dt} = -\alpha v + F(t), \quad (1)$$

where m is the mass of the particle, v is its velocity,

$$\alpha = 6\pi\eta a, \quad (2)$$

α is the damping constant, η is the dynamic viscosity, a is the radius of the sphere, and $F(t)$ is a randomly fluctuating force due to molecular collisions. We rewrite Eq. (1) to obtain

$$mx \frac{dv}{dt} = m \left[\frac{d(xv)}{dt} - v^2 \right] = -\alpha xv + xF(t). \quad (3)$$

The time average of Eq. (3) is

$$m \left\langle \frac{d(xv)}{dt} \right\rangle = m \frac{d\langle xv \rangle}{dt} = m\langle v^2 \rangle - \alpha\langle xv \rangle + \langle xF(t) \rangle. \quad (4)$$

Because $F(t)$ varies randomly (irrespective of the velocity or position of the particle),⁸ we have

$$\langle xF(t) \rangle = \langle x \rangle \langle F(t) \rangle = 0. \quad (5)$$

We also have

$$\frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} kT, \quad (6)$$

where k is Boltzmann's constant and T is the temperature. If we substitute Eqs. (5) and (6) into Eq. (4), we obtain

$$m \frac{d\langle xv \rangle}{dt} = kT - \alpha\langle xv \rangle, \quad (7)$$

so that

$$\frac{1}{2} m \frac{d^2\langle x^2 \rangle}{dt^2} + \frac{\alpha}{2} \frac{d\langle x^2 \rangle}{dt} = kT. \quad (8)$$

We let

$$\frac{d\langle x^2 \rangle}{dt} = w, \quad (9)$$

and obtain

$$\frac{dw}{dt} + \frac{\alpha}{m}w = \frac{2kT}{m}. \quad (10)$$

If we write $\gamma = \alpha/m$, we have

$$\frac{dw}{dt} + \gamma w = \frac{2kT}{m}. \quad (11)$$

We let

$$w = \frac{2kT}{\alpha} + ce^{-\gamma t}, \quad (12)$$

and Eq. (11) yields

$$\frac{dw}{dt} + \gamma w = -c\gamma e^{-\gamma t} + \frac{2kT\gamma}{\alpha} + \gamma ce^{-\gamma t} = \frac{2kT}{\alpha} \left(\frac{\alpha}{m} \right) = \frac{2kT}{m}, \quad (13)$$

so that Eq. (12) is a particular solution of Eq. (11). In our case the time t is large (in minutes) and the mass of the particles m is small. These conditions reduce the solution Eq. (12) to

$$w = \frac{2kT}{\alpha}. \quad (14)$$

We use Eqs. (9) and (14) and obtain

$$\frac{d\langle x^2 \rangle}{dt} = \frac{2kT}{\alpha}, \quad (15)$$

that is,

$$\langle x^2 \rangle = \frac{2kT}{\alpha}t. \quad (16)$$

If we use Eqs. (2) and (16) we have

$$\langle x^2 \rangle = \frac{2kT}{\alpha}t = \frac{2kT}{6\pi\eta a}t = \frac{kT}{3\pi\eta a}t. \quad (17)$$

Because $\langle r^2 \rangle = 2\langle x^2 \rangle$ in two dimensions, we have

$$\langle r^2 \rangle = \frac{2kT}{3\pi\eta a}t. \quad (18)$$

III. EXPERIMENTAL TECHNIQUES AND APPARATUS

To observe the motion of small Brownian particles, polystyrene microspheres with radii of 0.5, 1, 3, and 5 μm were purchased from Bang Laboratory.⁹ The major equipment used was an Olympus CKX41SF inverted optical microscope equipped with a 40 \times objective lens, a CCD, and a data collecting system (Hitachi camera) with a frame grabber to record a stream of frames.

Sample suspensions were made by suspending the polystyrene microspheres into various liquids at a concentration such that only one sphere was observed in the optical field. For the viscosity measurements 1 μm polystyrene microspheres were used. Liquids with different viscosities were used to suspend the polystyrene microspheres, for example,

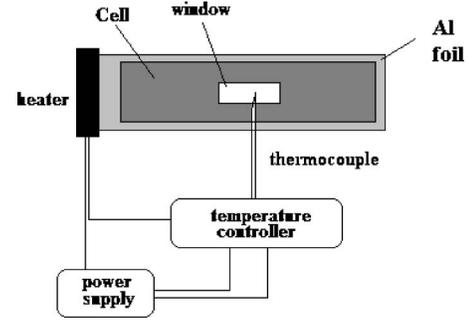


Fig. 1. Setup of the sample cell for temperature dependence measurements.

water, ethyl glycol (EG), cooking oil, and water/EG solution in varying concentrations. For size dependence measurements, each size of polystyrene microsphere was suspended in water. For temperature dependence measurements, 1 μm polystyrene microspheres were suspended in ethyl glycol.

Sample observation cells were made by first placing two large drops of cooking oil with high viscosity on a glass slide. One small drop of sample suspension was injected into the oil using a 1 ml syringe. Another glass slide was then carefully placed on top of the first slide. The suspension and oil then spread out and stabilized, allowing us to use this structure as our sample cell. The cooking oil isolates the suspension to insure that the particles in the suspension are in Brownian motion and not simply flowing with the liquid.

For temperature measurements a CIR-1013/120V cartridge heater was used to maintain the sample cell at different temperatures. The temperature was varied between 20 $^{\circ}\text{C}$ and 150 $^{\circ}\text{C}$, which is below the boiling point of ethyl glycol. The sample cell was wrapped with aluminum foil for uniform heating. A window was opened for data acquisition through the microscope. A K type thermocouple and an Omega CNi universal temperature controller were used to control the heating process. This setup is shown in Fig. 1.

The sample cells were placed under the microscope, observed, and recorded as a sequence of frames acquired by the frame grabber and the computer. The time interval between two frames was 1 s. A video of 5 min was taken for each measurement consisting of a series of 300 frames. The initial position of the microsphere was selected as the origin with pixel coordinate $O(x_0, y_0)$ in the frame. The square of the distance of the particle from $O(x_0, y_0)$ to $A(x, y)$ in each frame as shown in Fig. 2 is given by

$$r^2 = (x - x_0)^2 + (y - y_0)^2. \quad (19)$$

The time average value is given by

$$\langle r^2 \rangle = \frac{\left(\sum_{n=1}^N r_n^2 \right)}{N}, \quad (20)$$

where N is the number of frames. By using Eqs. (16) and (18) we have five parameters that can be measured. They are the temperature T , time t , viscosity η , radius a , and the time average of the square of the displacement $\langle r^2 \rangle$.

Because the exact distance in μm cannot be accurately obtained due to amplification effects of the microscope, pixels are used as the counting unit. The minimum resolution is 0.5 pixel measured from each spherical center.

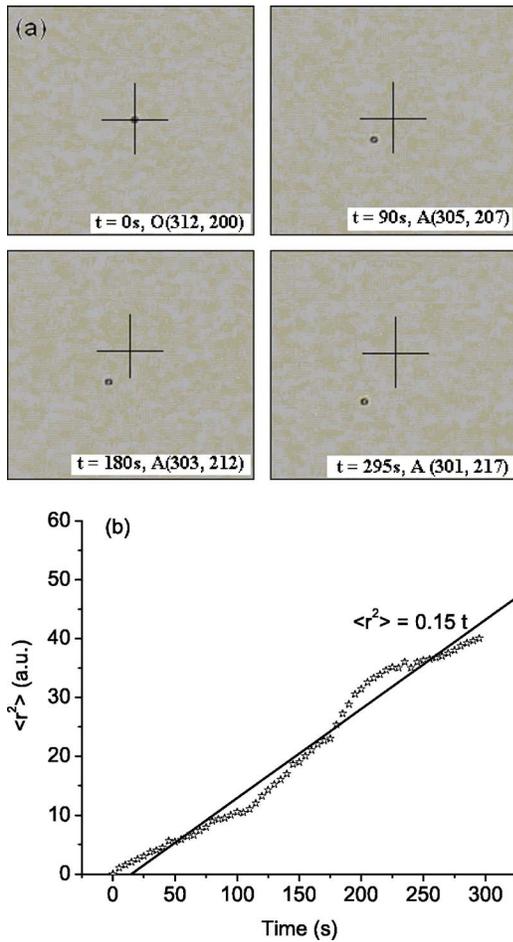


Fig. 2. Time dependence of Brownian motion using $1 \mu\text{m}$ microspheres. (a) Brownian motion of single microsphere in frame. (b) Plot of $\langle r^2 \rangle$ versus the time t showing a linear relation ($\sim 2\%$ slope error).

IV. RESULTS

The measurement of the time dependence of Brownian motion was performed at 20°C . Figure 2(b) shows the linear dependence of $\langle r^2 \rangle$ as predicted by theory. During the measurement, the motion in the z -direction (depth) was observed as a defocusing effect. Several measurements were taken and the results with less defocusing effect were used.

To investigate the size dependence of the Brownian motion, each size microsphere is used and the time dependence of $\langle r^2 \rangle$ is plotted in Fig. 3(a). In this case the temperature and the viscosity were constant, and therefore from Eq. (18) the slope of the linear fits reflect the dependence on the radius a . A linear fit gives a nonzero intercept in some cases, although the intercepts should all be zero theoretically. The nonzero intercept could be due to two-dimensional data obtained from three-dimensional motion, uncertainty in the data, and the time interval not being sufficiently long.

The size dependence of $\langle r^2 \rangle$ would contain large errors if it were determined by using data at the same time t for all size microspheres. Instead, we use the slope to determine the size dependence of $\langle r^2 \rangle$. From Eq. (18) the slope of $\langle r^2 \rangle$ is given by β_1/a , where $\beta_1 = 2kT/3\pi\eta$ is a constant. The values of the inverse slope were plotted against the radius a as shown in Fig. 3(b). A linear relation is found as predicted. See Table I.

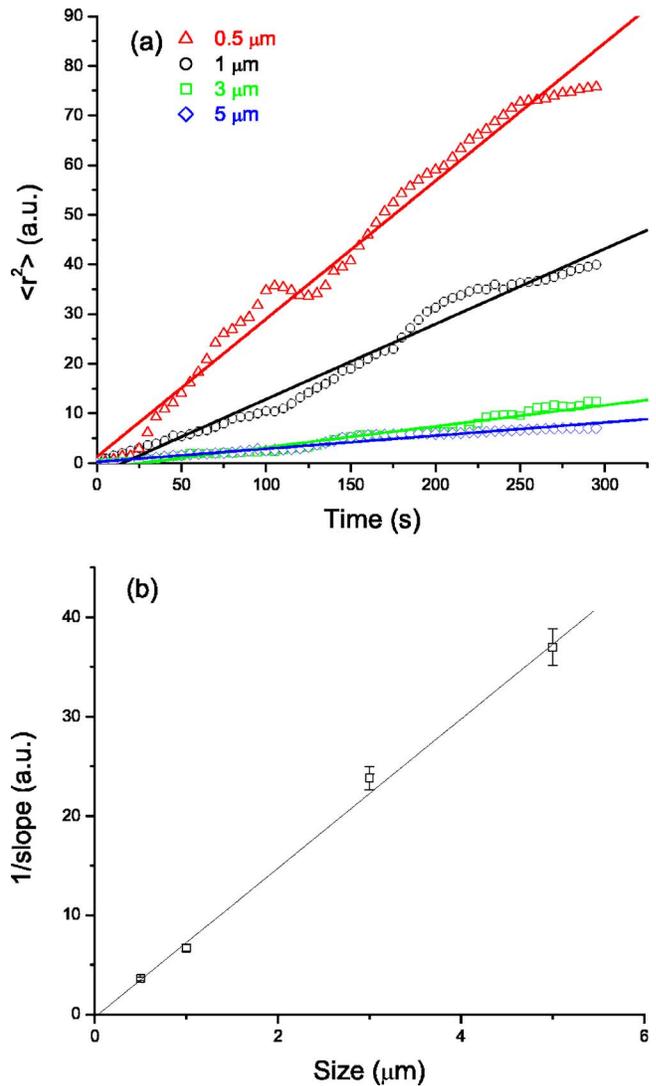


Fig. 3. Size dependence of Brownian motion. (a) $\langle r^2 \rangle$ versus t for 0.5, 1, 3, and $5 \mu\text{m}$ radii polystyrene microspheres. (b) The inverse slope versus a showing a linear relation (error bar is 5%).

The viscosity η is defined as the ratio of the shearing stress (F/A) to the velocity gradient dv_x/dz in a fluid:

$$\eta = \frac{(F/A)}{dv_x/dz}. \quad (21)$$

The SI unit of viscosity is Pascal second but is rarely used. The most common unit of viscosity is poise (P) after the French physicist Poiseuille, which is a dyne second per square centimeter ($\text{dyne}\cdot\text{s}/\text{cm}^2$), that is, $10 \text{ P} = 1 \text{ Pa}\cdot\text{s}$.

Table I. The values of the inverse slope for each size microsphere ($\sim 5\%$ error).

Radius (μm)	1/slope (arbitrary unit)
0.5	3.6
1	6.7
3	23.8
5	37

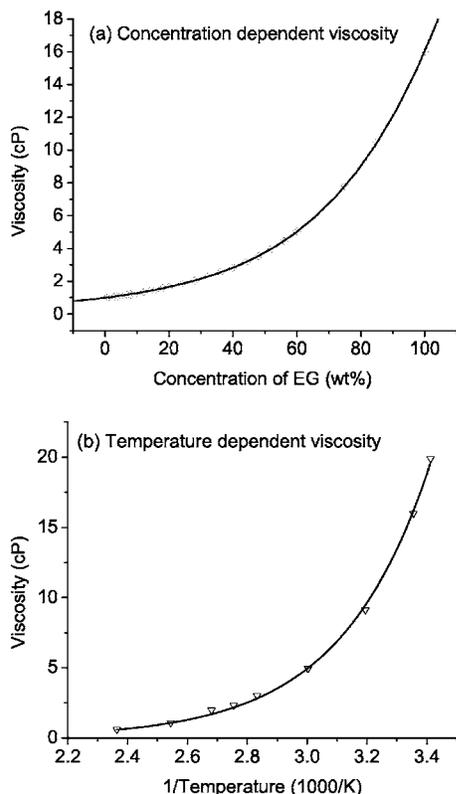


Fig. 4. (a) Viscosity of ethyl glycol in water with different concentrations. (b) Viscosity of ethyl glycol at different temperatures.

To investigate the viscosity dependence, six liquids with different viscosities were used as suspension for the spheres. At room temperature, $\eta=1$ cP for water, 16 cP for ethyl glycol, and 65 cP for cooking oil. To obtain more liquids with different viscosities, water and ethyl glycol (EG) were mixed. The relation between viscosity and wt % concentration of EG/water mixture is shown in Fig. 4(a).^{10,11} The mixtures were made to 60%, 75%, and 85% to obtain predicted viscosities of 5, 7.8, and 10.5 cP, respectively (see Table II). A best curve fit of the data shown in Fig. 4(a) was obtained and used to predict the viscosity at different concentrations. These three EG water solutions were also used as suspension liquids. The time dependence of $\langle r^2 \rangle$ of each suspension is shown in Fig. 5(a). An approximate linear relation with time was found for each viscosity. Because the size and temperature are constants, the slope in each plot reflects the viscosity dependence. From Eq. (18) the slope of the plot is given by β_2/η , where $\beta_2=2kT/3\pi a$ is a constant. A plot of the inverse slope versus η is shown in Fig. 5(b).

Table II. The values of the inverse slope for each suspension with the viscosity η ($\sim 3\%$ error).

Viscosity η (cP)	1/slope (arbitrary unit)
1	6.7
5	11.4
7.8	15.4
10.5	18.9
14	23.8
65	100

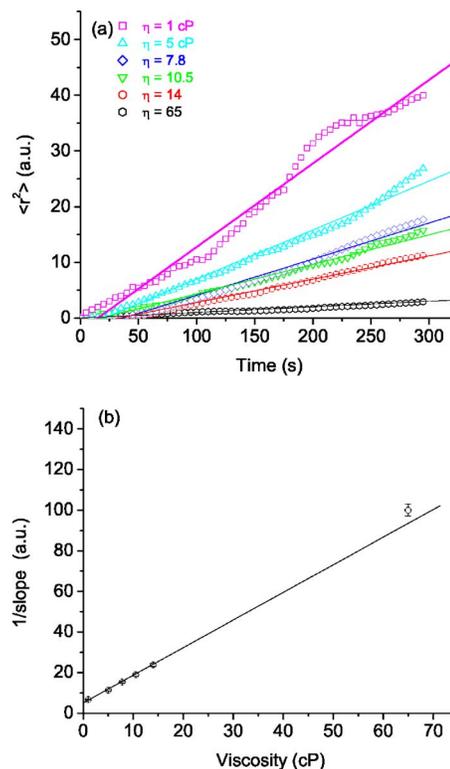


Fig. 5. Viscosity dependence of Brownian motion using $1 \mu\text{m}$ microspheres. (a) $\langle r^2 \rangle$ versus t for $\eta=1, 5, 7.8, 10.5, 14, 65$ cP. (b) The inverse versus η showing the inverse linear dependence of $\langle r^2 \rangle$ on η (error bar is 3%).

To investigate the temperature dependence, $1 \mu\text{m}$ polystyrene microspheres were suspended in EG. Measurements were taken after the temperature was equilibrated with a fluctuation of about $\pm 2^\circ\text{C}$ around the desired temperature. The time dependence of $\langle r^2 \rangle$ for the motion of the $1 \mu\text{m}$ microsphere is shown in Fig. 6(a) for various temperatures. A linear time dependence was observed at each temperature. The slope at each temperature was obtained by a linear fit. The viscosity of the liquid is a function of temperature, so this effect must be considered. For a constant radius, the slope is given by $\beta_3 T/\eta$, where $\beta_3=2k/3\pi a$ is a constant. The slope versus T plot is shown in Fig. 6(b). No linear relation is found because η is not a constant but a function of temperature.

For EG the temperature dependence of the viscosity is given by the Arrhenius equation^{12,13}

$$\eta = Ae^{E/kT}, \quad (22)$$

where A is a constant and E is an activation energy. The temperature dependence of the measured viscosity of EG is shown in Fig. 4(b).¹⁴ An exponential fit was obtained and suggests that the temperature dependence of the viscosity of EG fits Eq. (20) in the range from 20°C to 150°C . The viscosities of EG at each temperature were found from Fig. 4(b) and were multiplied by the slopes (see Table III); hence the product of the slope and η is given by $\beta_3 T A$ as shown in Fig. 6(b) a linear relation is found. Therefore $\langle r^2 \rangle$ is proportional to T and is consistent with Eq. (18).

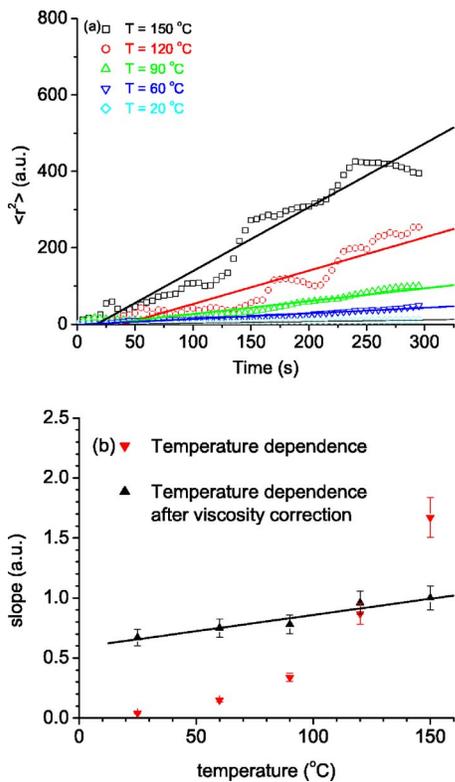


Fig. 6. Temperature dependence of Brownian motion using $1 \mu\text{m}$ microspheres. (a) $\langle r^2 \rangle$ versus t for $T=20, 60, 90, 120, 150$ °C. (b) The slope versus T . Data indicated with the symbol \blacktriangledown shows that $\langle r^2 \rangle$ increases with increasing T . Data indicated with the symbol \blacktriangle show a linear relation of $\langle r^2 \rangle$ versus T after the slopes are corrected for the temperature dependence of viscosity (error bar is 10%).

V. DISCUSSION

The dependence of the Brownian motion of small particles on the time, viscosity, size, and temperature is found to be

Table III. The values of the slope at temperature T ($\sim 10\%$ error).

Temperature (°C)	Slope (arbitrary unit)	Viscosity η at T (cP)	Corrected slope (arbitrary units)
25	0.042	16	0.67
60	0.15	5	0.75
90	0.34	2.3	0.78
120	0.87	1.1	0.96
150	1.67	0.6	1

consistent with Eq. (18). A large number of data need to be taken and analyzed by the students. To save time we divided the lab into three parts and had students determine the size and time dependence, the viscosity dependence, and the temperature dependence.

We found that defocusing due to the three-dimensional motion of the microsphere is one of the major problems during the experiment. If such motion appears, we must neglect it. To this extent we made sure that the motion was two-dimensional and consistent with our assumption.

We also found that even slight vibrations of the microscope table can greatly affect the quality of the data. All hands must be off the table when data is taken.

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