Brownian Movement and Avogadro's Number

A Laboratory Experiment

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Einstein's theory of Brownian movement[2] and its verification by Perrin[3] provided the definitive support for the kinetic–molecular theory.

Three technological advances make possible the replication of some classical experiments on Brownian movement in the advanced undergraduate laboratory. First, latex microspheres of known and accurate diameters are available commercially. Second, a television camera makes it possible to view microscope images of the spheres and to project them onto a monitor screen. This is the modern version of Perrin's *camera obscura*. Third, the ready availability of electronic calculators and microcomputers reduces greatly the required calculations.

An undergraduate laboratory project for the study of Brownian movement of latex spheres in aqueous suspension was developed by J. Webb.[4] With one student giving a signal every 30 s, his or her partner announced the coordinates of a sphere's position as seen in a 600× microscope with a calibrated eyepiece grid. A histogram was plotted from the data of 43 undergraduates and a best fit Gaussian curve drawn. From the root mean square (rms) of 458 displacements (random walks), Avogadro's number was calculated as 6.53×10^{26}/kmol ± 12%. Each student participated for 45 min during one of the eight laboratory periods.

The writer developed an experiment on Brownian movement that could be completed in one laboratory period by two students. The experiment was tested with students in the advanced undergraduate laboratory of the Physics Department at the University of Arizona.

Objectives

The objectives of the experiment are (1) to project and observe on a TV monitor the motions of latex microspheres, (2) to plot at regular time intervals the position of a microsphere, (3) to plot a histogram of the displacements, (4) to test the randomness of the displacement distribution, (5) to calculate the mean and rms (standard deviation) of the displacements, (6) to calculate Avogadro's number and to estimate its experimental uncertainty, and (7) to test the relationship between the rms displacement and the time interval.

Apparatus and Supplies

The experimental arrangement is shown in Figure 1. The TV camera is a black-and-white model with the lens removed. It is mounted 60 cm above a microscope with a 20× objective, with the eyepiece removed. Also needed are a TV monitor, a clock with a second hand, depression microscope slides, slide covers, nail polish, transparency sheets, felt-tip marking pens, a transmission diffraction grating, and normal-probability graph paper. A strong collimated light source is required as a microscope illuminator. A heat-absorbing glass or water cell should be placed between the illuminator and the microscope mirror. The latex microspheres are available from scientific supply houses; the smallest purchasable quantity will last a lifetime. The spheres that worked well for the writer had diameters of 0.93, 1.099, and 1.305 μm.

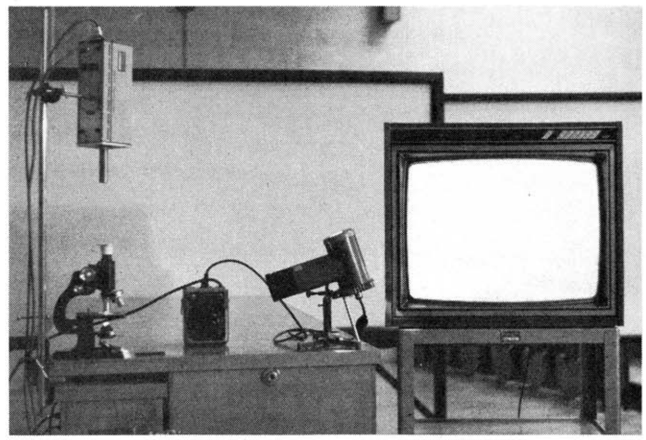

Figure 1. Experimental setup.

Experimental Procedure

The instructor or lab assistant prepares in advance the microscope slide with the latex spheres. A small drop of the commercial suspension is diluted in 25–50 mL of distilled H_2O. The cavity in a depression slide is filled with the very dilute suspension. A slide cover glass is placed over the filled depression and sealed with nail polish or some other waterproof cement. To keep the microspheres from settling out, the slide should be turned over daily. If the slide is rotated about its horizontal axis at a very slow rate, many of the spheres will stay suspended for several weeks.

With the slide on the microscope stage, the illuminator, the microscope mirror, the monitor brightness and contrast, and the microscope focus are adjusted until a few clear images of the spheres are seen on the monitor screen.

One of the laboratory partners adjusts the fine focus and is the timekeeper. A transparency is taped to the monitor screen. As the specified time is called, the second partner puts a dot at the center of the sphere's image, which is more easily located if the focus is adjusted so that there is a central bright diffraction spot.

In our pilot study, the time intervals were 15 and 30 s. The number of positions marked on one transparency was 26, which gave 25 displacements. The partners then traded roles. The positions on the transparency were labeled with consecutive numbers. A "random walk" of a sphere with a 1.10-μm diameter at 30-s intervals is shown in Figure 2. If the

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[2] Einstein, A. *Investigations on the Theory of the Brownian Movement;* Furth, R., Ed.; Cowper, A., Tr.; Dover: New York, 1956.
[3] Perrin, J. *Atoms;* Hammick, D., Tr.; Constable: London, 1923.
[4] Webb, J. *Phys Educ.* **1980,** *15,* 116.

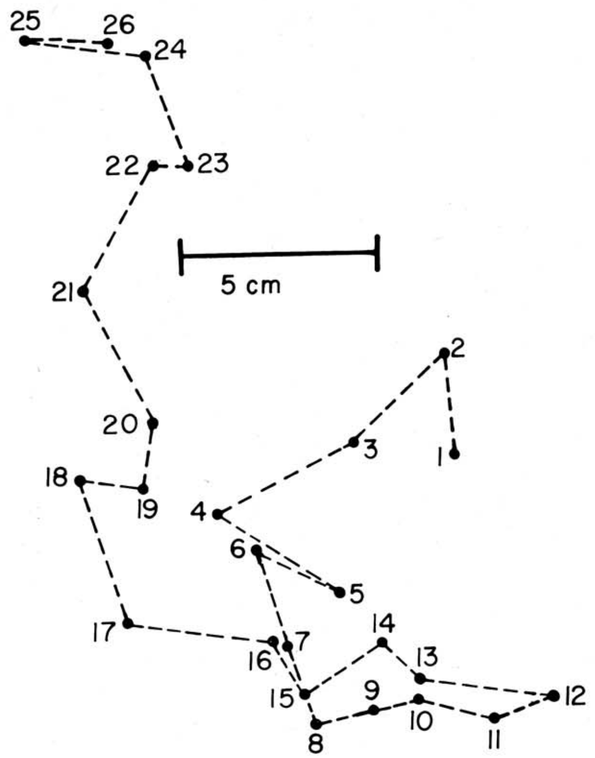

Figure 2. A "random walk" at 30-s intervals.

image of the sphere drifts off the screen, another sphere is selected and the positions are marked with a different number sequence.

The temperature of the suspension was approximated by placing the bulb of a laboratory thermometer between the top of the slide and the objective. To convert the apparent to actual displacements, the depression slide on the microscope stage was replaced by a 1000-cm^{-1} transmission grating. The distance between several lines of the grating image was measured on the monitor screen, and thus the magnification factor was determined.

The diameter of the latex microspheres is supplied by the manufacturer and appears on the bottle label. A 2- or 3-h lab period is more than adequate for each of two partners to obtain data for two time intervals. In the pilot study, the transparencies were photocopied on graph paper. If a copier is not available, then the transparency can be taped to a sheet of metric graph paper. If three copies of each transparency are made, each partner and the instructor can have a record of the original data by both students.

Analysis of Data

With an arbitrary origin on the graph, the x and y coordinates of each position are determined. The displacements are then obtained by subtracting the coordinate of a given position from the preceding one, with correct algebraic signs. The displacements are then sorted into groups or intervals, and the raw and cumulative frequencies are tallied. A frequency distribution for the 15-s data by two partners in the pilot study is shown in Table 1. The grouped data facilitates statistical computations and the drawing of a histogram[5].

Results

The histogram of the 100 displacements in Table 1 and the best fit Gaussian curve are shown in Figure 3. The goodness

[5] Bury, K. *Statistical Models in Applied Science;* Wiley: New York, 1975.

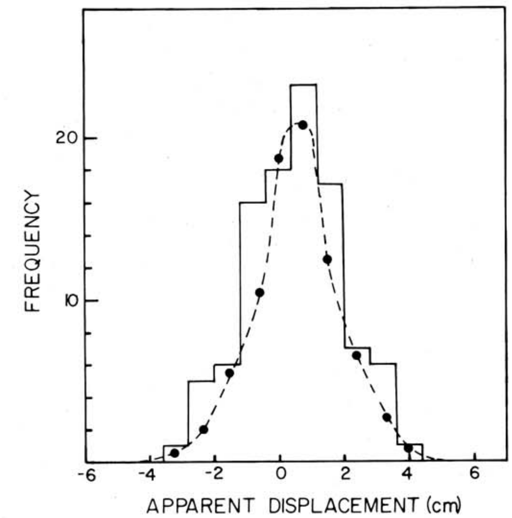

Figure 3. Histogram and best fit Gaussian curve for data of Table 1.

Table 1. Frequency Distribution of Microsphere Displacements on a TV Monitor, Observed by Two Students at 15-s Intervals[a]

Displacement range (cm)		Frequency	Cumulative frequency
−3.6	−2.81	1	1
−2.8	−2.01	5	6
−2.0	−1.21	6	12
−1.2	−0.41	16	28
−0.4	+0.39	18	46
0.4	1.19	23	69
1.2	1.99	17	86
2.0	2.79	7	93
2.8	3.59	6	99
3.6	4.39	1	100

[a] T = 296.3 °K, r = 0.550 × 10^{-6} m. Viscosity, η = 9.29 × 10^{-4} gm^{-1}s^{-1}. Displacement-screen calibration, 2.13 μm/cm.

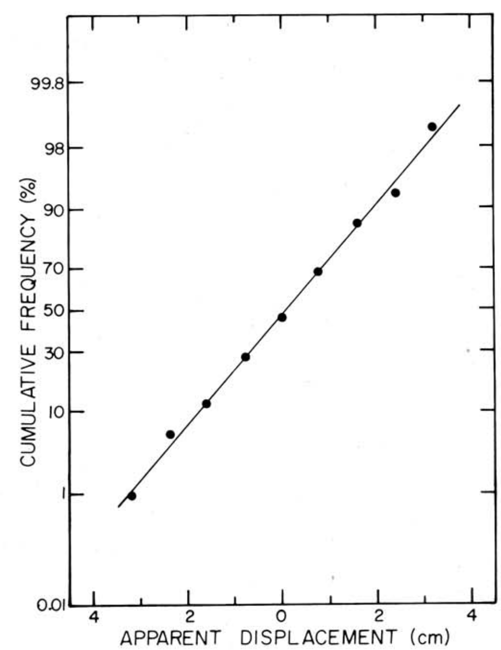

Figure 4. Graph of data from Table 1.

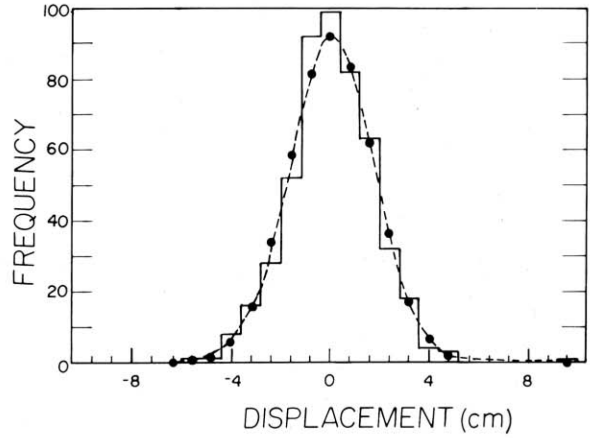

Figure 5. A computer-generated histogram and best fit Gaussian curve for 15-s displacements by 10 students.

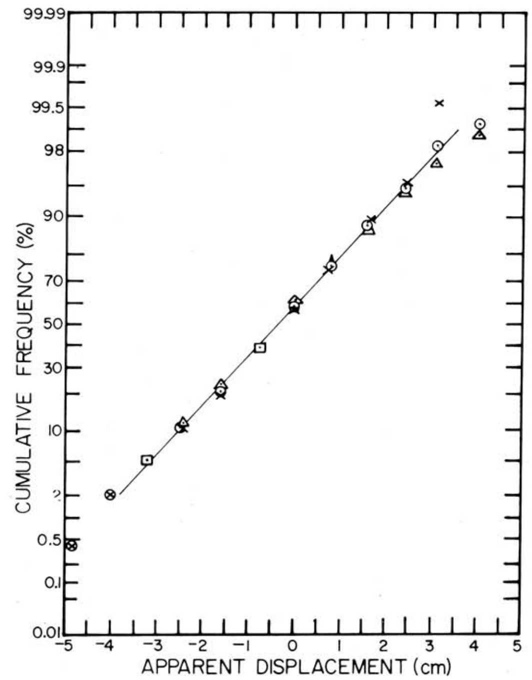

Figure 6. Graph of data used in Figure 5: X—displacements in the x direction; Δ—displacements in the y direction; O—pooled displacements.

of fit may be tested by the chi-square method. A simpler technique is to use arithmetic or normal probability graph paper. A plot of the data in Table 1 on such paper is shown in Figure 4. The straight line indicates that the distribution of the displacements is Gaussian. Thus, even as few as 100 data points are sufficient to establish the randomness of Brownian movement displacements.

There are now available many inexpensive pocket calculators with programs for basic statistical computations. Using the data of Table 1 with such a calculator, one obtains for the apparent displacements: mean = 0.48 cm; standard deviation = 1.50 cm. With the calibration of 2.13 μm/cm, the two values are 1.02 μm and 3.20 μm, respectively. The mean and standard deviation for the 30-s interval data of the same two students were -1.00 μm and 4.37 μm. The ratio of the standard deviations is 4.37/3.20 = 1.37, which agrees well with Einstein's theoretical prediction of 1.41.

The formula derived by Einstein for Avogadro's number is

$$N = \frac{RTt}{3\pi\eta r s^2}$$

Substituting the values shown in Table 1 into the formula above, gives $N = 7.5 \times 10^{26}$/kmol.

Another pair of students picked at random from the laboratory group had data for the 15-s interval, which resulted in $N = 6.03 \times 10^{26}$/kmol.

Since there was a large variation in the reported values of N, the data of the 10 individual observers were pooled into a single sample. The histogram of the 15-s displacements and the Gaussian fitted to it with a computer program are shown in Figure 5. The test with normal probability paper, as shown in Figure 6, is an excellent fit to a Gaussian distribution. This was also true for eight sets of data with a 30-s interval. The results for the entire 18 sets of data are summarized in Table 2. Shown also in Figure 6 are the plots of displacements in the x and y directions. The graph supports the assumption of displacement randomness in the two directions.

The largest source of random errors is in the pinpointing of the microsphere positions. The uncertainty in the rms displacement for the 15-s interval is 3%, and the uncertainty in the microsphere's radius is 1%. The timing accuracy depends primarily on the alertness and eye–hand coordination of the two partners throughout the experiment. A temperature variation of 0.5 °C will have its major effect on the value of viscosity, 1% or so. Another factor is the slight curvature of

Table 2. Brownian Movement, Summary of Class Results, University of Arizona, Spring 1987

No. of observers	t (s)	$\bar{X}$ (μm)	s (μm)	s^2 (μm)^2	$N \times 10^{26}$/kmol	S^2_{30}/S^2_{15}
10	15	0.42	3.54	12.6	6.23	1.86 (Experiment)
8	30	0.14	4.84	23.4	6.63	2.0 (Theory)
			weighted mean		6.41	

the monitor screen (although the late-model monitors have a flat one). A conservative estimate in the experimental uncertainty of N for two observers is ±15% with 30-s time intervals and, perhaps, as high as 20% for the 15-s trials.

Discussion and Summary

By plotting random walks of a latex microsphere image on a TV monitor, students obtain data from which Avogadro's number can be calculated. Although the values obtained for Avogadro's number vary considerably between observers, the students gain valuable experience with mathematical and graphical analysis for a Gaussian distribution. Challenging also is the error analysis and the unit conversion.

This experiment on Brownian movement used modern technology to replicate some of the classical work in one laboratory session. The experiment is suitable for the advanced undergraduate laboratory in chemistry and physics. It is probably also instructive to introduce students to the "nonrelativistic Einstein", who discovered order in the chaotic agitation of microscopic particles.

Acknowledgment

I am indebted to the following for encouragement, advice, and technical assistance: W. Bickel, D. Donahue, K. Hsieh, D. Kangas, and J. Kessler of the University of Arizona, and to R. Anderson of Western Michigan University.