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An Experiment to Measure Boltzmann's Constant

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We describe a simplification of Jean Perrin's classic experiment to determine Boltzmann's constant from the sedimentation equilibrium of colloidal suspensions. Perrin's complicated procedure for preparing suitable colloidal particles is avoided by using commercially available plastic spheres of specified diameter and density. The experiment is suitable for either an introductory or advanced laboratory.

INTRODUCTION

We describe in this paper an experiment to measure Boltzmann's constant. The experiment is especially suitable for the introductory laboratory since the theoretical basis for the method is quite simple and is given in many introductory physics texts. The method, suggested by Einstein and first performed by Perrin, entails observing, with a microscope, the equilibrium distribution of particles in a colloidal suspension. Suitable colloidal particles of uniform size and density are commercially avilable. A microscope slide is prepared as a container for the suspension and the equilibrium distribution is determined by counting the number of particles at various elevations in the chamber. Data obtained in half an hour of counting consistently give a determination of Boltzmann's constant, or equivalently, of Avagadro's number, to within 20% of the accepted values.

THEORY AND HISTORY

In 1905, Einstein proposed that observations of sedimentation equilibrium might be used to determine Boltzmann's constant.[1] In the second of his five papers on the theory of Brownian motion, Einstein digressed briefly from his primary topic of the motion of colloidal particles and devoted one paragraph "to determine how small a suspended particle must be in order that it may remain permanently suspended in spite of gravitation."[2] He showed that if a collection of particles, each of volume V and density ρ, is suspended in a liquid of density ρ_0, the number of particles per unit volume will assume the equilibrium distribution

$$n(h)=n(0)\exp[-V(\rho-\rho_0)gh/kT]. \quad (1)$$

Here $n(0)$ is the particle density at, say, the bottom of the vessel, $n(h)$ is the particle density at height h above the bottom, g is the acceleration of gravity, T is the absolute temperature, and k is Boltzmann's constant. An elementary derivation of this result, based on the concept of pressure and on the ideal gas equation, is given in many introductory texts.[3–5] The result is also an immediate onsequence of the canonical distribution of statistical mechanics, Einstein suggested that, with suitable suspensions, this exponential distribution might be observable. Boltzmann's constant can be determined since all the other quantities in Eq. (1) are either known or measurable.

Jean Perrin performed the suggested experiment in 1908.[6] The difficulty of the experiment is indicated in the following excerpt from the presentation speech for Perrin's 1926 Nobel Prize:

> He [Perrin] had for this purpose to prepare a system of very small particles, all of which, moreover, should have the same weight and the same size. He succeeded herein by using gamboge, a preparation obtained from a vegatable sap and which can be handled like soap. By rubbing the gamboge between his hands under water, Perrin obtained an emulsion which under the microscope proved to consist of a swarm of spherical particles of different size. This was by no means an easy operation which is proved by the fact that after several months of accurate and careful work Perrin was able to obtain from one kilogram of gamboge only some decigrams of particles of the desired size.[7]

After preparing the uniform particles, Perrin had still to accurately determine their volume. Since the diameter of the spherical particles was too small to be measured directly, he had to resort to several indirect methods to obtain their volume.[8]

However, once a suitable suspension was prepared and the particle volume was determined, Perrin's procedure for measuring $n(h)$ was quite simple and direct. We follow his procedure in our experiment. The suspension is placed in a small glass cell on a microscope stage and is viewed from above, with the microscope in the usual vertical position. Because of the very short depth of field, dh, of a high-power objective, the region in focus is a thin disk-shaped volume Adh, where A is the area of the field of view. Adjustment of the verical position of the microscope places the thin region under observation at various heights h within the suspension. At each height, the particle density $n(h)$ is determined by counting the particles in the field of view. Increments in height h are determined from a micrometer scale on the microscope drive. Using this procedure, Perrin verified the exponential form of the distribution and obtained values for Avagadro's number N_0, between 6.0×10^{23} and 8.0×10^{23} per gram-mole, in agreement with previous determinations from Planck's radiation law.

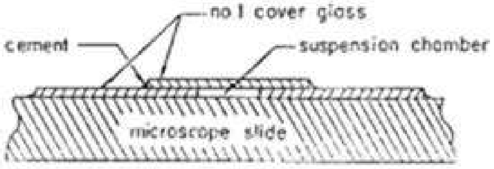

FIG. 1. Details of microscope slide.

Perrin continued his experimental research on colloidal suspensions for several years. In addition to the sedimentation method, he determined Avagadro's number from observations of both translational and rotational Brownian motion. It was for this extensive research that he received the 1926 Nobel Prize in physics.

PREPARATION OF SUSPENSION

For the exponential distribution to be observable, the height at which the concentration decreases by a factor of, say, $1/e$ must be somewhat larger than the depth of field of the microscope objective. Specifically, the approximately 2μ depth to field, dh, of a 40× objective requires that the concentration decrease by $1/e$ in at least 10μ. This requirement restricts the diameter and density of particles appropriate for the experiment. Polystyrene spheres available from Sargent–Welch for their Millikan apparatus have appropriate specifications: the diameter is $1.011\pm0.005\mu$ and the density ρ is 1.053 ± 0.004 g/cm^3.[9] With a water ($\rho_0=1.000$ g/cm^3) suspension of these particles at room temperature ($T=295$°K), and with the accepted value of Boltzmann's constant ($k=1.38\times10^{-16}$ erg/°K), Eq. (1) gives a $1/e$ decrease in concentration in $14.5\ \mu$. The distribution is easily expanded by using a suspending liquid slightly denser than water. We use an 11% solution of glycerol in water ($\rho_0=1.025$ g/cm^3) to prepare a suspension with an expected $1/e$ decrease in $27.4\ \mu$. Any greater expansion of the distribution would introduce an unacceptably large uncertainty in the factor $\rho-\rho_0$ since the density of the spheres is specified only to about 0.5%.

The plastic spheres are supplied at 5% concentration in a 10 ml bottle of water. Since one drop of this suspension in 25 ml of liquid yields a suitable concentration for the experiment, one bottle of the concentrated solution will supply many students for several years. Also, the volume of water in the single concentrated drop produces a negligible change in the density of the 25 ml of the chosen liquid.

PREPARATION OF SLIDE

The working distance, the distance from the front of the objective to the plane in focus, is approximately ½ mm for a 40× or 43× objective. Since we wish to bring the floor of the cell containing the suspension into focus, the distance from the floor of the cell to the top of the cover glass clearly must be less than the working distance. In practice, a somewhat shorter depth is desirable to help avoid accidentally breaking the cover glass when focusing on the floor of the cell.

A cell of the following construction works well. (See Fig. 1.) Two No. 1 square glass cover slips, thickness 130 to 170 μ, are cememted to the face of a plain microscope slide with a gap of 5 to 10 mm between them. The cement must be insoluble in the suspending liquid; we used Vaseline at first, but changed to a commercial sealant (xyelene) to make more durable samples. The open ends of the shallow trough between the cover slips are dammed with a fine ridge of the cement, taking care not to contaminate the center portion of the floor of the trough. A pipette or an eyedropper is used to fill the trough with the prepared suspension. The trough is then covered with a third No. 1 cover glass, which is cemented to the two supporting cover glasses. Additional cement is applied at the dammed ends of the cell to insure that the construction is leakfree.

The suspension in the completed cell must settle to equilibrium before observations are made. Although we did not observe the approach to equilibrium in detail, the water suspension gives good results after settling overnight and the glycerol-water suspension after 2 days. The slides, however, are not permanent. All of our slides, after giving good results over a period of days, were found to be useless on a subsequent day; all the spheres were at the floor of the cell. Absence of Brownian motion proved that the spheres were firmly stuck to the floor. The useful lifetime of most of the slides was 3 or 4 days, although a few lasted for more than a week and one lasted for over a month. If a way were found to prevent the spheres from adhering to the glass floor, permanent slides could be prepared.

OBSERVATIONAL PROCEDURES

Following Perrin, we examine the equilibrium suspension slides from above with a 40× or a 43× objective and a 10× eyepiece. The microscope must have a micrometer drive to measure increments in height. The illumination of the spheres can be either from the side, producing bright images on a dark field, or from below, producing dark images on a bright field. Counts can be taken either directly from the field of view or from photographs.

For visual observation, the side lighting with a dark field is the most comfortable. A piece of black paper is placed under the slide and the position of the high intensity lamp is adjusted to maximize the contrast. At the floor of the cell, with the concentrations and objectives we use, the spheres in the field of view number in the order of hundreds. As the microscope is moved upward, the concentration steadily decreases until in the upper regions of the cell, (h approximately 100 μ) there are either no spheres or just one or two lone stragglers. An acceptable order of magnitude value for k can be determined immediately by estimating the height at which the concentration is half that at the floor of the cell. For the water suspension, this occurs at less than 10 μ and for the 11% glycerol suspension at 10 to 20 μ above the floor, in agreement with Eq. (1) and the accepted value of k.

We use the following procedure for obtaining quantitative results. To facilitate the counting, an aluminum foil disk with four or five pinholes is placed at the focal plane of the eyepiece of the microscope. This mask restricts the field of view so that only a few spheres are seen through each pinhole at any one time. The visible spheres can now be easily counted at a glance and the number recorded. A new region is then brought into view through the pinholes by simply rotating the eyepiece, and another count is taken. At least 10 or 20 such determinations are made at one level in the suspension. This counting procedure is repeated at

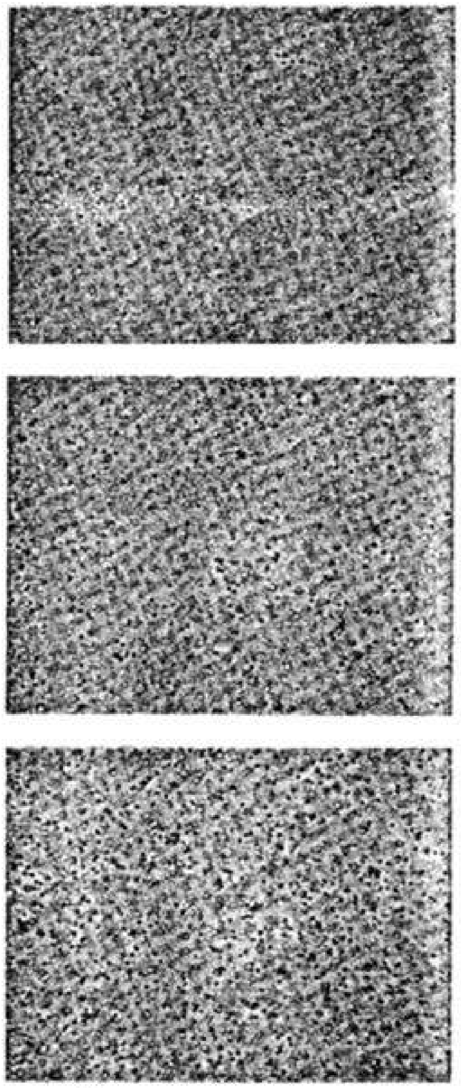

FIG. 2. Photographs of the equilibrium distribution of 1.011 μ diam polystyrene spheres suspended in water. The increment in micrometer setting for adjacent photos is 8 μ. Due to the 4/3 index of refraction of the water, the true height increment is 10.7 μ.

several levels separated by increments of about 5 μ. However, an increment of height read directly from the micrometer of the microscope is not the true distance between the two levels of observation in the suspension. Because of the 4/3 index of refraction of the suspending liquid, we have

$$h = 4/3h', \tag{2}$$

where h' is the micrometer reading and h is the true height in Eq. (1). An alternative counting procedure is to photograph the entire field of view (i.e., without the mask) at each level, and then to count the spheres from the photographic print. Figure 2 is a sequence of photographs of a water suspension, with bright field illumination.

Several precautions should be noted in either the direct or the photographic procedure. The decision to count a sphere or to not count it is dependent on the observer's subjective criterion for deciding when a sphere is in focus. This subjectivity does not affect the results as long as a consistent criterion is maintained for all levels. Counts made at the floor are larger than expected if a substantial number of particles are stuck to the surface and the counts are smaller than expected if the observation region substantially overlaps the volume of glass below the floor surface. Finally we find that upon reversing the direction of the micrometer drive our microscopes have several microns of free play. A significant error is avoided by continuously advancing the micrometer drive in the same direction when changing the level of observation.

RESULTS

Counts obtained from a distilled water suspension ($\rho_0 = 1.000$ g/cm^3) and from an 11% glycerol suspension ($\rho_0 = 1.025$ g/cm^3) are plotted in Fig. 3. The lines are least squares fits. These particular counts were obtained with the aid of the aluminum foil mask and, for each suspension, the total counting time was less than 1 h, well within the time available to the student in a single laboratory period. The slope of the fit to the water data yields

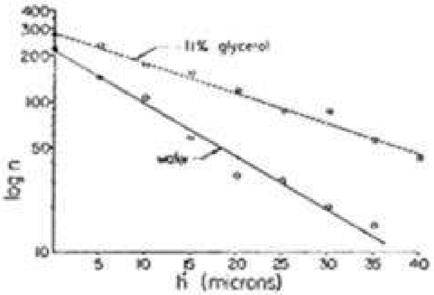

FIG. 3. Particle counts n as a function of micrometer setting h'.

1.57×10^{-16} erg/°K for Boltzmann's constant and the 11% glycerol data yield 1.47×10^{-16} erg/°K.

Although Fig. 3 shows only the results of two of our longest counting runs, we made a total of 15 runs with the water suspension and 3 with the 11% glycerol suspension. Most of these 18 runs had less than half as many counts as the runs in Fig. 3, and each took less than ½ h counting time. These runs gave values for k ranging from 1.16×10^{-16} to 1.72×10^{-16} erg/°K with an unweighted average of 1.43×10^{-16} erg/°K. Thus, with less than ½ h of counting, results are obtained consistently within 20% of the accepted value.

POSSIBLE EXTENDED PROJECTS

Although we have not computed uncertainty brackets for the experimental values of k, such a computation would be an interesting and challenging exercise in error analysis. The uncertainty is due primarily to inconsistent counting criterion, real statistical fluctuations in the number of particles present, error in micrometer value h', and uncertainty in the factor $\rho-\rho_0$.

Perrin worked with many different suspensions and, in the course of his observations, he investigated variations in all the parameters in Eq. (1). Similar investigations can be carried out in an introductory laboratory project or in the advanced undergraduate laboratory. Liquids other than water and 11% glycerol solution can be used to further investigate the dependence on ρ_0. The dependence on particle volume can be observed by preparing several suspensions, each with spheres of a different diameter. Eleven sizes of polystyrene spheres, ranging in diameter from 0.091 to 1.100 μ, are available from Dow Chemical.[10] The dependence on temperature can also be observed. Although a water suspension permits a relatively narrow window of temperature variations, other suspending liquids might allow a wider temperature range to be investigated. Finally, the suspension slides prepared for the sedimentation equilibrium experiment may also be used to investigate translational Brownian motion.[11]

ACKNOWLEDGMENTS

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[1] Neither Einstein nor Perrin actually refer to Boltzmann's constant k in their papers, but use instead Avogadro's number, $N_a=R/k$, where R is the molar gas constant. The convention of abbreviating R/N_a as k, although apparently introduced by Plank in his blackbody radiation papers, was not well established at the time.

[2] A. Einstein, *Investigations on the Theory of the Brownian Movement* (Dover, New York, 1956), p. 27.

[3] D. Halliday and R. Resnick, *Physics* (Wiley, New York, 1966), Pt. 1, pp. 608–611. See also Chap. 23, Prob. 42.

[4] F. W. Sears and M. W. Zemansky, *University Physics* (Addison-Wesley, Reading, Mass., 1970), 4th ed., p. 286.

[5] R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, Mass., 1964), Vol. 1, pp. 40.1–40.2.

[6] Although several brief notes appeared in 1908, a comprehensive report is J. B. Perrin, Ann. Chim. **18**, 1 (1909). An English translation is F. Soddy, *Brownian Motion and Reality* (Taylor and Francis, London, 1910).

[7] *Nobel Lectures, Physics, 1922–1941* (Elsevier, Amsterdam, 1965), p. 136.

[8] G. L. Trigg, "The Existence of Atoms," *Crucial Experiments in Modern Physics* (Van Nostrand Reinhold, New York, 1971), pp. 37–54. This Momentum Book, No. 23 in the Commission on College Physics Series, is an excellent reference for students performing this experiment. See also G. P. Harnwell and J. J. Livingood, *Experimental Atomic Physics* (McGraw-Hill, New York, 1933), pp. 89–92.

[9] The Sargent–Welch bottle only specifies the density as 1.05 g/cm^3 and the diameter as 1.01 μ. The manufacturer of the spheres, Dow Chemical, directed us to J. B. Yannas, Polymer Lett. **2**, 1005 (1964) for the quoted values.

[10] For more information contact Diagnostic Products Division of Dow Chemical Corp. P.O.B. 512, Midland, Mich. 48640.

[11] H. F. Meiners, ed., *Physics Demonstration Experiments* (Ronald, New York, 1970), Vol. II, pp. 817–819.