An experiment to measure Avogadro's constant. Repeating Jean Perrin's confirmation of Einstein's Brownian motion equation

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Note: This article is available on our website, *www.chem13news.uwaterloo.ca*. You might want to enter this document to copy Fig. 1 and enlarge it. See the experimental section, "Determine N for yourself".

In 1909, Jean Perrin (1870-1942), a Nobel Prize winning French physicist, reported his series of painstaking experiments to test the equations Albert Einstein had derived in the May 1905 paper that I described last month.[1] In this article I will describe Perrin's experimental proof[2] and show how you and your students can repeat Perrin's analysis as a dry lab experiment.

Early in the twentieth century Perrin had perfected techniques for producing small, spherical particles of uniform radius (in the range 0.1 – 5 μm (1 μm = 10^{-6} m)). He used gamboge, a latex from the tree, *Garcinia morella*. Adding water to a methanol solution of gamboge gives an emulsion of gamboge particles that are spherical and of various diameters. Repeated cycles of centrifugation allowed Perrin to select out gamboge particles of uniform diameter. A similar procedure works with mastic, a gum resin from a Mediterranean tree. Perrin developed methods for measuring the radius and density of these spherical particles.[3]

Confirmation of Einstein's equation

When Perrin learned of Einstein's 1905 predictions regarding diffusion and Brownian motion, he devised an experimental test of those relationships. His approach was simple. Using a microscope in a camera lucida setup,[4] he could observe and record the Brownian motion of a suspended gamboge particle in a liquid of a given viscosity and constant temperature. The camera lucida allows one to observe, at the same time, both the particle and its projection on a sheet of paper. Thus, Perrin and his assistant could mark the particle's position on a piece of graph paper at timed intervals. In his own words, "[We took] turns at the microscope, each dotting the granules every 30 seconds at the call of the other."[5] Three such "dottings" are shown in Fig. 1, in which the successive dots are joined by line segments.[6] In the left case, for example, the particle was tracked for 24 minutes — 48 segments of 30 seconds each.

Perrin used these tracks to test Einstein's predictions by calculating the value of Avogadro's constant, using the final equation in Einstein's paper,

$$N = \frac{t}{\lambda_x^2}\left(\frac{RT}{3\pi kP}\right), \qquad (1)$$

where R is the gas constant, 8.314 x 10^7 g cm^2 s^{-2} mol^{-1} K^{-1}; T is the absolute temperature, 290 K in most of Perrin's experiments; λ_x^2 is the mean square displacement in the x direction for periods of time, t; k is the viscosity, 0.011 g cm^{-1} s^{-1} at 290 K; and P is the radius of the microscopic particle.[7] If the values of N are the same for different conditions, this will constitute proof that Einstein's equation is correct.

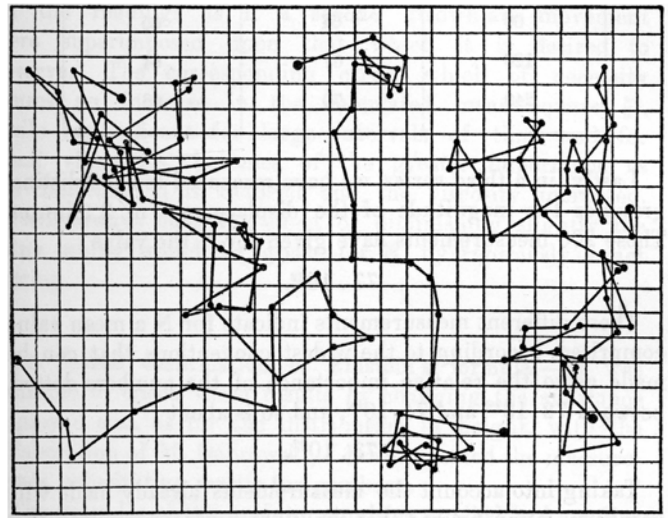

Fig. 1. These tracks of three particles are by J. Perrin.[6] The dots show the particle positions at 30-second intervals, with lines joining successive points. The scale is 1 division equals 0.0003125 cm. The particle radius is 0.52 μm.

Given a particle track such as those in the figure, the task is to evaluate λ_x^2, the mean square displacement *in the x direction*. The tracks are shown in two dimensions, call them x and y, the horizontal plane; if the particle moved up and down, as it assuredly did, the coordinates in the z direction could not be readily ascertained. That's okay, we don't need that information. Converting displacements from two dimensions to one dimension is straightforward. Consider a track such as one of those in Fig. 1. By the Pythagorean theorem, the square of the average distance travelled in the xy plane is equal to the square of the average distance travelled in the x direction plus the square of the average distance travelled in the y direction. That is,

$$\lambda_{xy}^2 = \lambda_x^2 + \lambda_y^2 . \qquad (2)$$

There is no preference for either the x or y direction. Therefore, the mean square projection along the x axis equals the mean square projection along the y axis. Hence,

$$\lambda_x^2 = \lambda_y^2 \quad \text{or} \quad \lambda_x^2 = \frac{1}{2}\lambda_{xy}^2 \qquad (3)$$

So to obtain the mean square displacement, λ_x^2, measure the length of each segment of the particle track in the xy plane, convert that segment length to the actual distance in centimetres by using the magnification factor and square that distance. Then find the average, or mean, of all those squared values and, finally, divide by 2. This gives the mean square displacement in the x direction. That's what Perrin and his assistants did for dozens of particles of different sizes in liquids of different viscosities.

Some of his results are given in Table 1.[8] These apply to a study of 50 particles in water (290 K, k = 0.011 g cm^{-1} s^{-1}) that were followed for two minutes each, while noting their position every 30 seconds. The mean square displacements are averages of 50 *different* particles, not multiple steps of the *same* particle. But that doesn't matter, given the randomness of Brownian motion. It's clear that Avogadro's constant is the same within experimental error in these four sets of measurements. Therefore, displacement due to Brownian motion depends on the elapsed time as Einstein had predicted. Also, the value calculated for the Avogadro constant, N, is within the range of values then accepted as valid.

Table 1. Results of Perrin's experiments on 50 particles[8]

Time intervals	λ_x^2	N/mol^{-1}	N_{mean}/mol^{-1}
30 s	45×10^{-8} cm^2	68×10^{22}	68×10^{22}
60 s	86.5×10^{-8} cm^2	70.5×10^{22}	
90 s	140×10^{-8} cm^2	71×10^{22}	
120 s	195×10^{-8} cm^2	62×10^{22}	

Note: I retain Perrin's practice of showing N as a multiple of 10^{22}. You'll find small errors if you attempt to calculate N from the given values of λ_x^2 !

In the summary table of all his work, Table 2,[9] Perrin indicates that he recorded 4,220 displacements. For comparison, in Fig. 1 the three tracks have a total of 118 displacements. The results in Table 2 show clearly that the value of N calculated by Einstein's equation is a constant, even when the viscosity varies 125-fold, and the particle size varies 26-fold. (The simple average for N in Table 2 is 68.9×10^{22} mol^{-1}, in good agreement with values Perrin obtained in his other methods of determining Avogadro's constant.) The constancy of N demonstrates that Brownian motion depends on viscosity and size of particle as Einstein had predicted; and that the nature of the particle and the nature of the solution, apart from its viscosity, are not factors, also as Einstein had predicted. Perrin concludes, "This remarkable agreement proves the rigorous accuracy of Einstein's formula and in a striking manner confirms the molecular theory."[9]

Table 2. Summary of Perrin's measurements of the Avogadro constant, N, using particles of various sizes in solutions of varying viscosity[9]

Relative viscosity	Nature of emulsion	Grain radius in μm	Number of displacements recorded	$N/10^{22}$ in mol^{-1}
1	I. Gamboge grains	0.50	100	80
1	II. Gamboge grains	0.212	900	69.5
4 to 5	III. Same grains as in II, but in 35% sugar solution	0.212	400	55
1	IV. Mastic grains	0.52	1,000	72.5
1.2	V. Very large mastic grains in 27% urea solution	5.50	100	78
125	VI. Gamboge grains in glycerine (1/10 water)	0.385	100	64
1	VII. Gamboge grains of very uniform equality (2 series)	0.367	1,500 120	68.8 64

If you read references 2a or 2b, you'll learn that Perrin analyzed his Brownian motion data in a couple other ways as well. Moreover, he used particles of uniform radius in a totally different way to deduce N, studying their distribution with height in a suspension in water. This distribution involves Avogadro's constant, and the value Perrin obtained in these analyses was also 70×10^{22} mol^{-1}. In summarizing all his work, Perrin settles on 70.5×10^{22} mol^{-1} as his best value of N.[10] Today's best value is, of course, 60.2×10^{22} mol^{-1}. It would be interesting to speculate why Perrin's value is 17% too high — but I'll restrain myself!

Determine N for yourself!

You and your students can use the information in Fig. 1 to calculate Avogadro's constant, just as Perrin did. First, to make it clear to your students what Brownian motion is, use an online demonstration,[11] or set up your own as described in the Letter to the Editor on page 2 of this issue. Explain that the tracks in Fig. 1 indicate the positions, at 30-second intervals, of a very small particle observed under a microscope for 24 minutes (left track), 15 minutes (middle track) and 20 minutes (right track).

Then proceed with the experiment. (See my sample analysis on the next page.) All you really need is a ruler with mm markings; a spreadsheet is useful but not essential. Here's what you do. Photocopy Fig. 1, enlarging it to 200% or more to get more precise measurements, and work out the magnification factor. For example, if you enlarge by a factor of 2, each division in Fig. 1 is about 6.7 mm wide. This corresponds to a true distance of 3.125×10^{-4} cm in Perrin's experiment, so the conversion factor would be

$$\frac{3.125 \times 10^{-4} \text{ true cm}}{6.7 \text{ mm measured}} = \frac{4.66 \times 10^{-5} \text{ true cm}}{\text{mm measured}}$$

Evaluate the actual conversion factor for your photocopy. Determine the average width of one division in mm by taking the average from several locations in the grid, both horizontal and vertical; you'll find that the grid is not as uniform as today's graph paper would be. There's an alternative way to enlarge Fig. 1. This article is available on our website, *www.chem13news.uwaterloo.ca*. Go into it, copy Fig. 1, paste it into a blank Word document, click on that copy and enlarge it by dragging one corner. You can enlarge it even more by cropping that enlarged figure leaving just the one track you want.

Set up a table (or spreadsheet) with these headings.

1. Segment number
2. Measured length (on paper) in mm
3. True length in cm
4. $Length^2$ in cm^2

On the photocopy, number the segments and enter these numbers in column 1 on your data table. (The data are most readily handled using a spreadsheet such as Excel.) Measure each segment length to the nearest mm and enter these in column 2. Convert these lengths to cm using the conversion factor (column 3), and then square those values (column 4). Finally, calculate the average of these squared distances and divide by 2. This is the value of λ_x^2. Substitute it into eq 1 and evaluate N. The temperature and viscosity in this case are given in the paragraph following eq 1. The particle observed in Fig. 1 had a radius of 0.52 μm, and the time interval is 30 s. Be sure to convert all length measurements to the same units (cm). Remind your students to include units and to ensure they are consistent, so cancellation occurs appropriately, when substituting into eq 1.

You can measure each track in Fig. 1 in several ways.

a) Use a time interval of 30 s as described above.
b) Use a time interval of *overlapping* 60-second periods. Measure the distance from the start of segment 1 to the end of segment 2, then from the start of segment 2 to the end of segment 3, and so forth.
c) Use a time interval of *non-overlapping* 60-second periods. Measure the distance from the start of segment 1 to the end of segment 2, then from the start of segment 3 to the end of segment 4, and so forth.
d) Repeat method (b) using 90-second time intervals.
e) Repeat method (c) using 90-second time intervals.
f) Repeat method (b) using 120-second time intervals.
g) Repeat method (c) using 120-second time intervals

Assign as many of these methods as you wish, but you may find that (a) is all you want to do. For example, you could divide your class into three groups and assign one track, by method (a), to each group.

My results are in Table 3. $N_{average} = (60.8 \pm 11.4) \times 10^{22}$ mol^{-1}, surprisingly close to the true value of 60.2×10^{22} mol^{-1}. It's not surprising that the standard deviation is large because Brownian motion is a random process and we're not considering many steps.

Acknowledgements

Thanks to Jean Hein, Herb Deruyter and Doug De La Matter for reading this article and giving helpful comments and suggestions.

Table 3. Analysis of tracks in Fig. 1

Track	Method	$\frac{\lambda_x^2}{10^{-8}\,cm^2}$ *	$\frac{N}{10^{22} mol^{-1}}$	$\frac{N_{avg}}{10^{22} mol^{-1}}$
Left	(a), 30 s	36.1	37	60.8 ±11.4
Left	(g), 120 s non-ovl	97.1	55	
Middle	(a), 30 s	19.7	68	
Middle	(f), 120 s overlap'g	76.3	70	
Right**	(a), 30 s	23.6	57	
Right	(e), 90 s non-ovl	67.4	60	
Right	(f), 120 s overlap'g	77.2	70	
Right	(g), 120 s non-ovl	77.9	69	

*Note: $\frac{\lambda_x^2}{10^{-8}cm^2}$ means that $\lambda_x^2 = 19.2 \times 10^{-8}$ cm^2 in the first entry

**Thanks to Jean Hein for measuring this one

A sample analysis

Table 4 gives an analysis of the middle track in Fig. 1, to illustrate the procedure. The figure was enlarged by a factor of nearly 3. Four measurements of several divisions — two measurements in each direction — gave an average of 9.63 mm per division. As each division corresponds to a true 0.0003125 cm, the factor for converting measured mm to true cm is

$$\frac{0.0003125 \text{ true cm}}{1 \text{div}} \times \frac{1 \text{div}}{9.63 \text{ measured mm}}$$

$= 3.245 \times 10^{-5}$ true cm for each measured mm.

The segments were numbered starting at the top left of the middle track. The length of each segment in the track was measured to the nearest mm with a mm ruler (column 2 in an Excel spreadsheet); these values were converted to true cm (column 3) using the factor above; and that length was squared (column 4). The average of the values in column 4 is 39.5×10^{-8} cm^2. This is the mean square displacement in the xy plane. Dividing by 2 gives the mean square displacement in the x direction, namely, $\lambda_x^2 = 19.7 \times 10^{-8}$ cm^2. Therefore, eq 1 gives the result

$$N = \frac{30 \text{ s}}{19.7 \times 10^{-8} \text{ cm}^2}\left(\frac{8.314 \times 10^7 \text{ g cm}^2 \text{ s}^{-1} \text{ mol}^{-1} \text{ K}^{-1} \times 290 \text{ K}}{3 \times 3.142 \times 0.011 \text{ g cm}^{-1} \text{ s}^{-1} \times 0.52 \times 10^{-4} \text{ cm}}\right)$$

$$= 68.1 \times 10^{22} \text{ mol}^{-1}.$$

Table 4. Analysis of middle track in Fig. 1 in 30-second steps

Segment #	Measured length in mm[a]	True length in cm[b]	Length^2 in cm^2
1	38	12.3×10^{-4}	152.1×10^{-8}
2	20	6.5×10^{-4}	42.1×10^{-8}
3	16	5.2×10^{-4}	27.0×10^{-8}
4	18	5.8×10^{-4}	34.1×10^{-8}
5	32	10.4×10^{-4}	107.8×10^{-8}
6	10	3.2×10^{-4}	10.5×10^{-8}
7	14	4.5×10^{-4}	20.6×10^{-8}
8	12	3.9×10^{-4}	15.2×10^{-8}
9	18	5.8×10^{-4}	34.1×10^{-8}
10	12	3.9×10^{-4}	15.2×10^{-8}
11	23	7.5×10^{-4}	55.7×10^{-8}
12	32	10.4×10^{-4}	107.8×10^{-8}
13	5	1.6×10^{-4}	2.6×10^{-8}
14	24	7.8×10^{-4}	60.7×10^{-8}
15	14	4.5×10^{-4}	20.6×10^{-8}
16	10	3.2×10^{-4}	10.5×10^{-8}
17	23	7.5×10^{-4}	55.7×10^{-8}
18	21	6.8×10^{-4}	46.4×10^{-8}
19	27	8.8×10^{-4}	76.8×10^{-8}
20	11	3.6×10^{-4}	12.7×10^{-8}
21	18	5.8×10^{-4}	34.1×10^{-8}
22	16	5.2×10^{-4}	27.0×10^{-8}
23	10	3.2×10^{-4}	10.5×10^{-8}
24	7	2.3×10^{-4}	5.2×10^{-8}
25	14	4.5×10^{-4}	20.6×10^{-8}
26	8	2.6×10^{-4}	6.7×10^{-8}
27	15	4.9×10^{-4}	23.7×10^{-8}
28	11	3.6×10^{-4}	12.7×10^{-8}
29	16	5.2×10^{-4}	27.0×10^{-8}
30	32	10.4×10^{-4}	107.8×10^{-8}

[a] The grid was enlarged such that 1 div = 9.63 mm as measured.
[b] The conversion factor is 0.00003245 true cm/(measured mm) (see text)

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References

1. *CHEM 13 NEWS*, April 2006, pages 14-15.
2. Jean Perrin described his studies on Brownian motion in two books that are available in English. a) J. Perrin, *Atoms*, translated by D.L. Hammick, second English edition, D. Van Nostrand, New York, 1923, pages 109-133. b) J. Perrin, *Brownian Motion and Molecular Reality*, is a translation, by F. Soddy, of Perrin's report in *Annales de Chimie et de Physique*, 8th series, September 1909, Ox Bow Press, reprint edition, 1990.
3. Reference 2a, pages 94-99; reference 2b, pages 24-38 gives an extensive explanation of the procedure.
4. The camera lucida was invented by William Hyde Wollaston in 1806. A modern description is on the internet at *http://www.microscopy-uk.org.uk/mag/indexmag.html?http://www.microscopy-uk.org.uk/mag/articles/drawing.html*. Or google "camera lucida microscope".
5. Reference 2b, page 62.
6. Reference 2b, page 64. A similar figure is in reference 2a, page 115, but differences in the 40-step track give a 12% lower value of N! I suspect the figure was redrawn for this later (1923) book without sufficient care.
7. I am using Einstein's notation. In Perrin's publications, note that he uses ξ^2 instead of λ_x^2 for the mean square displacement, ζ instead of k for the viscosity, and a instead of P for the particle radius.
8. Reference 2b, page 61. One column has been omitted for clarity.
9. Reference 2a, page 123.
10. Reference 2b, page 90.
11. a) *http://www.aip.org/history/einstein/essay-brownian.htm*; b) *http://www.microscopy-uk.org.uk/dww/home/hombrown.htm*. ■

Gwen Marbury wins teaching award

Gwen Marbury, who teaches at DeMatha Catholic High School in Hyattsville, Maryland, is the 2006 winner of the James Bryant Conant Award in High School Chemistry Teaching. This prestigious award is offered by the American Chemical Society to just one teacher in the United States each year. Congratulations, Gwen!

Although she started her chemistry career in an industrial lab, after 20 years, Gwen's inner voice pushed her into teaching. In 1995 she took up her position at DeMatha, an all-boys school. Her enthusiasm for chemistry and the stories she can tell from her industrial lab days help her keep her students interested in the subject. Her students appreciate her dedication. One says, "You can tell that she goes two extra miles to ensure that we understand the material. Ms. Marbury sincerely believes that each one of her students is a success story waiting to happen." Gwen herself says, "Probably since I have no children, working with [my students] is particularly gratifying to me. I very much enjoy sharing in their accomplishments and offering support in less favorable moments." *(Excerpted from* Chemical and Engineering News*, January 23, 2006, page 46.)*