High school students calculate Avogadro's constant using video projection of Brownian motion in milk

Herbert H. Deruyter, Waterloo Collegiate Institute, 300 Hazel Street, Waterloo ON N2L 3P2
Lewis J. Brubacher, Department of Chemistry, University of Waterloo, Waterloo ON N2L 3G1

[Students can find Avogadro's constant using milk, a stopwatch, a microscope, a video camera and a 1905 equation developed by Einstein.]

Introduction

One of Einstein's papers, published in his miracle year of 1905,[1] predicted that the incessant motion of molecules should impart an observable but random displacement to microscopic, suspended particles in a liquid. Building on Stokes' law of diffusion and van't Hoff's extension of the ideal gas law to dilute suspensions, Einstein argued that the mean square displacement of a suspended particle along one dimension is given by the equation:

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

Using the same symbols as Einstein, λ_x^2 represents the mean square displacement of a suspended particle in the *x*-direction for a length of time t, N is the Avogadro constant, R is the gas constant, T is the absolute temperature, k is the viscosity of the liquid, and P is the radius of the suspended particle. Since the quantities λ_x^2, t, T, k and P are measurable and the constant R is known, Einstein expressed the hope that other workers would soon use this same relation to determine the value of N.

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

Within three years Perrin used Einstein's Brownian motion equation to determine an experimentally derived value of Avogadro's constant. Perrin developed a technique for preparing uniform-sized particles of gamboge and mastic (plant resins). The motion of these particles in a dilute aqueous suspension were observed through a microscope. The location of a specific particle in the *x-y* plane was recorded at successive uniform time intervals to gain a value for λ_x^2. Substitution into Equation (2) showed that the displacement of these particles behaved as Einstein predicted, and led to a value for Avogadro's constant of $N = 7.15 \times 10^{23}\ mol^{-1}$.[2] These and related measurements convinced most of the remaining skeptics of the atomic structure of matter and earned Perrin the Nobel Prize for Physics in 1926.

Following Perrin's work numerous educators suggested methods for projecting images of Brownian motion for classroom viewing.[3,4] In the mid-1960s, Perrin's analysis of Brownian motion to estimate Avogadro's constant appeared in the undergraduate laboratory.[5−7] At this time, microscopic latex spheres of uniform diameter became commercially available thus making the laborious preparation of suspended particles unnecessary. However, viewing was limited to a single individual observing these particles through a microscope equipped with a graduated eyepiece or graticule. With the advent of video recording equipment, the movement of Brownian particles could be monitored on television screens.[8,9] More recently Salmon et al. and Newburgh et al. used video cameras, computers and image-analysis software to plot the displacement of plastic microspheres and estimate the value of N.[10,11] Regardless of the sophistication of the technologies used or the type of the microscopic particle observed, values of N ranged from 4.2 to $8.2 \times 10^{23}\ mol^{-1}$.

Brubacher wrote an accessible and concise description of Perrin's approach to illustrate how Perrin's original measurements of the displacement of Brownian particles could be used to obtain N.[12] Deruyter commented that Brownian motion of fat droplets in ordinary supermarket milk can be prepared quickly and observed readily by video projection in the classroom.[13] Here we present estimates of Avogadro's constant made by observing such milk preparations using microscopes and video projection equipment available in high schools. We provide two sets of data. The first set reports values of Avogadro's constant obtained by the authors to assess the merits of doing this laboratory activity with senior high school students. The second set reports results obtained by grade 12 science students.

Method

Milk samples were prepared by diluting 2% milk with de-ionized water to 0.2%. Students used suspensions diluted to 0.1%. A drop (about 40 − 50 μL) of the dilute milk suspension was added to the well of a glass cavity (depression) microscope slide and covered with a glass cover slip. The specimen was mounted on a compound light microscope fitted with a condenser and viewed using a 10× wide field ocular and a 40× objective lens. A VideoFlex camera was fitted to the eyepiece of the microscope using the adapter ring provided with the camera. The composite video output signal from the camera was directed to a Sony video projector. The image was projected onto large chart paper mounted on the wall (chalkboard). The equipment used in this experiment is illustrated in Figure 1.

Light from a 23-W compact fluorescent bulb about 20 cm away from the microscope was directed through the milk sample with

Figure 1. The equipment consists of a compound light microscope, VideoFlex camera, LCD projector and compact fluorescent light.

the microscope mirror to avoid the inevitable warming of the slide by a hot incandescent microscope light. The air temperature was measured in the immediate vicinity of the microscope slide using a laboratory thermometer. No observable change in ambient temperature was noted with the thermometer in the light stream. The temperature was recorded for each run.

The viscosity of the dilute milk suspensions was considered to be the same as water at the ambient temperature.[14] No observable difference was noted when the rate of flow of a 0.2% milk suspension was compared to the rate of flow of de-ionized water through the same partially closed valve of a burette.

A glass stage micrometer graduated in 0.01 mm[15] was used to calibrate the size of the image on the wall and to obtain the degree of magnification. Magnifications ranged from 11 060× to 13 430×. The diameters of the images of the fat droplets we monitored varied from 1.5 to 2.2 cm, corresponding to actual diameters of 1.2 to 2.0 μm.

The position of a projected fat droplet was marked every 30 s for a 10-min run to provide 21 successive locations. In our own experiments, one of us adjusted the microscope to keep the droplet in focus and mark time while the other recorded the position of the droplet on the wall chart and tracked the droplet continuously in order not to lose sight of it. Students worked in groups of three: one focused the microscope, the second marked time, while the third followed and marked the droplets on the screen. Several tracings of the outline of the droplet were measured to estimate the diameter of the droplet to the nearest millimetre. This necessarily required some "visual averaging" as the droplet did not pause for our convenience. Figure 2 illustrates one such record. The distance travelled during each interval was measured to the nearest millimetre. This distance was corrected for magnification to obtain the actual displacement (λ) of the droplet in the *x-y* plane. Each displacement was in turn squared (λ^2). The average of the squared displacements was calculated for the entire run. This average was then halved[12] to obtain λ_x^2, the mean square displacement in the *x*-direction. Substitution of this measured value into Equation (2) along with R and measurements of t, T, k and P delivered an estimate for Avogadro's constant.

Another fat droplet was then selected and the above procedure was repeated. Occasionally a droplet would get lost among a crowd of others, disappear from the plane of focus or migrate off screen. Runs with fewer than ten 30-s time intervals were discarded and a new run was started in its place. Students were asked to calculate one value of N by hand using an electronic calculator. Otherwise, Microsoft Excel was used to record and automate the calculations. The configuration of the spreadsheet is presented in the Appendix. Copies of this sheet could also be used to compile data manually.

Results

Figures 2 and 3 illustrate the record of a single run used to generate an estimate for N. Numbers label the consecutive positions of the projected image of a fat droplet at 30-s intervals. These displacements generate a value of 1.95×10^{-7} cm^2 for the mean square displacement (λ_x^2). Other relevant data for this run include: a magnification of 11 720 times, an ambient temperature of 26°C, and a viscosity of 0.008705 g cm^{-1} s^{-1}. The universal gas constant is 8.314×10^7 g cm^2 s^{-2} mol^{-1} K^{-1}. The circle just left of centre represents the traced outline of the fat droplet with a diameter of 2.0 cm. Corrected for magnification, this fat droplet has a radius of 8.5×10^{-5} cm. Equation (2) gives a value of N = 5.5×10^{23} mol^{-1} for this run.

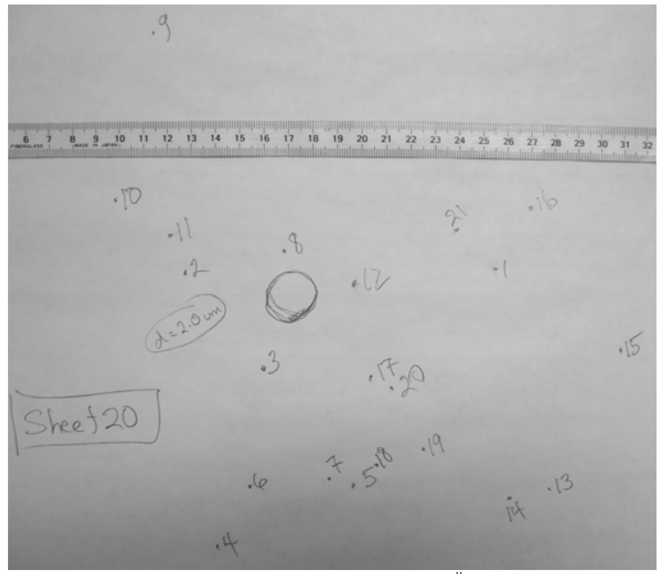

Figure 2. The original data record for Run #10 listed in Table 1.

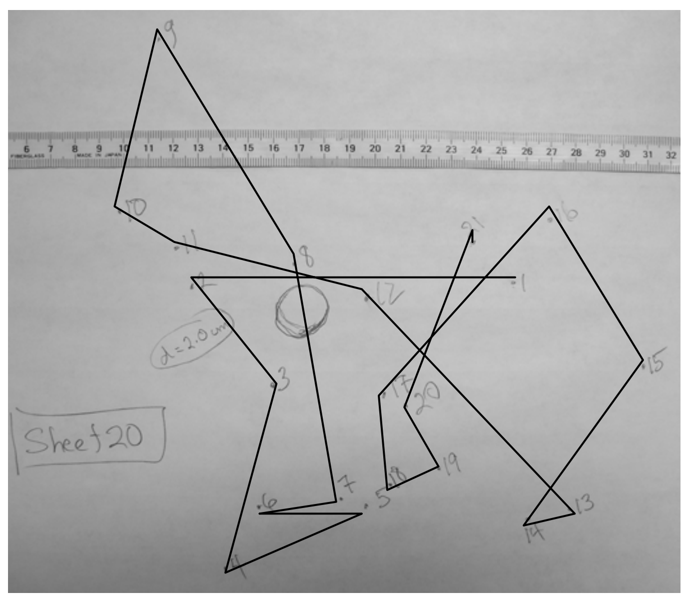

Figure 3. Connecting consecutively numbered positions yields the random walk of the fat droplet on screen.

The authors completed 26 runs and students completed 25 runs. Tables 1 and 2 list the two sets of values for Avogadro's constant. The values for N listed in Table 2 were calculated only after the students had collected the raw data for all 25 runs. The tables also provide the average and standard deviation for each set. Some runs were cut short when the fat droplet was lost from view or migrated off-screen.

Table 1. Values for Avogadro's constant obtained by the authors using Equation (2).

Run	Number of 30-s intervals in the run	$\frac{N}{10^{23}\,mol^{-1}}$
1	20	5.5
2	20	4.8
3	20	6.6
4	20	5.1
5	13	8.2
6	20	4.9
7	20	4.0
8	20	6.1
9	20	7.7
10	20	5.5
11	20	5.6
12	20	4.8
13	15	8.1
14	20	4.2
15	20	4.2
16	15	4.9
17	12	7.1
18	19	7.2
19	15	7.2
20	20	7.6
21	20	6.1
22	20	6.9
23	20	5.8
24	20	4.8
25	20	5.2
26	20	4.8
	Average	5.9
	St'd Deviation	1.3

Table 2. Values for Avogadro's constant obtained by students using Equation (2).

Run	Number of 30-s intervals in the run	$\frac{N}{10^{23}\,mol^{-1}}$
1	20	6.4
2	20	9.4
3	20	7.3
4	20	9.8
5	18	5.6
6	20	9.2
7	20	6.7
8	20	7.8
9	16	3.5
10	19	6.7
11	20	7.0
12	20	14.1
13	20	11.6
14	20	7.9
15	20	9.2
16	17	7.8
17	20	3.9
18	20	4.0
19	11	3.2
20	12	2.5
21	20	3.5
22	10	3.7
23	20	5.2
24	20	6.7
25	20	4.7
	Average	6.7
	St'd Deviation	2.8

Discussion

The average value of Avogadro's constant from both sets of data fall within the range reported in the literature noted earlier. The statistical nature of the data demands that the experiment be repeated several times, and consideration must be given to the collection of replicate sets of data in a timely manner. The 10-min duration of each run permits completion of several runs within a 1-hour high school laboratory period. The 30-s time interval generates 20 successive particle displacements. The benefits of this combination are illustrated graphically in Figure 4, which shows a plot of the mean square displacement against the number of intervals in a single run. Fluctuations in the mean diminish substantially in the first few intervals and are much reduced by the 20th time interval. The mean square displacement approaches a limit as the number of intervals grows. Though longer runs may gain greater precision, it comes at the cost of fewer runs and a larger number of truncated runs because fat droplets migrate off screen. Conversely, one might consider shorter runs of 10 or 15 points and accept the greater variability.

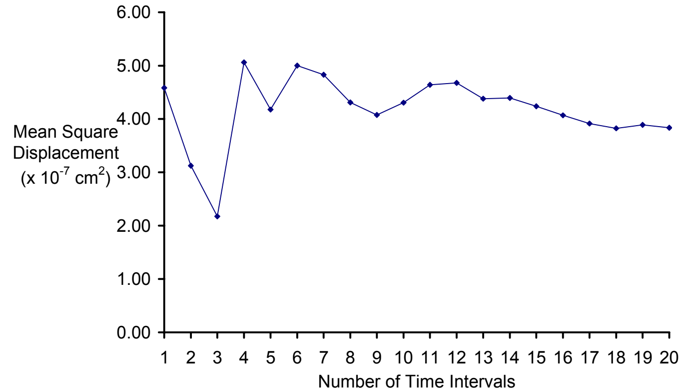

Figure 4. Mean Square Displacement (λ^2) as a Function of the Number of Time Intervals from Run 25, Table 2. Each point except the first represents an average. The first point is the squared displacement for the first 30-s time interval. The second point is an average of the first two squared displacements; the third point is an average of the first three squared displacements, and so on. The final point represents the average or mean square displacement of all twenty 30-s time intervals. The reduction in variation of the mean with successive intervals is interpreted to give a more reliable estimate for N.

Droplet diameters ranged from 1.2 to 2.0 μm, agreeing with the upper range of fat droplet diameters created by the two-stage homogenization of milk.[16] Smaller droplets move too fast to keep in focus. Measurements of the diameters of the fat droplets on screen were limited to two figures of precision and consequently restrict our estimates of Avogadro's constant to two digits as well. Rounding to two figures was done only in the final calculation for N. Though precision is limited to two significant figures the results presented in both sets of data are encouraging. Curiously, both sets of data show a small negative correlation between particle size and the magnitude of Avogadro's constant obtained. ($r = -0.46$, 24 degrees of freedom for the data in Table 1 and -0.52, 23 degrees of freedom for the data in Table 2). Newburgh et al. also reported this trend.[11] This dependence begs further exploration.

The sophistication of the analysis of the data obtained can be tailored to the needs of the particular student group. With a senior high school class we recommend the following: set up the equipment, prepare the slide, collect the data, calculate Avogadro's constant and emphasize the need for replication. More experienced students in an undergraduate program could obtain Avogadro's constant from the slope of the line obtained when the mean square displacement is plotted against the length of the time interval.[10, 11] The statistical properties of truly random data could also be explored.[6–11] For these latter approaches longer runs are desired. Regardless of the particular student audience in mind, the ease of preparation of the slide and measurement of the displacement of projected

Brownian particles commend this activity to the senior high school and undergraduate chemistry laboratory.

A number of curricular extensions and connections are associated with this work. Historically Perrin's original results represented an experimental corroboration of Einstein's theory of Brownian motion as presented by Equation (1). Einstein was correct in asserting that the mean square displacement of a microscopic particle had a functional dependence on t, T, k and P only. Perrin's confirmation of Einstein's work was largely responsible for closing the door on objections to the atomic structure of matter and now permitted chemists to determine the absolute masses of atoms and molecules. We sometimes forget that the firmly held ideas of today did not enjoy a smooth road to acceptance.

Finally, we echo the sentiment expressed by Newburgh et al.[11] and likewise close with the eloquent quotation from the biography of Einstein written by Pais. Pais writes, "One never ceases to experience surprise at this result, which seems, as it were, to come out of nowhere: prepare a set of small spheres, which are, nevertheless, huge compared with simple molecules, use a stopwatch and a microscope, and find Avogadro's number."[17] All of us, authors and students alike, felt that same "surprise".

Acknowledgments

This body of experimental work would not have been possible without the assistance and commitment of the AP Biology students at Waterloo Collegiate Institute. They arrived at school early to begin collecting data before the start of classes and returned for a second shift after school, only to do it again for a number of days. We appreciate the dedication, enthusiasm and promise of students such as Noor Al-Attar, Stellar Boo, Tayler Eaton, Helen Fan, Gordon Li, Ameena Meerasa, Sean Oh, Ann Sychterz and Shannon Walsh in doing this work. Thanks are also extended to Carolyn Knapp whose early assistance provided the assurance that this was worth pursuing.

Appendix — the spreadsheet used to calculate the Avogadro constant

Photocopy the following table for your students to use.

Table 1. Calculating the mean square displacement

Interval	Distance travelled on screen (cm)	Actual distance travelled (λ) (cm)	Square of actual distance travelled (λ^2) (Squared Displacement) (cm^2)
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14			
15			
16			
17			
18			
19			
20			
		Average λ^2	
		Average λ_x^2 (i.e. $\lambda_x^2 = \frac{1}{2}\lambda^2$)	

Table 2. Viscosity of water as a function of temperature.

Temperature (°C)	Viscosity (k) (g $cm^{-1}s^{-1}$)
20	0.01002
21	0.009779
22	0.009548
23	0.009325
24	0.009111
25	0.008904
26	0.008705
27	0.008513
28	0.008327
29	0.008148
30	0.007975

Table 3. Other relevant data.

Ambient temperature, T (K)	
Time interval, t (s)	30
Magnification factor	
Fat droplet diameter on screen (cm)	
Actual fat droplet radius, P (cm)	
Gas constant, R (g cm^2 s^{-2} $mol^{-1}K^{-1}$)	8.314×10^7

Avogadro's constant, $N = \frac{t}{\lambda_x^2}\left(\frac{RT}{3\pi kP}\right)$	

References

1. A. Einstein, *Annalen der Physik*, volume 17, pages 549-560, 1905. For an English translation see R. Fürth and A.D. Cowper, *Investigations on the Theory of the Brownian Movement*, Dover Publications, Inc., 1956, pages 1-18; or see *http://lorentz.phl.jhu.edu/AnnusMirabilis/AeReserveArticles/eins_brownian.pdf*
2. J. Perrin, *Atoms*, translated by D. L. Hammick, Second English Edition, D. van Nostrand; New York, 1923.
3. N.H. Black, *Journal of Chemical Education*, July 1928, pages 868-873.
4. H.C. Doane and W.A. Dow, *Journal of Chemical Education*, June 1929, page 1099.
5. F.E. Christensen, *American Journal of Physics*, volume 33, pages xxi-xxii, 1965.
6. J. le P. Webb, *Physics Education*, volume 15, pages 116-121, 1980.
7. G.P. Matthews, *Journal of Chemical Education*, March 1982, pages 246-248.
8. H. Kruglak, *Journal of Chemical Education*, August 1988, pages 732-734.
9. H.G. Kirksey and R.F. Jones, *Journal of Chemical Education*, December 1988, pages 1091-1093.
10. R. Salmon, C. Robbins and K. Forinash, *European Journal of Physics*, volume 23, pages 1-5, 2002. *http://physics.ius.edu/~kyle/K/Brownian/ejp133827.pdf*
11. R. Newburgh, J. Peidle and W. Rueckner, *American Journal of Physics*, volume 74, pages 478-481, 2006.
12. L.J. Brubacher, *Chem 13 News*, May 2006, pages 14-17.
13. H. Deruyter, *Chem 13 News*, May 2006, page 2.
14. Handbook of Chemistry and Physics, 52nd ed., R.C. Weast, The Chemical Rubber Company, Cleveland, 1972.
15. Carolina Biological Supply Company, *www.carolina.com.* Stage Micrometer, Catalogue No. 59-1430, US$52.
16. D. Goff, Homogenization of Milk and Milk Products, (2006) *http://www.foodsci.uoguelph.ca/dairyedu/homogenization.html.*
17. A. Pais, *Subtle is the Lord: The Science and Life of Albert Einstein*, Oxford University Press, Toronto, 2005, page 97. ■